Anions by Ion Chromatography

EPA 300.0/SW846-9056A/SW846-9056

DOCUMENT ID: HS-IC001, REV 9.3

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Date: 03/05/2020

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Date: 03/05/2020

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1) Identification of the Method and Applicable Matrices

1.1 This Standard Operating Procedure is used to determine the following common anions in water samples (wastewater, surface water, ground water, and non-potable water).

Bromide	Nitrite as N
Chloride	Nitrate/Nitrite as N
Fluoride	Ortho-Phosphate as P
Nitrate as N	Sulfate
Chlorate	

1.2 This analysis is applicable to aqueous samples, and soil sample leachates.

2) Scope Application and Summary of the Method

2.1 The sample is pumped through two different ion exchange columns, then a suppressor device, and into a conductivity detector. The two ion exchange columns, a pre-column or guard column and a separator column, are packed with low-capacity, strongly basic anion exchange resin. Ions are separated into discreet bands based on their affinity for the exchange sites of the resin. The suppressor is an ion exchange-based device that reduces the background conductivity of the eluent to a low or negligible level and also converts the anions in the sample to their more conductive acid forms. The separated anions in their acid forms are measured using an electrical-conductivity cell. Anions are identified based on their retention times compared to known standards. Quantitation is accomplished by measuring the peak height or area and comparing it to a calibration curve generated from known standards.

2.2 Soluble anions from soil samples are determined by the analysis of a 1:10 by weight DI water leachate of the sample and recorded in the prep batchs.

3) Definitions

3.1 Batch: Environmental samples that are prepared and/or analyzed together with the same process and personnel, using the same lot(s) of reagents. A **preparation batch** is composed of one (1) to twenty (20) environmental sample of the same quality systems matrix, meeting the above mentioned criteria and with a maximum time between the start of processing of the first and last sample in the batch to be twenty-four (24) hours. An **analytical batch** is composed of prepared environmental samples (extracts, digestates or concentrates) which are analyzed together as a group. An analytical batch can include prepared samples originating from various quality system matrices and can exceed twenty (20) samples.

3.2 Continuing Calibration Blank (CCB): Reagent water, or appropriate solvent, containing no analytes of interest.

3.3 Calibration Standard (CAL): A solution prepared from the primary dilution standard solution or stock standard solutions. The CAL solutions are used to calibrate the instrument response with respect to analyte concentration

3.4 Continuing Calibration Verification (CCV): The verification of the ICAL that is required during the course of analysis at periodic intervals. The CCV applies to both external standard and internal standard calibration techniques, as well as to linear and non-

linear calibration models.

3.5 Demonstration of Capability (DOC): procedure to establish the ability of the laboratory to generate acceptable accuracy and precision which is included in many of the EPA's analytical test methods. In general, an initial DOC procedure involves the analysis of four separate Laboratory Control Samples (LCS) as prescribed by the analytical method Each LCS must meet the specified LCS acceptance limits for percent recovery, and standard deviation. Ongoing DOC requirements are met by acceptable analysis of annual NELAC accepted proficiency test (PT) samples, or by the analysis of four LCS if PT samples are not available

3.6 Detectability Check Sample (DCS): a sample spiked at 2 to 3 times the calculated LOD (refer to SOP HS-QS006, LOD and LOQ), or alternatively spiked near the LOQ.

3.7 Exception Report: Appropriate comments reported with the associated sample batch that addresses sample anomalies such as demonstrated sample matrix effects.

3.8 Laboratory Control Sample (LCS): A sample matrix, free from the analytes of interest, spiked with known amounts of analytes or a material containing known and verified amounts of analytes.

3.9 Limit of Detection (LOD): an estimate of the minimum amount of a substance that an analytical process can reliably detect. The LOD is determined annually through the execution of a Method Detection Limit Study, and verified quarterly through the analysis of a Detectability Check Sample (DCS).

3.10 Limit of Quantitation (LOQ): The minimum levels, concentrations, or quantities of a target variable (e.g., target analyte) that can be reported with a specified degree of confidence. This defined concentration can be no lower than the concentration of the lowest calibration standard and can only be used if acceptable quality control criteria for this standard are met.

3.11 Linear Calibration Range (LCR): The concentration range over which the instrument response is linear, Study must be performed every six-months.

3.12 Matrix Spike (MS): A sample prepared by adding a known mass of target analyte to a specified amount of matrix sample for which an independent estimate of target analyte concentration is available.

3.13 Matrix Spike Duplicate (MSD): A second replicate matrix spike prepared in the laboratory and analyzed to obtain a measure of the precision of recovery for each analyte.

3.14 Matrix: The substrate (e.g., water, soil, etc.) which may contain the analyte of interest.

3.15 Method Blank (MBLK): A sample of a matrix similar to the batch of associated samples (when available) that is free from the analytes of interest and is processed simultaneously with and under the same conditions as samples through all steps of the analytical procedures, and in which no target analytes or interferences are present at

concentrations that impact the analytical results for sample analysis.

3.16 Method Detection Limit (MDL) study: a procedure described in 40CFR Part 136, Appendix B, that describes how to produce an MDL, a reporting element of certain EPA methods. The MDL study is one approach to determine the LOD.

3.17 NCAR: Nonconformance Corrective Action Report (refer to SOP HSQS003, current revision).

3.18 Quality Control Sample (QCS): A solution of method analytes of known concentrations that is used as the spiking solution for the LCS. The QCS is obtained from a source external to the laboratory and different from the source of calibrations standards. It is used to check laboratory performances with externally prepared test materials.

3.19 Reagent Water: Deionized (DI) reagent purified by filtration thru mix resin and carbon beds. For additional purification, the DI water is passed through an activated carbon filter with characteristics of Type I laboratory distilled water (daily resistance ≥17 megohms-cm).

3.20 Preparation Batch: A defined set of one to 20 client samples of the same matrix, meeting the batch definition criteria, and prepared for analysis within 24 hours. The preparation batch must also contain the required determinative method defined batch QC samples (e.g. method blank, laboratory control samples, matrix spikes, duplicates, etc.).

3.21 Retention Time Window: The length of time between sample injection and the appearance of a peak at the detector. The window of time is established for each analyte or group of analytes and is set for complete elution of analyte peaks. It is based upon a series of analyses and statistical calculations that establish the measured band on the chromatogram that can be associated with a specific analyte or group of analytes.

3.22 Second Source Calibration Verification (ICV): A standard obtained or prepared from a source independent of the source of standards for the ICAL. Its concentration should be at or near the middle of the calibration range. It is performed after the ICAL but prior to analyzing samples.

4) Safety

4.1 Lab Safety: Due to various hazards in the laboratory, safety glasses and laboratory coats or aprons must be worn at all times while in the laboratory. In addition, gloves and a face shield should be worn when dealing with toxic, caustic, and/or flammable chemicals.

4.2 Chemical Hygiene: The toxicity or carcinogenicity of each reagent used has not been precisely defined; however, each chemical used should be treated as a potential health hazard. Exposure to laboratory reagents should be reduced to the lowest possible

level. The laboratory maintains a current awareness file of OSHA regulations regarding the safe handling of the chemicals specified in this method. A reference file of data handling sheets (MSDS) is available to all personnel involved in these analyses.

