DETERMINATION OF SULFATE, CHLORIDE, BROMIDE, AND NITRATE USING THE DIONEX ION CHROMATOGRAPHY SYSTEM

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1. SCOPE AND APPLICATION

1.1. This method details the determination of sulfate, chloride, bromide, and nitrate, in aqueous matrices (drinking, fresh and saline surface waters, effluents, influents). The calibration range is from 0.25 to 120 mg Cl/L for chloride, 0.25 to 80 mg SO_4^{2-}/L for sulfate, 0.020 to 1.0 mg Br/L for bromide, and 0.080 to 10 mg N/L for nitrate. The range may be extended by dilution. The MDL for sulfate and chloride is 0.20 mg/L, for nitrate 0.050 mg N/L, and for bromide 0.013 mg/L. The PQL for chloride is 0.50 mg Cl/L, 0.50 mg SO_4^{2-}/L for sulfate, 0.040 mg Br/L for bromide, and 0.15 mg N/L for nitrate.

1.2. The aqueous tests covered are W-SO4-IC(-F), W-CL-IC(-F), W-Br-IC(-F), and W-NO3-IC(-F).

2. SUMMARY OF THE METHOD

2.1. This method is based on EPA method 300.0, Rev. 2.1 (1993).

2.2. Anions of interest are separated in an ion chromatograph using an anion-exchange column and potassium hydroxide eluent. Once separated, the anions pass through an anion suppressor where they are converted to their more conductive acid forms and the potassium hydroxide eluent is converted to less conductive water. The separated anions in their acid forms are measured by a conductivity detector and are identified on the basis of their retention times as compared to standards.

2.3. Depending on the needs of the analysis, two analysis methods are available: chloride, sulfate, and nitrate analysis on the AS18-4 µm 2x150 mm analytical column, and chloride, sulfate, and bromide analysis on the AS19-4 µm 2x250 mm analytical column. 2.5 µL injection volume and potassium hydroxide eluent are used in both methods. Each method uses a column guard to protect the analytical column. For the AS18 method, a Carbonate Removal Device (CRD) is installed after the suppressor to remove carbonate from the anion mixture. The AS19 method does not use the CRD.

2.4. Ion chromatography eliminates the need to use hazardous reagents and it effectively distinguishes among the halides (Br^-, Cl^-, and F^-) and the oxy-anions (SO_3^-, SO_4^-, NO_2^-, and NO_3^-).

2.5. For a description of possible interferences, see 300.0, Rev. 2.1 (1993).

3. EQUIPMENT AND SUPPLIES

3.1. Dionex Ion Chromatography System:

3.1.1. Dionex IC-5000+

3.1.2. Dionex AS-AP

3.1.3. PC with Chromeleon (version 7.2 or greater) software

3.1.4. Dionex AS 18-4 µm 2x150 mm column (Dionex P/N 076036) or Dionex AS 19-4 µm 2x250 mm column (Dionex P/N 083223).

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3.1.5. Dionex IonPac AG18-4µm 2x30 mm guard column (P/N 076037) or Dionex IonPac AG19-4µm 2x50 mm guard column (P/N 083225).

3.1.6. Thermo Scientific KOH Eluent Generation Cartridge (Dionex P/N 075778).

3.1.7. Dionex ADRS 600 2mm suppressor (Dionex P/N 088667).

3.1.8. Thermo Scientific 1 mL AS-AP syringe (Dionex P/N 074307) or Thermo Scientific 250 µL AS-AP syringe (Dionex P/N 074306).

3.1.9. Dionex CRD 200 200 µL (Dionex P/N 062986).

3.1.10. Dionex CR-ATC 500 Continuously Regenerated Anion Trap Column (Dionex P/N 075550).

3.2. Consumable parts used by the instrument which are either disposable after one use or frequently replaced:

3.2.1. Thermo Scientific 1.5 mL Polyprop vials (Dionex P/N 079812 100 pk).

3.2.2. Thermo Scientific PS 10 mL vials with cap (Dionex P/N 074228 100 pk).

3.2.3. High pressure VIPER PEEK fittings (P/N 22000-98001)

3.2.4. High Pressure VIPER ferrules (P/N 043276)

3.2.5. Assortment of PEEK tubing

3.3. Class A glassware and pipets for preparing samples, spikes, reagents, and standards.

3.4. 10 mL disposable syringes and 25 mm syringe filters (0.45 µm pore size), for prefiltering samples.

