

**Standard Operating Procedure for
 Determination of Anions By Ion Chromatography in Fresh/Estuarine/Coastal
 Waters
 (References Standard Methods 4110B)**

Document #: NASLDoc-026

**Revision 2019-1
 Effective May 1, 2019**

**I attest that I have reviewed this standard operating procedure and agree to comply
 with all procedures outlined within this document.**

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Revised by: _____ Date: _____

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Laboratory Supervisor: _____ Date: _____

Determination of Anions by Ion Chromatography in Fresh/Estuarine/Coastal Waters

1. SCOPE and APPLICATION

- 1.1 Ion Chromatography is a process that separates ion based on their affinity to the ion exchanger. The separated ion passes through a suppressor where they are converted to their highly conductive acid forms. The ions are identified based on retention times and measured by peak area.
- 1.2 A Method Detection Limit (MDL) of 0.08 mg Cl⁻/L, 0.09 mg SO₄/L, 0.02 mg Br/L was determined using the MDL method as specified in the EPA Federal Register 821-R-16-006, titled Definition and Procedure for the Determination of the Method Detection Limit, Revision 2.
- 1.3 The Quantitation Limit/Reporting Limit for Cl⁻ was set at 0.80 mg Cl⁻/L, SO₄ was set at 0.90 mg SO₄/L, Br was set at 0.08 mg Br/L
- 1.4 The method is suitable for Cl⁻ concentrations 0.08 to 200 mg Cl⁻/L, 0.09 to 200 mg SO₄/L, and 0.02 to 2.0 mg Br/L.
- 1.5 This procedure should be used by analysts experienced in the theory and application of Ion Chromatography analysis. Three months experience with an analyst, experienced in the analysis of anions in aqueous samples, is required.
- 1.6 This method can be used for all programs that require analysis of anions.
- 1.7 This procedure references Standard Methods 4110B.

2. SUMMARY

2.1 Filtered water samples are injected into a stream of eluent and passed through a series of ion exchangers. The separated anions are then passed through a suppressor device and are measured by conductivity.

3. DEFINITIONS

- 3.1 Acceptance Criteria – Specified limits placed on characteristics of an item, process, or service defined in a requirement document. (ASQC)
- 3.2 Accuracy – The degree of agreement between an observed value and an accepted reference value. Accuracy includes a combination of random error (precision) and systematic error (bias) components which are due to sampling and analytical operations; a data quality indicator. (QAMS)
- 3.3 Aliquot – A discrete, measured, representative portion of a sample taken for analysis. (EPA QAD Glossary)
- 3.4 Analytical Range – 5.0-200 mg Cl⁻/L, 5.0-200 mg SO₄/L, 0.06-2 mg Br/L.

- 3.5 Batch – Environmental samples, which are prepared and /or analyzed together with the same process and personnel, using the same lot(s) of reagents. An **analytical batch** is composed of prepared environmental samples (extracts, digestates, concentrates) and/or those samples not requiring preparation, which are analyzed together as a group using the same calibration curve or factor. An analytical batch can include samples originating from various environmental matrices and can exceed 20 samples. (NELAC/EPA)
- 3.6 Blank- A sample that has not been exposed to the analyzed sample stream in order to monitor contamination during sampling, transport, storage or analysis. The blank is subjected to the usual analytical and measurement process to establish a zero baseline or background value and is sometimes used to adjust or correct routine analytical results. (ASQC)
- 3.7 Calibrate- To determine, by measurement or comparison with a standard, the correct value of each scale reading on a device. The levels of the applied calibration standard should bracket the range of planned or expected sample measurements. (NELAC)
- 3.8 Calibration – The set of operations which establish, under specified conditions, the relationship between values indicated by a measuring device. The levels of the applied calibration standard should bracket the range of planned or expected sample measurements. (NELAC)
- 3.9 Calibration Blank – A volume of reagent water fortified with the same matrix as the calibration standards, without analyte added.
- 3.10 Calibration Curve – The graphical relationship between known values, such as concentrations, or a series of calibration standards and their analytical response. (NELAC)
- 3.11 Calibration Method – A defined technical procedure for performing a calibration. (NELAC)
- 3.12 Calibration Standard – A substance or reference material used to calibrate an instrument. (QAMS)
- 3.12.1 Initial Calibration Standard (STD) – A series of standard solutions used to initially establish instrument calibration responses and develop calibration curves for individual target analytes.
 - 3.12.2 Initial Calibration Verification (ICV) – An individual standard, which may be the same compound used as the calibrating standard, but not from the same vendor unless confirmed as different lots, analyzed initially, prior to any sample analysis, which verifies acceptability of the calibration curve or previously established calibration curve.
 - 3.12.3 Continuing Calibration Verification (CCV) – An individual standard, this may be the same as the calibrating standard, and is analyzed after every 10 field sample analyses.