4.3 Waste Management: The principal wastes generated by this procedure are the method-required chemicals and standards. It is the laboratory's responsibility to comply with all federal, state, and local regulations governing waste management by minimizing and controlling all releases from fume hoods and bench operations. Compliance with all sewage discharge permits and regulations is required. Laboratory procedures in SOP HS-SAF-001, Waste Disposal Procedures, must be followed.

4.4 Pollution Prevention: The materials used in this method pose little threat to the environment when recycled and managed properly. The quantities of chemicals purchased should be based on the expected usage during its shelf life. Standards and reagents should be prepared in volumes consistent with laboratory use to minimize the volume of expired standards or reagents to be disposed.

4.5 Job Safety Assessment

HAZARD ASSESSMENT		
Job Task #1:	**Hazards**	**Preventative Measures**
Sample handling.	Injury due lifting and placing samples on storage locations and broken sample containers.	Use proper lift technique and cart to move coolers and stools/stepladder when working reaching above shoulder height in sample storage cooler. When transporting samples always use sample carrier or properly inspected cart. Wear proper PPE when handling sample container and have spill kits available.
Job Task #2:	**Hazards**	**Preventative Measures**
Sample Testing and/or standard and reagent/solvent use.	Exposure to possible hazardous chemicals.	Wear gloves, safety glasses and lab coat. Work in fume hood and avoid skin contact with solvents/acids/reagents. Know location of safety shower, first aid kits, spill kits and fire extinguisher when handling flammable material.

5) Cautions

5.1 Routine preventative maintenance must be performed and documented to assure optimum instrument performance. Refer to the current revision of SOP HS-EQ004 for preventative maintenance schedules.

6) Interferences

6.1 Frequently compare calibration standard chromatograms to those of the column test chromatogram (received when the column was purchased) to insure proper separation and similar response ratios between the target analytes is observed.

6.2 Method interferences may be caused by contaminants in the reagent water, reagents, glassware, and other sample processing apparatus that lead to discrete artifacts or elevated baselines in an ion chromatogram. These interferences can lead to false

positive results for target analytes as well as reduced detection limits as a consequence of elevated baseline noise.

6.3 Samples that contain particles larger than 0.45 microns and reagent solutions that contain particles larger than 0.20 microns require filtration to prevent damage to instrument columns and flow systems.

6.4 Any anion that is only weakly retained by the column may elute in the retention time window of fluoride and potentially interfere. At concentrations of fluoride above 1.5 mg/L, this interference may not be significant; however, it is the responsibility of the analyst to generate precision and accuracy information in each sample matrix.

6.5 Close attention should be given to the potential for carry over peaks from one analysis that will affect the proper detection of analytes of interest in a second, subsequent analysis. It is the responsibility of the analyst to confirm that no late eluting peaks have carried over into a subsequent analysis thereby compromising the integrity of the analytical results.

6.6 Acetate, formate and other monovalent organic acid anions elute early and interfere with fluoride. Retention times of anions may differ when large amounts of acetate are present. Therefore this method is not recommended for leachates of solid samples where acetate is used for pH adjustment. Because acetate interferes, analysis of TCLP leachates for fluoride should be avoided.

6.7 When this method is used to analyze unfamiliar samples for any of the above anions, anion identification should be supported by the use of a fortified sample matrix covering the anions of interest.

6.8 Bromide and nitrite react with most oxidants employed as disinfectants. The utility of measuring these anions in treated water should be considered prior to conducting the analysis.

7) Personnel Qualifications and Responsibilities

7.1 General Responsibilities - This method is restricted to use by or under the supervision of analysts experienced in the method.

7.2 Analyst - It is the responsibility of the analyst(s) to:

- 7.2.1 Each must read and understand this SOP and follow it as written. Any deviations or non-conformances must be documented and submitted to the QA Manager for approval.
- 7.2.2 Produce method compliant data that meets all quality requirements using this procedure and the Data Reduction, Review and Validation SOP (HS-QS-009).
- 7.2.3 Complete the required initial demonstration of proficiency before performing this procedure without supervision.
- 7.2.4 Complete an ongoing demonstration of proficiency annually when continuing to perform the procedure.
- 7.2.5 The analysts must submit data for peer or supervisor review.

7.3 Section Supervisor - It is the responsibility of the section supervisor to:

- 7.3.1 Ensure that all analysts have the technical ability and have received adequate training required to perform this procedure.

7.3.2 Ensure analysts have completed the required initial demonstration of proficiency before performing this procedure without supervision.

7.3.3 Ensure analysts complete an ongoing demonstration of proficiency annually when continuing to perform the procedure.

7.3.4 Ensure analysts produce method compliant data that meet all quality requirements using this procedure and the Data Reduction, Review and Validation SOP.

7.4 Project Manager - It is the responsibility of the Project Manager to ensure that all method requirements for a client requesting this procedure are understood by the laboratory prior to initiating this procedure for a given set of samples.

7.5 QA Manager: The QA Manager is responsible for

7.5.1 Approving deviations and non-conformances

7.5.2 Ensuring that this procedure is compliant with method and regulatory requirements,

7.5.3 Ensuring that the analytical method and SOP are followed as written through internal method and system audits.

8) Sample Collection, Handling, and Preservation

8.1 Water samples are collected in plastic or glass. Volume collected should be sufficient to insure a representative sample, allow for replicate analysis, and minimize waste disposal.

8.2 Sample preservation and holding times for the anions are as follows:

Table 8.2 Common Anions, Analyte Preservation and Holding Time

Compound	Container	Preservative	Holding Time
Bromide	P,G	Cool to >0 to 6 ° C	28 days
Chloride	P,G	Cool to >0 to 6 ° C	28 days
Fluoride	P,G	Cool to >0 to 6 ° C	28 days
Nitrate as N	P,G	Cool to >0 to 6 ° C	48 hours
Nitrite as N	P,G	Cool to >0 to 6 ° C	48 hours
Nitrate + Nitrite as N	P,G	pH<2 w/ H2SO4, Cool to >0 to 6 ° C	28 days
Dissolved Ortho-Phosphate as P	P,G	Cool to >0 to 6 ° C	48 hours
Sulfate	P,G	Cool to >0 to 6 ° C	28 days
Chlorate	P,G	Cool to >0 to 6 ° C	28 days

Note: If the determined value for the combined Nitrate + Nitrite, as N, is >0.5mg/L, the sample must be reanalyzed, unpreserved, within holding time. This may require re-sampling.

9) Equipment and Supplies

9.1 Ion chromatograph:

9.1.1 Dionex ICS-2100

9.1.1.1 Dionex AS Autosampler
9.1.1.2 Dionex EO-Eluent Organizer
9.1.1.3 Dionex EluGen® Cartridges,
9.1.1.4 Eluent Pumps
9.1.1.5 Anion suppressor device: Dionex Anion Self-Regenerating Suppressor (ASRS Ultra II 4-mm, P/N 061561). The ASRS should be set to perform electrolytic suppression at a current setting of 112-mA using an external source DI water mode. Insufficient baseline stability may be observed using the ASRS in recycle mode.
9.1.1.6 Anion Guard Columns: Dionex IonPac® AG18 (4x50-mm, P/N 063154) or Dionex IonPac® AG18 (4x50-mm, P/N 060551) or equivalent. These columns functions as a protector of the analytical column.
9.1.1.7 Anion Analytical Columns: Dionex IonPac® AS18 (4x250-mm, P/N 063148) or Dionex IonPac® AS18 (4x250-mm, P/N 060549) or equivalent.
9.1.1.8 Carbonate Removal Device (CRD 200 – 4mm, P/N 062983)
9.1.1.9 Electrical Conductivity Detectors
9.1.1.10 Dionex Chromeleon Data System – Data acquisition and processing software.