3.5. Tools for instrument maintenance (at least adjustable wrenches, hex keys, and a sharp probing tool)

3.6. Parafilm

3.7. A properly calibrated analytical balance, spatula, and weigh boats for weighing dry standards and reagents

3.8. Disposable polystyrene beakers to use in preparing dilutions or spikes

3.9. Transfer pipettes

4. REAGENTS AND STANDARDS (SEE DEP SOPS NU-041 AND NU-042)

Note: Before preparing reagents or standards, or running samples, please read the safety notes in the safety/hazardous waste section of this SOP and the MSDS for the chemicals used in this analysis.

Note: Reagent and standard preparations must be documented in the Laboratory Information Management System (LIMS) 'Standard Preparation Tracker' module. Unique ID numbers for each standard and reagent are generated in the module and documented in

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the standard and reagent sheets submitted with each analysis folder. If available, a Certificate of Analysis for each purchased standard or reagent is maintained in the \\FLDEP1\DEAR\Labs\lab3\Chem_Data\Inorganic\Nutrients\REAGENT_PREP\IC\Certificates of Analysis folder. All containers holding standards or reagents must be labeled with their unique ID and expiration date.

Note: The volumes prepared for the reagents and standards may be altered by the analyst as necessary. The final concentrations of the constituents of a standard or reagent must not be changed.

4.1. Deionized (DI) water.

4.2. Eluent is automatically generated through the KOH Eluent Generator cartridge using DI water.

4.3. Other solvents (HPLC or ACS grade) for cleaning.

4.4. Stock Standards – Standards are prepared from ACS certified reagent grade materials, dried at 105 ºC for 24 hours and cooled in a desiccator. Holding time, 180 days. Store in refrigerator:

4.4.1. Stock Chloride, 10,000 mg Cl^-/L - Dissolve 21.0282 g potassium chloride in DI water and dilute to 1 L.

4.4.2. Stock Sulfate, 10,000 mg SO_4^{2-}/L - Dissolve 18.1402 g potassium sulfate in DI water and dilute to 1 L.

4.4.3. Stock Nitrate, 1000 mg N/L - Dissolve 3.6091 g potassium nitrate DI water and dilute to 500 mL.

4.4.4. Stock Bromide, 1000 mg Br^-/L, can be purchased (Ricca Chemical, cat# 1180-4, **1000 mg Br^-/L**). Alternative preparation method is to dissolve 1.2877 g of dried sodium bromide in DI water and dilute to 1 L.

4.4.5. 100 ppm Bromide Spike - Using a calibrated Eppendorf micropipet, place 1 ml of 1000 ppm Stock Bromide solution in 10 mL volumetric flask partially filled with DI water and dilute to mark with DI water. Holding time, 180 days. Store in the refrigerator.

4.4.6. Stock Carbonate, 10,000 mg $CaCO_3$/L – Dissolve 1.0606 g Na_2CO_3 in DI water and dilute to 100 mL. <u>This standard may be used only as a reference.</u>

<u>Note</u>: Large amounts of carbonate in samples are known to interfere with sulfate peak quantitation in the AS19 method. Carbonate may be added to an existing standard (see below) or prepared as a separate standard to be used as reference for evaluation of possible carbonate interferences.

4.5. Calibration Standards (Table 1) - Using a calibrated Eppendorf micropipet, place the appropriate volume of stock (4.4) for each analyte in a 250 mL volumetric flask partially filled with DI water and dilute to mark with DI water. Standards can also be prepared using instrument auto-dilution. Holding time, 30 days. Store in the refrigerator.

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Table 1.