- 3.13 Certified Reference Material (CRM) – A reference material one or more of whose property values are certified by a technically valid procedure, accompanied by or traceable to a certificate or other documentation which is issued by a certifying body. (ISO 17025)
- 3.14 Conditioning Blank- Reagent water (ASTM Type I) analyzed before the calibration curve to decrease the instrument blank and stabilize the column conditions.
- 3.15 Corrective Action – Action taken to eliminate the causes of an existing nonconformity, defect or other undesirable situation in order to prevent recurrence. (ISO 8402)
- 3.16 Deficiency – An unauthorized deviation from acceptable procedures or practices. (ASQC)
- 3.17 Demonstration of Capability – A procedure to establish the ability of the analyst to generate acceptable accuracy. (NELAC)
- 3.18 Detection Limit – The lowest concentration or amount of the target analyte that can be determined to be different from zero by a single measurement at a stated degree of confidence.
- 3.19 Duplicate Analysis – The analyses of measurements of the variable of interest performed identically on two sub samples (aliquots) of the same sample. The results from duplicate analyses are used to evaluate analytical or measurement precision but not the precision of sampling, preservation or storage internal to the laboratory. (EPA-QAD)
- 3.20 External Standard (ES) – A pure analyte (Ammonium Sulfate ($(\text{NH}_4)_2\text{SO}_4$)) that is measured in an experiment separate from the experiment used to measure the analyte(s) in the sample. The signal observed for a known quantity of the pure external standard is used to calibrate the instrument response for the corresponding analyte(s). The instrument response is used to calculate the concentrations of the analyte(s) in the unknown sample.
- 3.21 Field Duplicates (FD1 and FD2) – Two separate samples collected at the same time and place under identical circumstances and treated exactly the same throughout field and laboratory procedures. Analyses of FD1 and FD2 provide a measure of the precision associated with sample collection, preservation and storage, as well as with laboratory procedures.
- 3.22 Holding time – The maximum time that samples may be held prior to analysis and still be considered valid. (40 CFR Part 136) The time elapsed from the time of sampling to the time of extraction or analysis, as appropriate.
- 3.23 Injection- the sample aliquot that is drawn into the syringe and injected into the stream of eluent.
- 3.24 Laboratory Duplicates (LD1 and LD2) – Two aliquots of the same sample taken in the laboratory and analyzed separately with identical procedures. Analyses of LD1 and LD2 indicate precision associated with laboratory procedures, but not with sample collection, preservation, or storage procedures.

- 3.25 Laboratory Reagent Blank (LRB) – A matrix blank (i.e., Reagent water) that is treated exactly as a sample including exposure to all glassware, equipment, solvents, and reagents that are used with other samples. The LRB is used to determine if method analytes or other interferences are present in the laboratory environment, the reagents, or the instrument.
- 3.26 Laboratory Control Sample (LCS) – A sample matrix, free from the analytes of interest, spiked with verified known amounts of analytes from a source independent of the calibration standard or a material containing known and verified amounts of analytes. The LCS is generally used to establish intra-laboratory or analyst-specific precision and bias or to assess the performance of all or a portion of the measurement system. (NELAC)
- 3.27 Limit of Detection (LOD) – The lowest concentration level that can be determined by a single analysis and with a defined level of confidence to be statistically different from a blank. (ACS)
- 3.28 Limit of Quantitation (LOQ) – The minimum levels, concentrations, or quantities of a target variable (target analyte) that can be reported with a specified degree of confidence. The LOQ is set at 3 to 10 times the LOD such that it is \geq the lower standard. This is also referred to as the Quantitation Limit.
- 3.29 Linear Dynamic Range (LDR) – The absolute quantity over which the instrument response to an analyte is linear. This specification is also referred to as the Linear Calibration Range (LCR).
- 3.30 Material Safety Data Sheets (MSDS) – Written information provided by vendors concerning a chemical’s toxicity, health hazards, physical properties, fire, and reactivity data including storage, spill, and handling precautions.
- 3.31 May – Denotes permitted action, but not required action. (NELAC)
- 3.32 Method Detection Limit (MDL) – The minimum concentration of an analyte that can be identified, measured, and reported with 99% confidence that the analyte concentration is greater than zero (Standard Methods).
- 3.33 Must – Denotes a requirement that must be met. (Random House College Dictionary)
- 3.34 Precision – The degree to which a set of observations or measurements of the same property, obtained under similar conditions, conform to themselves; a data quality indicator. Precision is usually expressed as standard deviation, variance or range, in either absolute or relative terms. (NELAC)
- 3.35 Preservation – Refrigeration, freezing, and/or reagents added at the time of sample collection (or later) to maintain the chemical and or biological integrity of the sample.
- 3.36 Quality Control Sample (QCS) – A sample of analyte of known and certified concentration. The QCS is obtained from a source