9.1.2 Dionex Integrion HPIC
9.1.2.1 Dionex AS Autosampler
9.1.2.2 Dionex ICS-Series VWD
9.1.2.3 Dionex EluGen® Cartridge

9.2 In order to achieve comparable detection limits, the IC system must be properly maintained and must be capable of yielding a baseline with no more than 5 nS noise/drift per minute of monitored response over the background conductivity.

9.3 Nitrogen, zero grade or better.

9.4 Analytical balance, ±0.1 mg sensitivity (used to accurately weigh reagents).

9.5 Autosampler Vials, 1.5 ml capacity with Teflon lined crimp top.

9.6 Syringes, plastic, disposable, 10 mL - used during sample preparation.

9.7 Pipets, fixed, or variable, volume Eppendorf, various sized, calibrations verified per HS-EQ003.

9.8 Bottles, high-density polyethylene (HDPE), opaque or glass, amber, various sizes. For sampling and storage of calibration solutions.

9.9 Micro beakers, plastic, disposable - used during sample preparation.

9.10 Syringe filters, 30-mm Nylon, 0.45-µm.

10) Standards and Reagents

10.1 Note: All purchased standards according to manufacturer specifications. Store all standard solutions (remaining stock, composite and calibration) below 6 °C in glass containers having Teflon™ lined lids or in accord with the manufacturer's

recommended conditions. All purchased stock standard solutions must be replaced after reaching the manufacturer's expiration date assigned to the standard. All laboratory prepared standard solutions must be replaced after six months or sooner if routine QC indicates a problem or if required by reference method. An assigned expiration date of a lab prepared standard cannot exceed the manufacturer's expiration date for any component used in the standard formulation. When analyzing or preparing samples, all standards, lot numbers must be associated with the run batch or prep batch.

10.2 DI Water: Deionized (DI) water meeting purity characteristics of Type I laboratory distilled water (resistance >17 megohms-cm, anion free water). Water should contain particle sizes no greater than 0.20μm. Filter as necessary.

10.3 Stock Standard Solution, multi-anion 100-500 mg/L: Stock standards are purchased as certified solutions: Bromide, Fluoride, Nitrate as N, Nitrite as N and o- Phosphate as P all at 100 mg/L; Chloride and Sulfate at 500 mg/L.

10.3.1 Adhere to the manufacturer determined expiration date.

10.4 Second Source Stock Standard Solution, multi-anion 100-500 mg/L: Second source stock standards are purchased as certified solutions from a different sources as section 10.3 (i.e., different vendor, or if from the same vendor, obtain a different lot): Bromide, Fluoride, Nitrate as N, Nitrite as N and o- Phosphate as P all at 100 mg/L; Chloride and Sulfate at 500 mg/L.

10.4.1 Adhere to the manufacturer determined expiration date.

10.5 Working Calibration Standards – prepared from appropriate dilutions of the Stock Standard Solution (section10.3).

10.5.1 In a 100-mL volumetric flask, add the indicated amount of stock to ~50mL of DI water and dilute to volume.

10.5.2 Prepare fresh at each use.

Table 10.5 Initial Calibration Standards, Low-Level Curve

These standards are prepared in 100 mL volumetric flasks								
Anion	Stock (10.3) mL	Br^- mg/L	Cl^- mg/L	Fl^- mg/L	NO_3– mg/L	NO_2– mg/L	SO_4^{2-} mg/L	PO_4^{3-} mg/L
Level 1	0.1	0.1	0.5	0.1	0.1	0.1	0.5	0.1
Level 2	0.4	0.4	2.0	0.4	0.4	0.4	2.0	0.4
Level 3*	2.0	2.0	10.0	2.0	2.0	2.0	10.0	2.0
Level 4**	4.0	4.0	20.0	4.0	4.0	4.0	20.0	4.0
Level 5***	10	10.0	50.0	10.0	10.0	10.0	50.0	10.0
Level 6	20	20.0	100	20.0	20.0	20.0	100	10.0

*Low Level CCV.

**LCS/LCSD, MS/MSD and ICV are at 4ppm/20ppm.

***High level CCV.

10.6 Calibration Verification Standards (ICV/LCS/CCV) are prepared at the same concentration as the Levels in Calibration Standard (Table 10.5)
- 10.6.1 The CCV is prepared from the Stock Standard Solution (10.3)
- 10.6.2 The ICV is prepared from the Second Source Stock Standard Solution (110.4).

11) Calibration and Standardization

11.1 Perform Support Equipment Calibration Checks:
- 11.1.1 Balance Calibration Checks must be performed prior to balance use as per SOP HS-EQ001, current revision.
- 11.1.2 Quarterly Pipet Calibration checks must be current for the micro-pipets when they are used to measure portions of DI water or standard solutions required in this procedure. Quarterly pipet calibration checks are performed according to SOP HS-EQ003, current revision.

11.2 Operating Conditions for IC analysis: The analytical approach involves the use of a guard and analytical column. The IC operating conditions are given as Table 11.2 below:

Table 11.2 Perform Support Equipment Calibration Checks:

IC Conditions	Column: IonPac® AG20, AS20
Flow rate:	1.0 mL/minute
Injection volume:	20 µL
Makeup gas:	Helium
Detection:	conductivity detector

- 11.2.1 Note: Once optimized and calibrated, the same IC conditions must be used for analysis of all standards, samples, blanks and QC samples.

11.3 Initial Calibration Curve: External standard calibration is used. Six standards are used at the concentrations outlined in Table 10.5.

11.4 The calibration is processed using the linear calibration model:
- 11.4.1 For a linear calibration curve (y = ax + b), the analyst should not force the line through the origin, but leave the intercept calculated. In addition, do not include the origin (0,0) as a calibration point. In order to be used for quantitative purposes, a correlation coefficient, r, must be greater than or equal to 0.995. For non-linear fit using least square fit, r2 must be greater than or equal to 0.990.
- 11.4.2 Retention Time Windows: The width of the retention time window used to make identifications should be based upon measurements of actual retention time variations of standards over the course of a day. Three times the standard deviation of a retention time can be used to calculate a suggested window size for each analyte. However, the experience of the analyst should weigh heavily in the interpretation of chromatograms.

11.5 Initial Calibration Verification (ICV): Verify each new Initial Calibration using a second source standard (ICV) at or near the midpoint of the curve. Agreement with the new curve should be ±10% of the true value of the second source standard.

11.6 Continuing Calibration Verification (CCV):

11.6.1 Verify calibration by injecting a CCV standard (10) prior to conducting any sample analyses. A CCV must also be injected at intervals of not more than once every ten samples and at the end of the analysis sequence. CCVs must be analyzed at two levels on days when a full multipoint calibration is not preformed. Analyst must alternate the CCV level between high and low standards.

11.6.2 If the response of any analyte varies from the expected values by more than ± 10%, then the test must be repeated using fresh standard. If the results are still more than ± 10%, then an entirely new calibration curve must be prepared for that analyte.