	Chloride		Sulfate		Nitrate		Bromide	
	fin. conc.	**stock vol.**	**fin. conc.**	**stock vol.**	**fin. conc.**	**stock vol.**	**fin. conc.**	**stock vol.***
STD1	0.25 ppm	6.25 µL	0.25 ppm	6.25 µL	0.080 ppm	20.0 µL	0.020 ppm	50.0 µL
STD2	0.50 ppm	12.5 µL	0.50 ppm	12.5 µL	0.10 ppm	25.0 µL	0.040 ppm	10.0 µL
STD3	1.0 ppm	25.0 µL	1.0 ppm	25.0 µL	0.20 ppm	50.0 µL	0.050 ppm	12.5 µL
STD4	2.5 ppm	62.5 µL	2.5 ppm	62.5 µL	0.50 ppm	125 µL	0.08 ppm	20.0 µL
STD5	5.0 ppm	125 µL	5.0 ppm	125 µL	1.0 ppm	250 µL	0.20 ppm	50.0 µL
STD6	12 ppm	300 µL	8.0 ppm	200 µL	1.0 ppm	250 µL	0.40 ppm	100 µL
STD7	30 ppm	750 µL	20 ppm	500 µL	2.5 ppm	625 µL	0.50 ppm	125 µL
STD8	120 ppm	3000 µL	80 ppm	2000 µL	10 ppm	2500 µL	1.0 ppm	250 µL

*100 ppm Br spike solution (4.4.5) is used for preparing STD1, 1000 mg Br^-/L stock standard (4.4.4) is routinely used for preparing the rest of the standards but the 100 ppm Bromide Spike can also be used (adjust the volumes accordingly).

Note 1: 100 ppm of carbonate (2500 µL of Stock Carbonate 4.4.6.) may be added to STD8 for research purposes only.

Note 2: STD2 is also used as a PQL-level standard and is called PQCK5 when used as such.

Note 3: STD8 is also used as a high concentration check standard, CHCKHI4, as a part of the initial QC.

Note 4: STD4 is also used as CHCK1 standard in combination with the INT_STD (4.7) for interference check.

4.6. CHCK2 standard (Table 2) - Using a calibrated Eppendorf micropipet, place the appropriate volume of stock (4.4) in a volumetric flask partially filled with DI water and dilute to mark with DI water. Holding time, 30 days. Store in the refrigerator.

Table 2.

	Volume Prepared	Chloride		Sulfate		Nitrate		Bromide	
		fin. conc.	**stock vol.**	**fin. conc.**	**stock vol.**	**fin. conc.**	**stock vol.**	**fin. conc.**	**stock vol.**
CHCK2	**1000 mL**	20 ppm	2000 µL	20 ppm	2000 µL	0.80 ppm	800 µL	0.20 ppm	200 µL

4.7. Interference Check Standard, INT_STD (Table 3) - Prepare in 250 mL volumetric flask using the indicated amounts of stock standard (4.4). Holding time, 30 days. Store in the refrigerator.

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Table 3.

	INT_STD		
	Stock	**fin. conc.**	**stock vol.**
Chloride	(4.4.1.)	2.5 ppm	62.5 µL
Sulfate	(4.4.2.)	2.5 ppm	62.5 µL
Nitrate	(4.4.3.)	0.5 ppm	125 µL
Bromide	(4.4.4.)	0.08 ppm	20 µL
Fluoride	100 ppm	1 ppm	2500 µL
Nitrite	1000 ppm	1 ppm	250 µL
Phosphate	1000 ppm	1 ppm	250 µL
Carbonate	(4.4.6)	10 ppm	250 µL

4.8. A certified quality control (ALTQC) sample is prepared following the manufacturer's instructions. See the manufacturer's certificate for concentration and expiration date. Depending on the certified concentration, The ALTQC sample may be further diluted to bring its concentration within the calibration range. Store in the refrigerator.

5. SAMPLE PREPARATION PROCEDURE (SEE DEP SOP NU-033)

5.1. All samples are stored on ice or at ≤ 6 °C (not frozen). Samples to be analyzed for bromide and/or chloride **only** do not require the above storage.

5.2. Samples should be analyzed for chloride, bromide, or sulfate within 28 days of collection date. Samples should be analyzed for nitrate within 48 hours of collection. If samples are analyzed outside these hold times, results must be reported with the Q qualifier code and appropriate comment.

5.4. Remove the samples from the refrigerator following the proper protocols to preserve the samples chain of custody. Allow the samples to come to room temperature before pouring them into the autosampler vials.