external to the laboratory and different from the source of calibration standards. It is used to check laboratory performance with externally prepared test materials. Also referred to as CRM.

- 3.37 Run Cycle – Typically a day of operation – the entire analytical sequence from sampling the first standard to the last sample of the day.
- 3.38 Sample Volume- Amount of sample injected into the stream of eluent.
- 3.39 Sample Tray –Metal tray that holds auto analyzer vials containing samples or standards. The user identifies each vial in the operating software.
- 3.40 Sample Tray Holder – An automated carousel that contains up to six sample segments. This carousel spins in clockwise manner to move the sample trays into position for analysis.
- 3.41 Sensitivity – The capability of a test method or instrument to discriminate between measurement responses representing different levels (concentrations) of a variable of interest.
- 3.42 Shall – Denotes a requirement that is mandatory whenever the criterion for conformance with the specification requires that there be no deviation. (ANSI)
- 3.43 Should – Denotes a guideline or recommendation whenever noncompliance with the specification is permissible. (ANSI)
- 3.44 Standard Reference Material (SRM) – Material which has been certified for specific analytes by a variety of analytical techniques and/or by numerous laboratories using similar analytical techniques. These may consist of pure chemicals, buffers, or compositional standards. The materials are used as an indication of the accuracy of a specific analytical technique. Also referred to as CRM.

4 INTERFERENCES

- 4.1 Any substance in a sample that has a retention time that coincided with the retention time of any anion.
- 4.2 A high concentration of anion can cause interference with resolution and possibly cause carryover to other ions. Dilute sample and reanalyze.
- 4.3 Contaminants in reagent water.





5 SAFETY

- 5.1 Safety precautions must be taken when handling reagents, samples and equipment in the laboratory. Protective clothing including lab coats, safety glasses and enclosed shoes must be worn. In certain situations, it will be necessary to also use gloves and/or a face shield. If solutions come in contact with eyes, flush with water continuously for 15 minutes. If solutions come in contact with skin, wash thoroughly with soap and water. Contact Solomons Rescue Squad (911) if emergency treatment is needed and also inform the CBL Associate Director of Administration and Facilities Maintenance of the incident. Contact the CBL

Associate Director of Administration and Facilities Maintenance if additional treatment is required.

- 5.2 The toxicity or carcinogenicity of each reagent used in this procedure may not have been fully established. Each chemical should be regarded as a potential health hazard and exposure should be as low as reasonably achievable. Cautions are included for known hazardous materials and procedures.
- 5.3 Do not wear jewelry when troubleshooting electrical components. Even low voltage points are dangerous and can injure if allowed to short circuit.
- 5.4 The following hazard classifications are listed for the chemicals used in this procedure. Detailed information is provided on Material Safety Data Sheets (MSDS).