11.7 Continuing Calibration Blank (CCB): This blank is run after the CCV to evaluate whether carryover from previous samples or a CCV has occurred or whether the calibration has drifted. The CCB should be < ½ the PQL.

12) Sample Preparation/Analysis

12.1 Sample Preparation – recommend pre-filter all samples using a 0.45 µ filter. Document filter lots used in sample sequence log along with all standards and reagents, such as eluent.

12.2 IC analysis of aqueous samples -

12.2.1 Transfer a 1-ml aliquot of filtered sample (or diluted sample) into autosampler vial and load onto the instrument autosampler. Create an analytical sequence for all samples and required QC samples. The autosampler will load approximately 100 µL into the sample loop and auto-inject a 20 µL aliquot of the loaded sample. This process is repeated for each sample in the sequence.

12.2.2 Identification of an analyte occurs when a peak from a sample falls within the retention time window of the target analyte.

12.2.3 If the resulting chromatogram fails to produce adequate resolution, except for preserved samples or if identification of specific anions is questionable, analyze a matrix spike of the sample to confirm the anion identification.

12.3 IC analysis of soil samples:

12.3.1 Weigh out 5 grams of soil sample into a digestion tube. Record to nearest 0.1g in logbook. Add 50 mL DI water to sample. Cap and shake vigorously for 2 – 3 minutes. Centrifuge the sample afterwards or let it settle. Decant a sufficient volume of liquid and filter using a 0.45µ membrane filter. Document prep in pre batch containing sample weight, water volume and filter lots and analyze as in sections 12.2.1 thru 12.2.3. A 10x preparation factor is applied to yield an mg/Kg solid result.

12.3.1.1 Note: The nature of the sample matrix may require that varying sample amount are used in this step. In such cases, a 1:10 ratio of

sample to DI water must be maintained. Any deviation must be recorded in the sample preparation batch in LIMS.

12.4 Example calculations for constituent concentration are provided section 15.

12.5 If the responses exceed the calibration range of the system, dilute the sample and reanalyze. NOTE: Using the sequence scanner in LIMS will flag by sample ID those RPDs outside 30% with a code #120.

12.6 If during analysis, there is a need to manually integrate the peak (due to high salt concentration, co-elution, etc.), refer to CE-QA002 Corporate SOP for Manual Integration, or to HS-QS016 Houston Laboratory SOP for Manual Integration, whichever is most current.

12.7 If any carryover is suspected due to a higher anion sample just preceding the sample, then the sample is rerun after a CCV/CCB to check for potential carryover effect. If the concentration of the run matches, then it can be used as confirmation. If it is less than the original, then the rerun is reported.

12.8 Each sample analysis must be bracketed with an acceptable initial calibration, calibration verification standard(s) and initial calibration blank (every 10 samples).

12.9 Build an analytical sequence table with the Dionex Chromeleon software and initiate instrument operation. The Typical Analytical Sequence:

- 12.9.1 Initial Calibration curve samples, including the ICV or
- 12.9.2 Initial CCV/CCB (alternating between a high and low standard on day without initial multipoint calibration)
- 12.9.3 Method Blank (MBLK)
- 12.9.4 LCS
- 12.9.5 Client sample
- 12.9.6 Client Matrix Spike
- 12.9.7 Client Matrix Spike Duplicate
- 12.9.8 Client samples (5)
- 12.9.9 Initial CCV/CCB (alternating between a high and low standard on day without initial multipoint calibration)
- 12.9.10 Client samples (10 or less)
- 12.9.11 Initial CCV/CCB (alternating between a high and low standard on day without initial multipoint calibration)

13) Troubleshooting and Maintenance

13.1 Review of Retention Time data: Shifts in retention time is inversely proportional to concentration. Nitrate, phosphate and sulfate will exhibit the greatest degree of change, although all anions can be affected. In some cases this peak migration may produce poor resolution or make peak identification difficult.

- 13.1.1 Should more complete resolution be needed between any two co-eluting peaks be required, the eluent can be diluted. This will spread out the run, however, and will cause late eluting anions to be retained even longer.
- 13.1.2 The analysts must verify that this dilution does not negatively affect performance by repeating and passing all the QC criteria in Section 16.

13.1.3 As a specific precaution, upon dilution of the eluent, a peak for bicarbonate may be observed within the retention time window for bromide that will negatively impact the analysis.

13.1.4 Eluent dilution will reduce the overall response of an anion due to chromatographic band broadening which will be evident by shortened and broadened peaks. This will adversely affect the LODs for each analyte.

13.2 When a change of >15% for the RT for sulfate is observed, it may indicate the guard column requires attention. Clean or replace the column.

14) Data Reduction and Reporting

14.1 Data is collected with "Chromeleon" data acquisition software. This software provides the sequence log of run order for the data to be collected from the IC detector.

14.1.1 For each new analytical sequence, a new folder is opened (e.g. IC-1).

14.1.2 Chromeleon processes the calibration curve and all associated sample and QC data.

15) Calculations

15.1 QC Calculations: LIMS calculates the percent recovery for various QC samples (LCS) according to the following equations:

15.1.1 % Recovery, %R (for MS and MSD Samples)

$$\%R = \frac{(SSR - SR)}{SA} \times 100$$

Where:
SSR = Spiked Sample Result (mg/L or mg/kg).
SR = Sample Result (unspiked).
SA = Spike Amount Added (mg/L or mg/kg).

15.1.2 % Recovery, %R (for standards and LCS)

$$\%R = \frac{SSR}{SA} \times 100$$

Where:
SSR = Spiked Sample Result (mg/L or mg/kg).
SA = Spike Amount Added (mg/L or mg/kg).

15.1.3 RPD (for precision or duplicate evaluation)

$$RPD = \frac{|SR_1 - SR_2|}{½(SR_1 + SR_2)} \times 100$$

Where:
SR_1 = Sample result for duplicate 1.

SR_2 = Sample result for duplicate 2.

15.2 Sample Concentration Calculation

15.2.1 Aqueous sample

Conc (mg/L) = Instr reading (mg/L) * DF

Where DF = Dilution Factor

15.2.2 Solid Sample

Conc (mg/kg) = Instr reading (mg/L) * DF * PrepFac

Where DF = Dilution Factor
PrepFac = Prepation Factor, normally 10 (0.5 g to 50 mL DI water)

50 /0.5 = 10

16) Quality Control, Acceptance Criteria and Corrective Action

16.1 Initial Demonstration of Capability (IDOC)
- 16.1.1 Purpose: Verify the ability to produce data of acceptable precision and bias for a specific instrument type, matrix, method, and analyst.
- 16.1.2 Frequency: Initially during method development, and any time there is a significant change in instrument type, personnel, methodology, or matrix
- 16.1.3 Acceptance Criteria: Four aliquots at one (1) to four (4) time the limit of quantitation and analyzed according to the method either concurrently or over a period of day. Calculate mean recovery and standard deviation for each analyte of interest. Compare recovery and standard deviation to the corresponding acceptance criteria for precision and accuracy in the method (if applicable) or to lab-generated acceptance limits. If any one compound does not achieve acceptance criteria, the performance is unacceptable for
- 16.1.4 Corrective Action: Identify and correct the source of error. Reanalyze the demonstration.