5.5. Samples for the IC are pre-diluted based on conductivity. See section 6.3. for detailed instructions.

5.6. For each batch –

- One batch may contain up to 20 samples.
- Prepare one MBLK (8.5.1).
- Prepare one matrix spike for every 10 samples (see 8.5.3). Add the appropriate amount of spiking solution (Stock Standards 4.4.) into a 10 mL portion of a selected sample. Prepare either a duplicate sample, if the components are known to be above the practical quantitation limit (PQL), or one matrix spike in duplicate.

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- Prepare one laboratory fortified blank (LFB) following the same procedure substituting DI water for the sample.
- Effluents are batched separately. Make sure that an effluent sample is spiked to represent the batch.

6. SAMPLE ANALYSIS/QUANTITATION

6.1. Preparing the Instrument:

6.1.1. Ensure that the pump, eluent generator compartment, DC compartment, and the autosampler are powered on.

6.1.2. The DC compartments are kept at a constant temperature of 30 C. The compartment doors should be kept shut at all times unless doing maintenance. The DC compartment doors should never be opened during analysis.

6.1.2. Turn on the computer. Unplug the network cable. Login under the local account THERMO_IC_PC\Thermo_IC. Use username .”\Thermo_IC.” There is no password: simply hit Enter to login. Run instrument under this local account. Use flash drive to transfer data or connect to the network and login under Lab_Nutrients account. Data processing in Chromeleon and printing can be performed under Lab_Nutrients account, but the instrument should only be run under the local account with network cable unplugged. Always log off before switching to another account.

6.1.3. Connect all the compartments to Chromeleon 7.

6.1.3. Perform daily or weekly maintenance detailed in sections 10.2 and 10.3.

6.1.4. Once temperature of the DC compartment stabilizes at 30 C, change the pump flow rate, eluent concentration, and suppressor to the corresponding initial settings of the method to be used (Table 4). The pump flow rate should be increased gradually, in increments of 0.5 mL/min. See the weekly maintenance for guidance.

Table 4. Instrument Methods

Method/Column	**AS18-4 µm**		**AS19-4 µm**	
	Time (min)	**Value**	**Time (min)**	**Value**
Temperature	All	30.0 C	All	30.0 C
Flow Rate	All	0.38 mL/min	All	0.38 mL/min
Eluent Concentration	Initial	17.0 mM	Initial	20.0 mM
	0 → 6.5	17.0 mM	0 → 9	20.0 mM
	6.5	30.0 mM	9.0	50.0 mM
	6.5 → 7.0	30.0 mM	9.0 → 10.0	50.0 mM

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	7.0	60.0 mM	10.0	75.0 mM
	7.0 → 8.0	60.0 mM	10.0 → 11.0	75.0 mM
	8.0	17.0 mM	11.0	20.0 mM
	8.0 → 11.0	17.0 mM	11.0 → 16.0	20.0 mM
Suppressor	All	57 mA	All	71 mA

Note: Gradient step time interval and concentrations must be kept consistent throughout an analytical run. As the column ages, analytes retention times change. The timings of the eluent concentration changes have to be adjusted accordingly to maintain optimal elution conditions.

Note: As the suppressor ages, the suppressor current may be increased to improve its performance (see Dionex Suppressor manual).

6.2. Preparing a Sample Queue:

Note: It is important that all system folders, sequences, methods, and processing methods are kept together. Do not mix system 1 with system 2 or vice versa.

6.2.1. Click the "Data" Module. All instrument data folders are organized in two folders: System_1 and System_2. Sequence, template, and method files are System-specific and should always be used only within one System folder.

6.2.2. To create a run sequence, right-click on the appropriate subfolder in the Sequences folder and select New Sequence.

6.2.3. Alternatively, copy one of the templates available in the Templates folder and paste it in the appropriate subfolder of the Sequences folder for the same System.

6.2.3. Go to the last run of the system, then copy and paste the instrument method and the processing method into the new sequence.

6.2.4. In the Instrument Method column, select the method that was pasted into the sequence. Then press F9 to populate all the rows with this method.

6.2.5. In the Processing Method column, select the processing method that was pasted into the sequence. Then press F9 to populate all the rows with this processing method.