Table 1

Chemical	Health Hazard	Fire Hazard	Instability Hazard	Specific Hazard	
Potassium Sulfate	0	0	0		
Sodium Chloride	1	0	0		
Sodium Bromide	2	0	0		
Methane sulfonic Acid	3	1	0	COR,IRR	
Potassium Hydroxide	3	0	0	COR,IRR	

On a scale of 0 to 4 the substance is rated on four hazard categories: health, flammability, reactivity, and contact. (0 is non-hazardous and 4 is extremely hazardous)

HAZARD RATING

Health Hazard - Blue: 4 – deadly, 3 – extreme danger, 2 – hazardous, 1 – slightly hazardous, 0 – normal material

Fire Hazard - Red: Flash Points: 4 – below 73° F, 3 – below 100° F, 2 – below 200° F, 1 – above 200° F, 0 – will not burn

Instability Hazard - Yellow: 4 – may detonate, 3 – Shock and heat may detonate, 2 – violent chemical change, 1 – unstable is heated, 0 - stable

Specific Hazard - White: Acid = ACID, Alkali = ALK, Corrosive = COR, Oxidizer = OXY

6 EQUIPMENT AND SUPPLIES

- 6.1 Dionex ICS-5000+ Reagent-Free Ion Chromatography System. Chromeleon 7.2 operating software on a computer running Microsoft Windows 7 operating system.
- 6.2 Refrigerator, capable of maintaining 4 +/- 2°C.
- 6.3 Lab ware – All reusable lab ware (glass, Teflon, plastic, etc.) should be sufficiently clean for the task objectives. This laboratory cleans all lab ware related to this method with a 10% HCl (v/v) acid rinse.

7 REAGENTS AND STANDARDS

- 7.1 Purity of Water – Unless otherwise indicated, references to water shall be understood to mean reagent water conforming to Specification D 1193, Type I. Freshly prepared water should be used for making the standards intended for calibration. The detection limits of this method will be limited by the purity of the water and reagents used to make the standards.
- 7.2 Purity of Reagents – Reagent grade chemicals shall be used in all tests. Unless otherwise indicated, it is intended that all reagents shall conform to specifications of the Committee on Analytical Reagents of the American Chemical Society, where such specifications are available. Other grades may be used, provided it is first ascertained that the reagent is of sufficiently high purity to permit its use without compromising the accuracy of the determination.

7.3 Methane Sulfonic Acid

Doinex EGC III MSA Methanesulfonic Acid Eluent Generator Cartridge purchased from Thermo Fisher Scientific. Product#074535, CAS#1310-58-3.

7.4 Potassium Hydroxide

Dionex EGC III KOH Potassium Hydroxide Eluent Generator Cartridge purchased from ThermoFisher Scientific. Product#074532, CAS#73-75-2.

7.5 Bromide Stock Standard–

Sodium Bromide	0.6438 g
Reagent water	up to 500 mL

In a 500 mL volumetric flask, dissolve 0.6438 g of Sodium Bromide in ~400 mL of reagent water. Dilute to 500 mL with reagent water (1mg Br/mL). Write name of preparer, preparation date, standard manufacturer, manufacturer lot number in the Analytical Standard log book. Make fresh every 6 months.

7.6 Chloride Stock Standard –

Sodium Chloride	0.8243 g
Reagent water	up to 500 mL

In a 500 mL volumetric flask, dissolve 0.8243 g of Sodium Chloride in ~400 mL of reagent water. Dilute to 500 mL with reagent water (1mg Cl⁻

/mL). Write name of preparer, preparation date, standard manufacturer, manufacturer lot number in the Analytical Standard log book. Make fresh every 6 months.

7.7 Sulfate Stock Standard –
Potassium Sulfate
Reagent water

0.9070 g
up to 500 mL

In a 500 mL volumetric flask, dissolve 0.9070 g of Potassium Sulfate in ~400 mL of reagent water. Dilute to 500 mL with reagent water (1mg SO₄/mL). Write name of preparer, preparation date, standard manufacturer, manufacturer lot number in the Analytical Standard log book. Make fresh every 6 months.

8 SAMPLE COLLECTION, PRESERVATION, AND STORAGE

8.1 Water collected for anions should be filtered through a Whatman GF/F glass fiber filter (nominal pore size 0.7 µm), or equivalent.

8.2 Water collected for anions should be stored at 4°C. The sample container should be clean and sample rinsed.

8.3 Anion samples may be stored up to 28 days at 4°C.

9 QUALITY CONTROL

9.1 The laboratory is required to operate a formal quality control (QC) program. The minimum requirements of this program consist of an initial demonstration of laboratory capability and the continued analysis of laboratory instrument blanks and calibration standard material, analyzed as samples, as a continuing check on performance. The laboratory is required to maintain performance records that define the quality of data generated.

9.2 Initial Demonstration of Performance

9.2.1 The initial demonstration of capability (iDOC) – is used to characterize instrument performance (MDLs) and laboratory performance (analysis of QC samples) prior to the analyses conducted by this procedure.