16.2 Continuing Demonstration of Capability
- 16.2.1 Purpose: Verify the ability to produce data of acceptable precision and bias for a specific instrument type, matrix, method, and analyst.
- 16.2.2 Frequency: A. Annual to re-qualify analyst for analysts. If period greater than one year has lapse since the last performance of analysis than Initial Demonstration must be performed.
- 16.2.3 Acceptance Criteria: Four consecutive LCS analysis meeting stated LCS criteria or successful PT study.

16.3 Retention Time Window Width:
- 16.3.1 Purpose: Ensures that the chromatographic system is operating reliably and that system conditions have been optimized for the target analytes in the standards and sample matrix to be analyzed.

16.3.2 Frequency: At method development and after major instrument maintenance (i.e. column replacement, temperature program changes)
16.3.3 Acceptance Criteria: RT Window is determined as ±3 times the standard deviation of the RT for the analyte of interest obtained from the ICAL and several CCVs analyzed over a 24 hour period. However, the experience of the analyst should weigh heavily in interpreting chromatograms.
16.3.4 Corrective Action: N/A

16.4 Initial Calibration:
16.4.1 Purpose: Establishes the calibration curve for the quantification of the analytes of interest.
16.4.2 Frequency: A new curve must be generated when the ICV or CCV criteria are not met, or after major instrument maintenance such as column replacement or changes in operating conditions.
16.4.3 Acceptance Criteria:
16.4.3.1 Initial calibration curve must have 5-points minimally for all analytes (7 are used in this procedure); generate r >0.995
16.4.3.2 If non-linear fit (second order) is used, the COD ≥ 0.99 and six calibration points are required.
16.4.4 Curve Failure Corrective Action: Check standards and or perform maintenance as necessary to correct problem, then generate new curve

16.5 Initial Calibration Verification (ICV).
16.5.1 Purpose: Establishes the calibration curve for the quantification of the analytes of interest.
16.5.2 Frequency: Prior to sample analysis, following significant instrument maintenance, and as required by instrument QC performance.
16.5.3 Acceptance Criteria: The new ICAL curve must have a correlation coefficient equal to or greater than 0.995 with a minimum of 6 calibration points
16.5.4 Corrective Action: Identify and correct the source of error. Perform the ICAL again and reanalyze all affected samples.

16.6 Retention Time Window Position:
16.6.1 Purpose: Assists in the identification of analytes of interest.
16.6.2 Frequency: Set the absolute RT position for each analyte of interest using the mid-point of the ICAL. Reset the absolute RT position for each analyte of interest daily using the first CCV analyzed each day.
16.6.3 Acceptance Criteria: The RT must be ±10% of the previous RT window.
16.6.4 Corrective Action: Re-analyze the CCV. If the acceptance criteria are not met on re-analysis, determine the source of error and perform corrective action.

16.7 Continuing Calibration Verification (CCV)
16.7.1 Purpose: Verifies that instrument response is reliable and has not changed significantly from the current ICAL. On days when multipoint calibration is not performed, analyst must alternate CCV levels between a high and low level standards.
16.7.2 Frequency: beginning of sequence, after every 10 sample injections and at end of a sequence.
16.7.3 Criteria: The acceptance range for CCV is 90 - 110 percent recovery.
16.7.4 Corrective Action: If outside these ranges, perform corrective action to solve

the source of the error, and then re-analyze all samples since the last acceptable CCV. If the CCV fails high, only the bracketed samples that are non-detect can be reported.

16.8 Calibration Blank (CCB):
- 16.8.1 Purpose: Determines the zero point of the calibration curve for all initial and continuing calibrations. Please place CCB after CCV in the analytical sequence.
- 16.8.2 Frequency: At the beginning of each sequence, after every 10 samples and at the end of each sequence.
- 16.8.3 Acceptance Criteria: No analytes detected > ½ LOQ
- 16.8.4 Corrective Action: Identify and correct the source of error. Reanalyze all affected samples.

16.9 Method Blank (MB)
- 16.9.1 Purpose: Assess background interference or contamination in the analytical system that may lead to high bias or false positive data.
- 16.9.2 Frequency: Analyze the Method Blank (MB) with each batch of 20 or less field samples processed through the entire method within a normal work shift.
- 16.9.3 Criteria: All analytes must be less than the quantitation limit or ½ the quantitation limit depending QA plan associated with the samples. In addition, solvent blanks should be run after samples suspected of being highly contaminated to determine if sample carryover has occurred. The method blank results must be less than the method quantitation limit, or no more than 5% of sample concentration, or 5% of regulatory limits, whichever is greater.
- 16.9.4 Corrective Action: If above the limit, if it is an indication of instrument drift, the baseline must be reset and the samples since the previous acceptable blank must be re-analyzed. If contamination is indicated, all affected batch samples must be reprocessed. Samples that are non-detect will not require reprocessing.

16.10 Laboratory Control Sample (LCS) or Lab Fortified Blank (LFB): The LCS is prepared from a calibration standard.
- 16.10.1 Purpose: Evaluates the performance of the entire analytical system, including all preparation and analysis steps. Assesses the ability of the laboratory/analyst to successfully recover the target analytes from a clean matrix. LCS must contain all target analytes.
- 16.10.2 Frequency: Analyze the LCS/LFB with each batch of 20 or less field samples processed through the entire method within a normal work shift.
- 16.10.3 Criteria: Refer to table 22.2 for the acceptance range.
- 16.10.4 Corrective Action: The LCS/LFB results must be within the acceptance range. If outside this range perform corrective action to solve the source of the error, and re-prepare and re-analyze the sample batch unless the LCS/LFB fails high and the samples are non-detect.

16.11 Matrix Spike, Matrix spike duplicate (If field sample is not available to perform both an MS and MSD, then perform an LCS and LCSD.
- 16.11.1 Purpose: Assesses the performance of the method on a particular matrix.
- 16.11.2 Frequency: Matrix spikes will be analyzed at the frequency of one spike for

each 10 samples analyzed by Method 300.0 and one spike for each 20 samples analyzed by Method 9056A. If fewer than 20 samples are in a batch, at least one spike will be included for method 9056A and If fewer than 10 samples are in a batch, at least one spike will be included for Method 300.0. If insufficient sample is available for a MS and MSD, then an LCS duplicate must be analyzed and used for the RPD and percent recovery. When duplicate LCS's are used, the same control limits as duplicate matrix spikes will apply.

16.11.3 Acceptance Criteria: Spike recovery and RPD criteria are specified in the Table 22.2.

16.11.4 MS/MSD % Recovery Criteria Failure Corrective Action: If the MS and MSD have recoveries which are outside the target range, the poor recoveries in the MS and MSD may be due to matrix effects. The LCS, surrogate recoveries and calibration results must all be evaluated in order to determine if matrix interference is present or if method performance is poor. Note that the MS and MSD are used to evaluate the matrix effect, not to control the analytical process. If both the Matrix Spike and Matrix Spike Duplicate are found to be out of control for the same analyte, a matrix effect is likely confirmed (assuming the LCS passes). If recoveries of the MS/MSD pair are suspicious (laboratory error, etc) another set of MS/MSD must be re-extracted with the sample batch. For instance, if both matrix spikes exhibit low recovery but good precision then it can be assumed that matrix interference is present. However, if precision between the MS and the MSD is poor, technique error must be eliminated as a possible source of error before the data can be accepted. If matrix interference is highly suspected corrective action is not necessary.
MS/MSD RPD Criteria Failure Corrective Action: If the RPD fails, the data must be evaluated for error and perform sample/batch QC reprocessing if necessary

16.12 Duplicate Samples

16.12.1 Purpose: Provides information on the heterogeneity of the sample matrix. Also determines the precision of the analytical process for that matrix.