6.2.6. Name the sequence with the format YYMMDD_S#. For AS-19 method, the file should be named YYMMDD_S2_AS19. If there are more than one sequence used on the same date, add a letter "A", "B", "C," etc. after the date to differentiate between the sequences, e.g. 180605A_S1.

6.2.7. Beginning with the calibration curve, enter your run sequence.

An example run sequence includes:

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CAL STDs STD1-STD8 (4.5)
BLK_carryover (DI water, 4.1)
INT-STD (Interference check standard, 4.7)
CHCK1 (STD4, 4.5)
PQCK5 (STD2, 4.5)
ALTQC (4.8)
CHCKHI4 (STD8, 4.5)
CHCK2 (4.6)
BLK (DI water, 4.1)
Batched samples (up to 20), including an MBLK, an LFB**,** matrix spike(s), and sample or matrix spike duplicate (for matrix spikes and spiking instructions see section 5.6.) **Bracketing checks and blanks must be added for every 10 samples.**
CHCK2 (4.6)
BLK (DI water, 4.1)

6.2.8. In the "Type" column, the calibration standards (4.5) should be set to "Calibration Standard."

6.2.9. The "Level" column indicates whether a given vial contains a calibrant. Set each standard to its corresponding level. (STD 1 is level 1, STD 2 is level 2, etc.)

6.2.10. The initial QC (4.6-4.8) should be set to "Check Standard" in the "Type Column.

6.2.11. All samples should have a status of "Idle." It will change to "Finished" when the sample analysis has completed.

6.2.12. Save sequence. Press "Start" at the top when the sequence is ready to be run.

6.3. Sample Preparation:

6.3.1. Samples for the IC are pre-diluted based on conductivity or salinity. Use Table 5 as a guide. This can be done either manually or through auto-dilutions.

Table 5.

Conductivity (μS/cm)	Salinity (PPTh)	Dilution Factor
0-500	0-0.20	nil
500-999	0.21-0.40	2
1000-2999	0.41-2.0	10
3000-9999	2.1-4.3	20
10,000-14,999	4.4-8.6	40
15,000-19,999	8.7-10.7	50
20,000-29,999	10.8-21	100
30,000+	22-43	200

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Samples to be analyzed for nitrate only should not generally be diluted according to conductivity. If time before sample expiration permits, these samples should be screened at a 1:10 dilution factor to determine the most appropriate dilution factor.

6.3.2. Samples with particulates should be pre-filtered with a 0.45 µm syringe filter. If samples need to be filtered, the MBLK and CHCK1 should also be filtered.

6.4. Running over multiple days:

6.4.1. The IC is capable of running over multiple days, as long as it does not run out of DI water used for eluent generation. These bottles can be easily re-filled while the run is in progress.

6.4.2. If running over multiple days, perform all of the daily maintenance indicated in (10.3) at the beginning of every day.

6.4.3. When running samples over multiple days, run the PQCK5 standard once every 24 hours (see 8.6.). If it fails, shut down the run and begin again with a new calibration curve.

6.4.4. When creating a sequence that will use a previously generated calibration, find the sequence that contains the original calibration data and copy the calibration rows into the "Insert Calibration" row of the new sequence.

6.4.5. Whenever the system's conditions have been changed (such as the pump being stopped), run the QC indicated in section 8.7. before proceeding with new injections.

6.4.6. If a run requires more cups than the maximum capacity of the autosampler, simply begin again at the first completed vial on the autosampler – replace the injected vials with new vials.

6.5. Shutdown:

6.5.1. The IC pump, EG, CR-TC, suppressor, and temperature should not be shut off day to day.

6.5.2. For normal weekends, the parameters can be lowered to conserve resources. This is done using the "S#_Weekend" method. This method is purely for automated lowering of system parameters. No data should be collected using this method.

Note: The instrument will continue to draw water from the eluent water reservoirs. Make sure to refill the reservoirs before leaving for weekend. Consult your supervisor if you are planning to leave the instrument unattended for more than two days.

6.5.3. If there is a long weekend or the IC does not need to be ran for 3+ days, the IC can be turned off in the following order: Suppressor → CR-TC → EG → Pump. This will make equilibrating the following week take longer but may be necessary to prevent the system from running out of DI water.