9.2.2 Linear Dynamic Range – LDR (Linear Calibration Range) should be established using appropriate six or seven point calibration curve.

9.2.3 Quality Control Sample (QCS/SRM) – When using this procedure, a quality control sample is required to be analyzed at the beginning of the run and every batch, to verify data quality and acceptable instrument performance. If the determined concentrations are not within $\pm 3s$ of the certified values, performance of the determinative

step of the method is unacceptable. The source of the problem must be identified and corrected before either proceeding with the initial determination of MDL_s or continuing with analyses.

9.2.4 Method Detection Limits (MDL_s) – Initial MDL_s should be established for Anions using a spiked water sample, typically two to ten times the estimated MDL and no more than ten times higher than the estimated MDL. Process a minimum of seven spiked samples and seven blank samples through all steps of the method. The samples used for the MDL must be prepared and analyzed in at least three batches on three separate calendar dates. If multiple instruments are used for this analysis, MDL_s must include data/calculations from all instruments.

9.2.4.1 Make all computations as specified in the analytical method and express the final results in the method-specified reporting units.

9.2.4.2 Calculate the sample standard deviation (S) of the replicate spiked sample measurements and the sample standard deviation of the replicate method blank measurements from all instruments to which the MDL will be applied.

9.2.4.3 Compute the MDL_s (the MDL based on spiked samples) as follows:

$$MDL_s = t_{(n-1, 1-\alpha=0.99)} S_S$$

Where:

MDL_s = the method detection limit based on spiked samples

$t_{(n-1, 1-\alpha=0.99)}$ = the Student's t-value appropriate for a single-tailed 99th percentile

t statistic and a standard deviation estimate with n-1 degrees of freedom.

S_S = sample standard deviation of the replicate spiked sample analyses.

9.2.4.4 Compute the MDL_b (the MDL based on method blanks) as follows:

If none of the method blanks give numerical results for an individual analyte, the MDL_b does not apply. A numerical result includes both positive and negative results, including results below the current MDL, but not results of “ND” (not detected) commonly observed when a peak is not present in chromatographic analysis.

If some (but not all) of the method blanks for an individual analyte give numerical results, set the MDL_b equal to the highest method blank result. If more than 100 method blanks are available, set MDL_b to the level that is no less than the 99th percentile of the method blank results. For “n” method blanks where n ≥ 100, sort the method blanks in rank order. The (n * 0.99) ranked method blank result (round to the nearest whole number) is the MDL_b. For example, to find MDL_b from a set of 164 method blanks where the highest ranked method blank results are ... 1.5, 1.7, 1.9, 5.0, and 10, then 164 x 0.99 = 162.36 which rounds to the 162nd method blank result.

Therefore, MDL_b is 1.9 for n =164 (10 is the 164th result, 5.0 is the 163rd result, and 1.9 is the 162nd result). Alternatively, you may use spreadsheet algorithms to calculate the 99th percentile to interpolate between the ranks more precisely.

If all of the method blanks for an individual analyte give numerical results, then calculate the MDL_b as:

$$MDL_b = \bar{X} + t_{(n-1, 1-\alpha=0.99)} S_b$$

Where:

MDL_b = the MDL based on method blanks

\bar{X} = mean of the method blank results (use zero in place of the mean if the mean is negative)

$t_{(n-1, 1-\alpha=0.99)}$ = the Student’s t-value appropriate for the single-tailed 99th percentile t statistic and a standard deviation estimate with n-1 degrees of freedom.

S_b = sample standard deviation of the replicate method blank sample analyses.

9.2.4.5 The verified MDL is the greater of the MDL_s or MDL_b. If the verified MDL is within 0.5 to 2.0 times the existing MDL and fewer than 3% of the method blank results (for the individual analyte) have numerical results above the existing MDL, then the existing MDL may optionally be left unchanged. Otherwise, adjust the MDL to the new verification MDL. (The range of 0.5 to 2.0 approximates the 95th percentile confidence interval for the Initial MDL determination with six degrees of freedom.)

9.2.4.6 The MDL should be determined annually, whenever there is a significant change in instrumental response or a significant change in instrument configuration. Data for annual MDL calculation and verification is analyzed at least quarterly, throughout the year.