16.12.2 Frequency: Once per preparation batch.

16.12.3 Frequency: Duplicates (as MS/MSD or LCS/LCSD) are analyzed on a frequency of one duplicate for each batch of 10 or less samples extracted and analyzed.

16.12.4 Criteria: Acceptance limits for the water matrix and soil matrix are 20 % RPD.

16.12.5 Corrective Action: If the duplicate results are outside the acceptance limits for relative percent deviation, first determine if the cause is a system error; if so, correct the problem and repeat the duplicate. If not, the LCSD RPD must fall within the acceptance criteria in order for the data to be accepted. The sample results must be flagged to indicate the QC failure as matrix interference.

16.13 Method Detection Level (MDL) or Detection Limit Procedure

16.13.1 Purpose: To establish the method detection limit, see SOP HS-QS006 for detail on MDL, LOD and LOQ procedures.

16.13.2 Frequency: Establish the initial MDL of an instrument by process a minimum of 7 spiked aliquots at the appropriate matrix spike level and 7 method blank samples through all steps of the method. The samples used for the MDL must

be prepared in at least three batches on three separate calendar dates and analyzed on three separate calendar dates. After analysis determine the MDLs (spiked MDL) and MDLb (blank MDL). Select the highest MDL as the initial MDL. MDL must be determined for each analyte per matrix per method.

16.13.3 Ongoing Data Collection: On a quarterly basis, two MDL spikes must be prepared at the MDL spiking level and analyzed. Ensure minimum of seven spiked samples and seven method blanks are completed for the annual verification. If only one instrument is in use, a minimum of seven spikes are still required.

16.13.3.1 If new instrument is added to group of instruments, analyze a minimum of two spike replicates and two method blanks. If both blank MDL and are below the MDL then instrument is considered valid. Combine new spied samples with existing MDL and recalculate the MDL. If the recalculated MDL does not vary by the specified factor then existing MDL is validated. If either one of these conditions are not met, then than the MDL must be regenerated.

16.13.4 Annual Verification

16.13.4.1 Recalculate the MDLs and MDLb from the spike samples and method blank from the last twenty four months, but only data with the same spiking level. Include initial MDL if data was within 24 months.

16.13.4.2 If the verified MDL is the greater of MDLs or MDLb. If the verified MDL is within 0.5 to 2.0 times the existing MDL and fewer than 3% of the method blank have numerical results above the existing MDL, then the existing MDL may be left unchanged. Otherwise adjust the MDL to the new verified MDL.

16.13.5 Current MDLs may be found in the Limits tab of each testcode in LIMS.

16.14 Limit of Detection (LOD) Verification

16.14.1 Purpose: Validates the established Detection Limit.

16.14.2 Frequency: Prior to sample analysis and verified quarterly Verification must is performed on each instrument. The LOD is spiked at 2-3 times the detection limit for single compound analyses and 1-4 times the detection limit for multi-analyte standards. Sample must be taken through all preparatory steps such as digestion, extraction clean-up, etc.

16.14.2.1 With each MDL study, all compound must be confirmed at a concentration equal to 1-2 time the calculated MDL. To achieve this confirmation multiple concentration may need to be analyzed. Remaining quarterly checks may be performed at 2-3 times the MDL until the next MDL study.

16.14.3 Acceptance Criteria: The apparent signal to noise ratio at the LOD must be at least three and the results must meet all method requirements for analyte identification (e.g., ion abundance, second-column confirmation, or pattern recognition.) For data systems that do not provide a measure of noise, the signal produced by the verification sample must produce a result that is at least three standard deviations greater than the mean method blank concentrations.

16.14.4 Corrective Action: Repeat the Detection Limit Determination and LOD

Verification at a higher concentration or perform and pass two consecutive LOD verifications at a higher concentration and set the LOD at the higher concentration.

16.14.5 Current LOD values may be found in LIMS under the QA Section in the Limit Manager feature.

16.15 Limit of Quantitation (LOQ) Establishment and Verification:

16.15.1 Purpose: Validates the lower quantitation limit of the analysis. Can be performed at 1-2 X the LOQ. Sample must be taken through all preparatory steps such as digestion, extraction clean-up, etc.

16.15.2 Frequency: Prior to sample analysis and verified quarterly.

16.15.3 Acceptance Criteria: Data must empirically demonstrate precision and bias at the LOQ using LCS control limits.

16.15.4 Corrective Action: Identify and correct the source of error, reanalyze the LOQ. If failure persists re-evaluate the appropriateness of the LOQ.
Initial Demonstration of Proficiency – The laboratory must demonstrate initial proficiency with each sample preparation and determinative method combination it utilizes, by generating data of acceptable accuracy and precision for target analytes in a clean matrix. The laboratory must also repeat the following operation annually and whenever new staff members are trained or significant changes in instrumentation are made.

16.15.5 LOQ at time of SOP creation is found in Table 22.1 of this SOP. For latest LOQ confirmation values, see Limit Manager feature in LIMS under the QA Section.

16.16 Data anomalies must be reported using batch Data Review exception reporting or via NCAR reporting. NCARs must be submitted to the department supervisor or QA manager.

16.17 Linear Calibration Range (LCR) - The LCR must be determined initially and verified every six months or whenever a significant change in instrument response is observed or expected. The initial demonstration of linearity must use sufficient standards to insure that the resulting curve is linear. The verification of linearity must use a minimum of a blank and three standards. If any verification data exceeds the initial values by ±10%, linearity must be reestablished. If any portion of the range is shown to be nonlinear, sufficient standards must be used to clearly define the nonlinear portion.

17) Data Records Management

17.1 All data is stored electronically and/or hard copy for 5 years, or 10 years for the state of Louisiana. Data will also be held longer per client's request.

17.2 All analytical sequence IDs and standard preparation information must be recorded in the Run logbook. Hardcopy computer printouts of analytical sequences and raw data must be retained and initialed by the analyst (electronic initials are acceptable). To simplify standard and reagent tracking, analyst must attempt to use single lots of reagents and standards.

17.3 Complete all pertinent sections in the respective logbooks. If not-applicable then line

out the section and "Z" out or "X" out all large sections of the worksheet that are not used. Make all corrections with single line through, date and initial. Make NO obliterations when manually recording data.

17.4 Logbooks are controlled. Never remove a page from a logbook. Completed logbooks are returned to the QA department when filled and no longer needed in the work area.

17.5 SOP effective date is the date noted in the header or last signature date, whichever is most recent.

18) Contingencies for Handling Out of Control Data

18.1 When method required QC exceedances occur, in every case where sample data quality are affected, the source of the QC exceedance must be determined, corrected and sample reanalysis carried out when possible.

18.2 When affected sample analysis can not be repeated due to limitations (i.e. sample availability, or if reanalysis can only be performed after expiration of a sample hold time), the reporting of data associated with exceeded QC data must be appropriately flagged and narrated. This documentation is necessary to define for the data user the effect of the error has upon the data quality of the results reported (e.g. E flag data indicate the result to be only an estimate).