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6.6. Quantitation/Calculations:

6.8.1. The instrument will give analysis results for: Chloride in mg Cl^-/L, Sulfate in mg SO_4^{2-}/L, Nitrate in mg N/L, and Bromide in mg Br^- mg/L.

6.8.2. The QC Manager calculates recoveries for spikes and QC standards as well as relative percent differences (RPD) for duplicate samples and spikes.

6.8.3. The individual calibration standards are prepared according to section 4. The calibration is calculated by the instrument software for each component and is included in the analysis report. It also includes a correlation coefficient to evaluate the fit. The fit is cubic.

7. POST-RUN PROCEDURE

7.1. After the sequence has finished, double click the first chromatogram with the analytes. This will open the "Data Processing" tab.

7.2. In "Presets" at the top, click the "Calibration and Results" window. Click the first analyte peak in the chromatogram and then click the "Calibration" tab at the bottom. Check the correlation coefficient.

7.3. As a column ages, the retention times of all peaks shift. Review the chromatogram of the INT_STD and check that the retention time windows and the processing method parameters are positioned appropriately in relationship to the peaks. Ask your supervisor to adjust them if necessary.

7.4. Review each chromatogram to check for peak shape, integration, and peak results. The tab "Peak Results" at the bottom will also display the results.

7.4.1. Be particularly careful to check chromatograms where peak quantitation is marked as "n.a." The software will assign the "n.a." quantitation to both non-detects and peaks with areas above calibration curve. Check the chromatogram and the peak area to distinguish between the two.

7.4.2. Chromatograms with large peaks should be reviewed with particular care: such peaks may interfere with quantitation or even identification of neighboring peaks.

7.4.3. Additionally, large peaks may appear with shifted retention time and, as a result, may be mis-identified.

7.4. Click the "Summary" tab at the bottom to view all the results in the sequence for the selected analyte. To see the results for a different analyte, click the corresponding peak on the chromatogram.

7.5. After checking all the chromatograms, click "Report Designer" under "Data Processing" to access the needed printouts. The report folder must contain:

- The sequence located in the "Bench Sheet" tab.

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- The peak results located in the "Summary" tab.
- A printout of all calibration curves in the "Calibration" tab.
- The chromatograms of all the initial QC in the "Peak Analysis" tab.

When printing, make sure everything is in black and white and double sided. For all printouts (except the initial QC chromatograms), click the Chromeleon head at the top left of the screen, choose print, select "Current Injection," and make sure the right sheet is selected to be printed.

For the initial QC chromatograms, follow the same procedure but click "Current Sequence" instead of "Current Injection" and make sure the yellow vial with the asterisk and the green vial with the check mark are selected. Then print.

7.6. To print the method, click the "Instrument Method" tab above "Data Processing." Then print using the Chromeleon icon at the top left.

7.7. To print the processing method, click the "Data Processing" tab, Click "Calib. & PM" tab in Presets. Then click the "Detection" tab. Use the Chromeleon head to print and uncheck all options to print except for the "Detection" page. Click "OK" to print.

7.8. Generate an export file for QC Manager using the "Summary" tab of Report Designer. Click the Chromeleon head, Export, and "Current Injection." Select the appropriate parent folder in the \\FLDEP1\DEAR\LABS\Lab3\Chem_data\Inorganic\Nutrients\Dionex_IC \S1\ or \\FLDEP1\DEAR\LABS\Lab3\Chem_data\Inorganic \Nutrients\ Dionex_IC\Data\S2\. Select the "Text format (Results)(.txt)" option needed for QC Manager. Click "OK." The export file will appear in the selected folder under its own folder named in the same way as the sequence, e.g. 180605A_S2_AS19.

In the folder, give the text file a name made of the sequence name with an addition of an analyte code, e.g. 180605A_S2_AS19_CS . Use the following analyte code: "_CS" for chloride and sulfate, "_N" for nitrate, and "_B" for bromide.