9.3 Assessing Laboratory Performance

- 9.3.1 Laboratory Reagent Blank (LRB) – The laboratory must analyze at least one LRB with each batch of samples. The LRB consists of Nanopure water treated the same as the samples. Analyte found in LRB indicates possible reagent or laboratory environment contamination. LRB data are used to assess and correct contamination from the laboratory environment
- 9.3.2 Quality Control Sample (QCS)/ Standard Reference Material (SRM) – When using this procedure, a quality control sample is required to be analyzed at the beginning of the run and every batch, to verify data quality and acceptable instrument performance. If the determined concentrations are not within $\pm 3s$ of the certified values, performance of the determinative step of the method is unacceptable. The source of the problem must be identified and corrected before either proceeding with the initial determination of the MDL or continuing with the analyses. The results of these QCS/SRM samples shall be used to determine batch acceptance.
- 9.3.3 The QCS are obtained from a source external to the laboratory and different from the source of calibration standards.
- 9.3.4 Control Charts – The Accuracy Control Chart for QCS/SRM samples is constructed from the average and standard deviation of the 20 most recent QCS/SRM measurements. The accuracy chart includes upper and lower warning levels ($WL=\pm 2s$) and upper and lower control levels ($CL=\pm 3s$). These values are derived from stated values of the QCS/SRM. The standard deviation (s) is specified relative to statistical confidence levels of 95% for WLs and 99% for CLs. Enter QCS/SRM results on the chart each time the sample is analyzed
- 9.3.5 Calibration Verification, Initial and Continuing (ICV/CCV) – Immediately following calibration (ICV) and following every 10 samples (CCV), one calibration verification of a CRM falling within the middle of the curve is analyzed to assess instrument performance. The CCVs are to be within the expected value $\pm 3s$. Failure to meet the criteria requires correcting the problem, including reanalysis of any affected samples. If not enough sample exists, the data must be qualified if reported.

9.4 Assessing Analyte Recovery - Percent Recovery

- 9.4.1 Analyte recovery is assessed through percent recoveries of laboratory spikes of samples.

9.4.2 Percent Recovery = (Actual value/Expected value) X 100.

9.5 Assessing Analyte Precision – Relative Percent Difference

9.5.1 Analyte replication is assessed through duplicate analyses of samples – Relative Percent Difference.

9.5.2 $RPD = (|Laboratory\ Duplicate\ Result\ 1 - Laboratory\ Duplicate\ Result\ 2|) / [(Laboratory\ Duplicate\ Result\ 1 + Laboratory\ Duplicate\ Result\ 2) / 2] \times 100$

9.6 Corrective Actions for Out of Control Data

9.6.1 Control limit – If one measurement exceeds Accuracy Control Chart CL, repeat the analysis immediately. If the repeat measurement is within the CL, continue analyses; if it exceeds the CL, discontinue analyses and correct the problem.

9.6.2 Warning limit – If two out of three successive points exceed Accuracy Control Chart WL, analyze another sample. If the next point is within WL, continue analyses; if the next point exceeds the WL, evaluate potential bias and correct the problem.

9.6.3 Trending – If seven successive Accuracy Control Chart measurements are on the same side of the central line, discontinue analyses and correct the problem.

9.6.4 When external QCS samples are out of control, correct the problem. Reanalyze the samples analyzed between the last in-control measurement and the out-of-control one.

9.6.5 When external CCV samples are out of control, correct the problem. Reanalyze the samples analyzed between the last in-control measurement and the out-of-control one.

9.7 General Operation - To assure optimal operation and analytical results, the Reagent Blank and CCV are tracked daily in the raw data file, copied to Reagent Blank and CCV Control Charts.

Table 2

QC Indicator	Acceptance/ Action Limits	Action	Frequency (Batch)
Correlation Coefficient	≥ 0.995	If <0.995, evaluate data points of the calibration curve. If any data point is outside established limits, reject as outlier.	1 per batch if acceptable.
Quality Control Sample (QCS)/ Certified Reference Material (CRM)	± 10%	If QCS value is outside ± 10% of the target value reject the run, correct the problem and rerun samples.	Beginning of run and every 20 samples.