18.3 All analysts must report sufficient comments in laboratory data review checklist for exceeded QC associated with sample results so that project management can further narrate and ensure data qualifiers (flags) are properly assigned to the reported data.

18.4 NCARs must be issued for QC system exceedances. Matrix interferences are reported using the analyte reporting comment section in LIMS or using the Laboratory Data review checklist.

19) Corrective Action for Out-Of-Control Data

19.1 See table 24.3 and section 16 of this SOP for Corrective actions for handling out of control data.

20) Training

20.1 Training to perform the procedures for this method should take the following into consideration:

20.1.1 Review literature (see references section). Read and understand this SOP. Also review the applicable SDS for all reagents and standards used. Following the reviews, observe the procedure performed by an experienced analyst at least three times.

20.1.2 The next training step is to assist in the procedure under the guidance of an

experienced analyst. During this period, the analyst is expected to transition from a role of assisting, to performing the procedure with minimal oversight from an experienced analyst.

20.1.3 Perform initial Demonstration of Capability (IDOC) study as described above for water samples. Summaries of the IDOC are reviewed and signed by the supervisor. Copies may be forwarded to the employee's training file. For applicable tests, IDOC studies should be performed in order to be equivalent to NELAC's Initial Demonstration of Capability.

20.2 Training is documented following *SOP CE-QA003*).

20.3 When the analyst training is documented by the supervisor on internal training documentation forms (HS-QAFORM010 and HS-QAFORM038) the supervisor is acknowledging that the analyst has read and understands this SOP and that adequate training has been given to the analyst to competently perform the analysis independently.

21) Method Performance

21.1 Method performance is determined by:
- 21.1.1 The performance of MDL, LOD, AND LOQ study.
- 21.1.2 Quality control standards in each batch of data.
- 21.1.3 Performance Evaluation Samples.

22) Summary of Changes

Table 22.1 Summary of Changes

Revision Number	Effective Date	Document Editor	Description of Changes
9.3	03/05/2020	G. Moulton	Added Training in section 20
9.3	03/05/2020	G. Moulton	Updated section on method performance
9.3	03/05/2020	G. Moulton	updated section on corrective action for out of control data sec 19
9.3	03/05/2020	G. Moulton	Updated table numbers due to addition of more headers in the SOP.
9.3	03/05/2020	G. Moulton	Removed no longer needed verbiage on equipment and instrument no longer in use in section 9.
9.3	03/05/2020	G. Moulton	Removed repeated definitions in section 3.
9.3	03/05/2020	G. Moulton	Removed task 3 form section 4 in job safety assessment.
9.3	03/05/2020	G. Moulton	Corrected sec 11.3 to say six standards.
9.3	03/05/2020	G. Moulton	Added chlorate to list of elements in section 1.
9.2	11/20/2018	G. Moulton	Updated to new cover page and added new QA Manager
9.2	11/20/2018	G. Moulton	Modified headers of sec 1 and 2
9.2	11/20/2018	G. Moulton	Modified sec 17.1 storage time for data.
9.2	11/20/2018	G. Moulton	Modified sec 21.6 and 21.7
09.2- Section	10/15/2018	C.Stoike	Duplicate frequency defined for one in every 10 field

16.12.3			samples (10%)
09.2- Sections 3.11 & 16.17	10/15/2018	T. Yen	Linear Dynamic Range (LDR) study every 6 months or with major instrument modification.
09.2- Section 16.9.2	10/15/2018	T. Yen	Method Blank (MB) frequency defined as for every batch of 20 or less field samples during normal work shift.
09.2- Section 16.10.2	10/15/2018	T. Yen	Lab Control Sample/Lab Fortified Blank frequency defined as for every batch of 20 or less field samples during normal work shift.
09.1- Section 10.5	06/30/2017	T. Yen	New CCV levels identified on Table 10.5.
09.1- Section 11.6, 12.9 & 16.7	06/30/2017	T. Yen	Alternating between high and low CCV on days when initial calibration was not preformed.
09.1- Section 16.2.2	06/30/2017	T. Yen	DOC period on one calendar year or IDOC must be repeated.
09.1- Section 16.13	06/30/2017	T. Yen	LOD ate1-2 x for certain projects.
09.1- Section 21	06/30/2017	T. Yen	References updated.
09.1- Section 22	06/30/2017	T. Yen	Table 22.7 update with MDL, LOD and Linear Range criteria and corrective action.
09.0	05/15/2015	T. Yen	New SOP format, Lab Director and Inorganics Manager.
09.0 – Sections 3.14, 3.15, 3.23, 3.26	05/15/2015	T. Yen	Surrogate use removed.
09.0 – Sections 16.11 & 16.12	05/15/2015	T. Yen	QC frequency for 300.0 at 10%.
09.0- Section 22	05/15/2015	T. Yen	Updated references.
08.2	08/15/2013	T. Yen	Document format change.
08.2	08/15/2013	T. Yen	Signature Page – QA Manager and Lab Director
08.2 –Sections 12.1 & 12.3.1	08/15/2013	T. Yen	Document syringe and filter lot numbers.
08.2 –Sections 16.14	08/15/2013	T. Yen	New section on linear dynamic range.
08.2 -Section 17.2	08/15/2013	T. Yen	Analyst must make an effect not to use multiple lots of a reagents, solvents, standards or spikes in the preparation or the analytical batch.
08.2 -Section 17.5	08/15/2013	T. Yen	SOP effective date defined.
08.2 – Section 22	08/15/2013	T. Yen	Appendices updated.
08.1	12/15/2011	J. Cady	Minor document revision.
08.0	01/15/2011	R. Pierrot	Updated document to new format. Added level 6 to the calibration table. Revised Section 16 to clarify requirements. Revised the soil preparation procedure to reflect the laboratory practice of 5 grams to 50 mL (12.3.1). Added language allowing the variation in sample amounts for soil preps, as required by matrix. Added the option for variable volume pipettes (9.7)

23) References and Related Documents

23.1 Method 300.0, Determination of Inorganic Anions by Ion Chromatography, USEPA, EMSL – ORD, Cincinnati, Ohio, Revision 2.1, August 1993.

23.2 Method 9056A, Determination of Inorganic Anions by Ion Chromatography, USEPA OSWER, Test Methods for Evaluating Solid Waste Physical/Chemical Methods, Revision 1, February 2007.

23.3 Method 9056, Determination of Inorganic Anions by Ion Chromatography, USEPA OSWER, Test Methods for Evaluating Solid Waste Physical/Chemical Methods, Revision 0, September 1994.

23.4 Dionex Reference Library, May 2006 (CD-ROM)

23.5 ICS3000 Ion Chromatograph Operator's Manual, Rev 01, May 2005, Dionex Corporation, Sunnyvale, CA.

23.6 Current TNI Standards.

23.7 Current Department of Defense Quality Systems Manual.

23.8 EPA MDL Procedure, **Definition and Procedure for the Determination of the Method Detection Limit, Revision 2,** EPA 821-R-16-006. December 2016.