7.9 Export the chromatogram files to the Nutrients network folder. In the "Data" module, click the sequence then File → Send to. Select the appropriate folder for the IC instrument used at \\FLDEP1\DEAR\LABS\Lab3\Chem_data\Inorganic \Nutrients\Dionex_IC\ \S1\Raw_data\ or \\FLDEP1\DEAR\LABS\Lab3\Chem_data\Inorganic \Nutrients\ Dionex_IC\ S2\Raw_data\. Place the directory into the appropriate subdirectory for month and year. Uncheck the "Include 3D and MS raw data" option and then click "Start."

7.10. The amount of manual reprocessing will be minimal. Try to manually reprocess as few chromatograms as possible. If a chromatogram must be manually reprocessed, note this on the sequence report, along with an explanation of the reason. Print out a copy of the chromatogram with and without manual reprocessing applied and include them in the report. For the chemistry section's policy on manual integration, see DEP SOP CM-018.

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8. QUALITY CONTROL/DATA ASSESSMENT AND ACCEPTANCE CRITERIA FOR QUALITY CONTROL MEASURES (SEE DEP SOPS NU-038 AND NU-043)

8.1. For method performance and acceptance criteria for QC measures, corrective action for out-of-control data, and contingencies for handling out-of-control or unacceptable data, refer to the following DEP SOPs NU-038 and NU-043.

8.2. A new calibration is performed at the beginning of every analytical run (typically once a week or as needed.) The working calibration range is verified every time a new calibration is performed. The correlation coefficient for every component reported must be equal to or greater than 0.995. The acceptance limits for the recoveries for each calibrant above the PQL are 90 - 110 %. For the PQL-level standard acceptance limits are 70 - 130%. Acceptance limits below the PQL are 50 – 150%, with the additional requirement that the result is above MDL. This results in the effective acceptance limits of 80 – 150% for 0.25 ppm Cl and SO4 and 65 – 150% for 0.02 ppm Br.

8.3. Certain QC samples must be run at the beginning of each new calibration. These are:

8.3.1. A second source (ALTQC, 4.8.). The acceptance limits for the recovery of the ALTQC are 90 - 110 %.

8.3.2. A PQL-level check standard (STD2, 4.5). Acceptance limits for the recovery of the PQL are 70 - 130 %. The PQCK5 standard serves both as a PQL-level check and as a spike for the ongoing MDL/PQL verification for chloride, sulfate, and bromide.

8.3.4. An Interference Check Standard (4.7), which has acceptance limits of 85 - 115 % recovery. This should be run with a CHCK1 (STD4, 4.5), which has the same levels of each analyte. In case of failures, comparison between the two can help distinguish between an interference and a calibration problem. The acceptance limits on the CHCK1 are 90 - 110 % recovery.

8.3.5. A blank to check for carryover. This is simply DI water, and is run immediately after the highest calibration standard. The carryover blank has the same acceptance limits as other blanks.

8.3.6. A CCV with the same values as the upper limit of calibration, the CHCKHI4 (STD8, 4.5). This has the same acceptance limits as other CCVs, 90 - 110 % recovery.

8.4. Each run should include a bracketing CCV (CHCK2) and a CCB (DI water) every 10 samples.

8.4.1. Acceptance limits for the recovery of the check standards are 90 -110 %.

8.4.2. Results for all blanks (MBLK/CCB/BLK) must be less than the MDL and greater than –MDL.

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8.5. Certain QC must be run for every batch of up to 20 samples:

8.5.1. A method blank (MBLK). This consists of DI water that is prefiltered with a syringe filter if samples are filtered.

8.5.2. Precision must also be demonstrated so run either a duplicate sample or duplicate matrix spike with each batch of 20 samples to demonstrate that the relative percent difference (RPD) is < 20 %.

8.5.3. For each batch of 20 samples, two matrix spikes of different samples and an LFB must also be analyzed to ensure that analyte recovery is within acceptable ranges (see section 5.6). Follow the standard spiking protocol for duplicates and spikes. Acceptance limits for matrix spike recoveries and LFB recoveries are 90 - 110 % for aqueous matrices. If the concentration of the analyte in a QC sample is greater than four times the spiked amount, the corresponding matrix spike recovery is not reported.

Spike a 10 mL aliquot of sample (or DI water for LFBs) with all analytes at the appropriate spiking level. Spiking level for each analyte should be the same for the LFB and the matrix spikes.