Initial Calibration Verification (ICV)	± 10%	Recalibrate if outside acceptance limits.	Beginning of run following standard curve.
Continuing Calibration Verification (CCV)	± 10%	If outside 10%, correct the problem. Rerun all samples following the last in-control CCV.	After every 20 samples.
Method Blank/Laboratory Reagent Blank (LRB)	≤ Method Quantitation Limit	If the LRB exceeds the quantitation limit, results are suspect. Rerun the LRB. If the concentration still exceeds the quantitation limit, reject or qualify the data, or raise the quantitation limit.	Following the ICV and after every 20 samples following the CRM.
Laboratory Fortified Sample Matrix Spike	± 10%	If the recovery of any analyte falls outside the designated acceptance limits and the QCS is in control, the recovery problem is judged matrix induced. Repeat the LFM and if the sample results are again outside the acceptable recovery range, the sample should be reported with a “matrix induced bias” qualifier.	1/10 (Spike or duplicate)
Laboratory Duplicate	±10%	If the RPD fails to meet the acceptance limits, the samples should be reanalyzed. If the RPD again fails to meet the acceptance limits, the sample must be reported with a qualifier identifying the sample analysis result as not having acceptable RPD for duplicate analysis.	1/10 (Spike or duplicate)

10 CALIBRATION AND STANDARDIZATION

10.1 Calibration – Daily calibration must be performed before sample analysis may begin. Six or seven point calibrations are used with the calibrations that cover the analytical range. The following outlines the preparation of the working standards.

10.2 Chloride Working Standards-

In a 100 mL volumetric flask add the corresponding volume of stock standard from Table 3 in ~40 mL reagent water. Dilute to 100 mL with reagent water. Write name of preparer, preparation date, standard manufacturer, manufacturer lot number in the Analytical Standard log book. Make fresh every 3 months. Store at 4° C.

Table 3

Chloride Stock Standard Volume (mL)	Chloride Concentration (mg/mL)
0.5	5.0
1.0	10.0
2.0	20.0
3.0	30.0
4.0	40.0
10.0	100.0
20.0	200.0

10.3 Sulfate Working Standards-

In a 100 mL volumetric flask add the corresponding volume of stock standard from Table 4 in ~40 mL reagent water. Dilute to 100 mL with reagent water. Write name of preparer, preparation date, standard manufacturer, manufacturer lot number in the Analytical Standard log book. Make fresh every 3 months. Store at 4° C.

Table 4

Sulfate Stock Standard Volume (mL)	Sulfate Concentration (mg/mL)
0.5	5.0
1.0	10.0
2.0	20.0
3.0	30.0
4.0	40.0
10.0	100.0
20.0	200.0

10.4 Bromide Working Standards –

In a 100 mL volumetric flask add the corresponding volume of stock standard from Table 5 in ~40 mL reagent water. Dilute to 100 mL with reagent water. Write name of preparer, preparation date, standard manufacturer, manufacturer lot number in the Analytical Standard log book. Make fresh every 3 months. Store at 4° C.

Table 5

Bromide Stock Standard Volume (mL)	Bromide Concentration (mg/mL)
0.00625	0.0625
0.0125	0.125
0.025	0.25
0.05	0.50
0.10	1.00
0.20	2.00

10.2 The instrument prepares a standard curve for each set of calibrators. A graph plotting measured $\mu\text{S}^*\text{min}$ against standard concentration is presented. One standard value for each and every standard is incorporated in the curve. The coefficient of determination (Pearson's r value) for the calibration curve as well as the calculated concentration of each calibrator is reviewed. The calculated value of each calibrator must be within ten percent of the expected value. The coefficient of determination (Pearson's r value) for the calibration curve must be greater than 0.995.