24) Tables, Diagrams, Flowcharts and Validation Data

Table 24.1 300.0 Anion Calibration Acceptance Limits, including ICV

Analyte – water matrix	Low CCV mg/L	SPK mg/L	Low %	High %
Bromide	4.0	10.	90	110
Chloride	20.0	50.0	90	110
Fluoride	4.0	10	90	110
Nitrate-N	4.0	10	90	110
Nitrite-N	4.0	10	90	110
Ortho-Phosphate-P	4.0	10	90	110
Sulfate	20.0	50	90	110
Nitrate/Nitrite – N	8.0	20	90	110

For MDLs (DLs) see QA or LIMS for latest MDLs.

Table 24.2 300.0 Aqueous Spike Levels and Acceptance Limits

Analyte – solid matrix	LCS & MS Spike, mg/L	Low %	High %	RPD %
Bromide	4.0	90	110	20
Chloride	20.0	90	110	20

Fluoride	4.0	90	110	20
Nitrate-N	4.0	90	110	20
Nitrite-N	4.0	90	110	20
Ortho-Phosphate-P	4.0	90	110	20
Sulfate	20.0	90	110	20
Nitrate/Nitrite – N	8.0	90	110	20

For MDLs (DLs) see QA or LIMS for latest MDLs.

Table 24.3 300.0 Solid Spike Levels and Acceptance Limits

Analyte – solid matrix	LCS & MS Spike, mg/L	Low %	High %	RPD %
Bromide	40	90	110	20
Chloride	200	90	110	20
Fluoride	40	90	110	20
Nitrate-N	40	90	110	20
Nitrite-N	40	90	110	20
Ortho-Phosphate-P	40	90	110	20
Sulfate	200	90	110	20
Nitrate/Nitrite – N	80	90	110	20

For MDLs (DLs) see QA or LIMS for latest MDLs.

Table 24.4 9056A Anion Calibration Acceptance Limits, including ICV

Analyte – water matrix	Low Level, mg/L	High Level, mg/L	Low %	High %
Bromide	4.0	10.	90	120
Chloride	20.0	50.0	90	120
Fluoride	4.0	10	90	120
Nitrate-N	4.0	10	90	120
Nitrite-N	4.0	10	90	120
Ortho-Phosphate-P	4.0	10	90	120
Sulfate	20.0	50	90	120
Nitrate/Nitrite – N	8.0	20	90	120

For MDLs (DLs) see QA or LIMS for latest MDLs.

Table 24.5 9056A Aqueous Spike Acceptance Limits

Analyte – solid matrix	LCS & MS Spike, mg/L	Low %	High %	RPD %
Bromide	4.0	80	120	20
Chloride	20.0	80	120	20
Fluoride	4.0	80	120	20

Nitrate-N	4.0	80	120	20
Nitrite-N	4.0	80	120	20
Ortho-Phosphate-P	4.0	80	120	20
Sulfate	20.0	80	120	20
Nitrate/Nitrite – N	8.0	80	120	20

For MDLs (DLs) see QA or LIMS for latest MDLs.

Table 24.6 9056A Solid Spike Acceptance Limits

Analyte – solid matrix	LCS & MS Spike, mg/L	Low %	High %	RPD %
Bromide	40	80	120	20
Chloride	200	80	120	20
Fluoride	40	80	120	20
Nitrate-N	40	80	120	20
Nitrite-N	40	80	120	20
Ortho-Phosphate-P	40	80	120	20
Sulfate	200	80	120	20
Nitrate/Nitrite – N	80	80	120	20

For MDLs (DLs) see QA or LIMS for latest MDLs.

Table 24.7 Summary of Calibration and QC Procedures for EPA Method 300.0 / SW9056A

QC Check	Minimum Frequency	Acceptance Criteria	Corrective Action
Minimum five - point initial calibration for all analytes.	Initial calibration prior to sample analysis.	r ≥0.995	Correct problem then repeat initial calibration. No samples shall be analyzed until ICAL has passed.
Retention Time window position establishment	Once per multipoint calibration.	Position shall be set using the midpoint standard of the ICAL curve when ICAL is performed. On days when ICAL is not performed, the initial CCV is used.	NA
Second-source (ICV) calibration verification, all analytes.	Once immediately following three-point initial calibration.	All analytes within ± 10% of expected value.	Correct problem and/or prepare fresh ICV, then rerun ICV. If that fails, repeat initial calibration. No samples shall be analyzed until ICV has passed.

QC Check	Minimum Frequency	Acceptance Criteria	Corrective Action
Retention Time (RT) window width	At method set-up and after major maintenance (e.g., column change).	RE width is ±3 times standard deviation for each analyte RT over the 24-hour period	Calculated for each analyte.
Retention time window verified for each analyte.	Each calibration verification	± 10% of previous RT.	Prepare and analyze a fresh calibration curve
Calibration verification (CCV and CCB)	CCV and CCB daily before samples and then after every 10 injections and at the end of the analysis sequence. CCV levels must be alternated between the high and low level standards on days when no initial calibration is performed.	All reported analytes within ± 10% of expected value for CCV; analytes in CCB < ½ PQL.	Correct problem, repeat calibration verification and reanalyze all samples since last successful calibration verification.
Demonstration of ability to generate acceptable accuracy and precision using four replicate LCS.	Annually, Once per analyst.	Recovery ±10% of expected value	Recalculate results; locate and fix problem with system, then rerun the demonstration for those analytes that did not meet criteria.
Method blank.	One method blank must be analyzed for every 20 or less field samples	No analytes detected above <1/2 LOQ	Correct problem, and then re-analyze method blank and all samples processed with the contaminated blank.
LCS for all analytes.	One LCS per analytical batch of 20 or less field samples. .	Recovery at ± 10% of expected value for method 300.0. Recovery at ±20% of expected value for SW9056A	Correct problem, and then re-analyze the LCS and all samples in the affected analytical batch.
MS	One MS per every 20 or less field samples per matrix. For Method EPA300.0, one in every 10 or less field samples must be spiked.	Recovery ± 10% of expected value for EPA300.0, and ±20% for SW9056A	Describe in Laboratory Review Checklist.

QC Check	Minimum Frequency	Acceptance Criteria	Corrective Action
LCD/MSD	One duplicate (or MSD) per every 20 or less field samples per matrix. For Method EPA300.0, one in 10 or less field samples must be spiked.	RPD <20%	Describe in Laboratory Review Checklist.
MDL Study	Once per 6 months.	Follow procedure in EPA publication EPA 821-R-16-006, **Definition and Procedure for the Determination of the Method Detection Limit, Revision 2.**	Repeat MDL level spike twice every quarter. Compile data annually with spike standards and method blanks.
LOQ/LOD Study	Once per 3 months.	In LOD must be greater than MDL and less than or equal to PQL. Generally performed ate 2-4 times the MDL concentration. Note some project QA Plans require the LOD to be at 1-2 the MCL concentration. LOQ may be analyzed at 1 or 2 times the LOQ. All compounds must achieve LCS control limits.	LOD does not have acceptance limits, but all method analytical criteria must be achieved. Repeat LOQ if LCS limits are not achieved.
Linear Calibration Range (LCR). If any portion of the range is shown to be nonlinear, sufficient standards must be used to clearly define the nonlinear portion.	The LCR must be determined initially and verified every six months or whenever a significant change is made in the instrumentation.	If any verification data exceeds the initial values by ±10%, linearity must be reestablished.	Repeat LRC if limits are not achieved or revised Linear range in LIMS. Not even if linear is confirm to be greater than upper calibration, lab will not report greater than upper calibration limit.