11 PROCEDURE – DAILY OPERATIONS QUALITY CONTROL

- 11.1 Instrument constantly runs in idle mode. Initiate Chromeleon 7.2 software.
- 11.2 In the software on the Home tab turn off the pump flow, eluent generator and suppressor by clicking the toggle switch next to each module.
- 11.3 Discard any water remaining in the eluent reagent bottle from the previous analytical run. Fill the eluent reagent bottle with fresh reagent water.
- 11.4 Discard any water remaining in the syringe bottle from the previous run. Fill the syringe bottle with fresh reagent water.
- 11.5 Prime the pump by opening the purge valve $\frac{1}{4}$ turn.
- 11.6 Under the instrument tab in the software, in UMD ICS5000 Anions tab under Pump 1 tab prime pump for at least 500 seconds at a flow rate of 5.00 mL/min, click prime button to initiate pump prime.
- 11.7 Once prime is completed close purge valve.
- 11.8 Under the home tab turn pump on and set flow rate at 0.250 mL/min.
- 11.9 Under the home tab turn on eluent generator and set concentration to 10mM KOH.
- 11.10 Under the home tab turn on suppressor and set current at 13mA.
- 11.11 Temperature controls should remain on.
- 11.12 Check the pressure under the pump_1 tab. Pressure must be at ~ 2000 psi otherwise the pump will shut off.
- 11.13 Under the sampler tab prime syringe at least 20 cycles to ensure no bubbles are in the syringe and water line.
- 11.14 Allow instrument to equilibrate for one hour.
- 11.15 After one hour, under the CD-Left tab, total signal should be at $\sim 0.300 \mu\text{S}$.
- 11.16 Gather working standards from refrigerator. Assess standards and remake anything that has exceeded the time over which it is considered stable.
- 11.17 Begin daily bench sheet documentation.
- 11.18 Check salinity values for each sample. Based on the salinity values the sample may require dilution.

Table 6

Salinity Value (ppt)	Dilution Factor
0.3-0.4	X2
0.5-1.75	X5

1.76-3.9	X10
>3.9	X20

- 11.19 Load working standards and samples into clean sample rinsed 10mL auto sampler vials.
- 11.20 Under the sampler tab tray controls, remove each tray from instrument and load each tray with standards and samples. Instrument is loaded as follows: standards, CRM, blank then samples. Throughout the analytical batch, samples are chosen as laboratory duplicates and laboratory spikes to assess analyte precision and analyte recovery, respectively. Insert corresponding trays back into instrument.
- 11.21 Under the Data tab in the Anions folder for 2019 create a sequence from the menu bar. A window will pop up click on Anions, enter the number of samples and name the folder the analysis date.
- 11.22 Copy and paste the Instrument Method, Processing Method, and Report Template from a previous sequence into the sequence just created.
- 11.23 Under the new sequence in the name column enter the standards and the names of the samples loaded. Instrument is loaded as follows: Two conditioning blanks, standards, CRM, blank then samples. Standard Reference Material (SRM) samples are analyzed every 20 samples, and Laboratory Reagent Blanks (LRB) are analyzed every 20 samples following CRM.
- 11.24 In the instrument method column select the 10-45mMGrad_1 method. Copy down for all.
- 11.25 In the processing method column select Anions_1. Copy down for all.
- 11.26 The last injection should be water blank and the instrument method should be LowFlow20Mm_Iso.
- 11.27 In the type column for the standards change the drop down selection to read calibration standard. All other samples should remain as unknown.
- 11.28 In the level column for the standards change the drop down selection to one for the lowest standard through seven for the highest standard.
- 11.29 In the position column enter the tray position that each standard and sample corresponds with.
- 11.30 Volume column should be set at 10 μ L.
- 11.31 Save run.
- 11.32 Click start.
- 11.33 As calibration curves are produced by the instrument, review them for acceptability. The instrument software prepares a standard curve for each Anion. A graph plotting measured μ S*min against standard concentration is presented. If acceptance criteria are not met the entire curve shall be reanalyzed. One standard value for each and every calibrator is incorporated in the curve.
- 11.34 If results fall outside acceptance limits, the sample should be reanalyzed. If sample result exceeds the highest standard of the highest calibration range, the samples will need to be diluted and reanalyzed.

12 DATA ANALYSIS AND CALCULATIONS

- 12.1 Upon completion of all analysis, under the Report Designer tab print Summary Report. Under the Electronic Report tab export Peak integration Report, Calibration Report, and Summary Report. Results are exported to a DATA folder on the desktop. The file is named by the analysis date. The report file for analytical batch of January 1, 2017 would be named 010117. The file is saved as a PDF file.
- 12.2 The instrument software has calculated final sample concentration from the designated standard curve. Dilution will require further calculation before the data can be finalized. The analyst examines each row of data. Results are eliminated that are outside the limits of the calibration range.

13 REFERENCES

- 13.1 Parsons, T.R., Y. Maita and C.M. 1984. A Manual of Chemical and Biological Methods for Seawater Analysis, Pergamon Press, Elmsford, N.Y.
- 13.2 Kerouel, R. and A. Aminot. 1987. Procédure optimisée hors-contaminations pour l'analyse des éléments nutritifs dissous dans l'eau de mer. Mar. Environ. Res 22:19-32.