Spike N3:

Analyte	Spike Level (mg/L)	Stock Conc. (mg/L)	Amount of Stock (µL)
Sulfate/Chloride	30	10,000	30
Nitrate	5.0	1000	50
Bromide	0.5	100	50

Matrix spikes and LFBs are named using the following format: SampleID_Cl spike code_SO4 spike code_NO3 spike code_Br spike code. For example, 1234567_N3_N3_N3. If an analyte is not analyzed in the batch, the corresponding spike code is omitted.

8.6. The IC can run over more than one day if the calibration range is checked and confirmed to be acceptable. This can be done by running a PQCK5 standard at least every 24 hours when samples are being analyzed.

8.7. If the instrument running has been briefly interrupted, for example the pump was shut down and re-started, the calibration must be checked before running new samples. This is done by running a CCV, a PQCK5 standard, and a CCB. If the instrument conditions are expected to change after the interruption, a new calibration must be analyzed.

9. DATA ARCHIVAL

9.1. The raw data is archived in paper format. A report folder is created for each analytical run. Occasionally more than one run may be in one folder. The folder is labeled with the test (IC-SO4, Cl, etc.), export filename/s (e.g. 180605A_S2_AS19_CS) and initials of the analyst.

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9.2. Each report folder should contain the following items - results report(s), bench sheet(s), backlog(s), reagents and standard sheets, the calibration reports, chromatograms for initial QC, method parameters, chromatogram processing parameters and QC assessments uploaded from QC Manager to LIMS at the time of test authorization.

9.3. The report folders are on file with the nutrients and general chemistry supervisory personnel. Periodically, the files are moved to the State Records Center for long time storage according to DEP SOP LB-006.

9.4. Instrument raw data files, *.cmbx, are backed up and stored on the Nutrients drive under \\FLDEP1\DEAR\LABS\Lab3\Chem_data\Inorganic \Nutrients\Dionex_IC\.

9.5. IC instrument data excel transfer files for upload to QC manager are stored in electronic format located on the Nutrients drive: \\FLDEP1\DEAR\Labs\Lab3\Chem_Data\Inorganic\Nutrients\Dionex_IC\.

9.6. If available, a Certificate of Analysis for each purchased standard or reagent is maintained in the \\FLDEP1\DEAR\Labs\lab3\Chem_Data\Inorganic\Nutrients\REAGENT_PREP\IC\Certificates of Analysis folder.

9.7. Method validation data is on file with the supervisor. Digital copy is also stored on the network, under an appropriate sub-folder in \\fldep1\dear\Labs\Lab5\Chemistry\Inorganic\Nutrient\Validations.

10. MAINTENANCE

Note: All major maintenance must be recorded in the instrument maintenance manual.

10.1. Keep the instrument clean and free of dust as much as possible. If eluent or sample is spilled, be sure to clean it up immediately.

10.2. Weekly maintenance. Perform the following maintenance procedures before you calibrate the instrument for the first time in a calendar week:

10.2.1. Check the expiration date and the EGC % remaining in the Eluent Generator tab of the Instruments module of the Chromeleon Console.

10.2.2. Turn the system off using the controls of the Home tab of the Instruments module of the Chromeleon Console in the following order: Suppressor → CR-TC → EG → Pump. The Compartment and Column temperature should remain on at 30 C. Turn the temperature on if it is off.

Important: Make sure the EG is turned off right away after the CR-TC has been turned off. Running the EG while the CR-TC is on will deplete and ruin the CR-TC.

10.2.3. Empty and rinse and refill the DI water reservoirs that supply water to the pumps and AS-AP. The DI water used for this purpose must be sonicated

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for 30 min prior to use to reduce air and carbonate content. High content or air/carbonate in DI water may result in formation of bubbles, which in turn can lead to unstable injection volume, baseline noise, and inconsistent analyte recoveries.

10.2.4. Prime the pump to prevent air from going through the system:

Open the corresponding system's purge valve, go to the "Pump" tab for that system, click "Prime," then "Execute despite warning." Wait a few minutes until all the bubbles go to waste. Click "Stop," **close the purge valve**, set the pump to 0.15 mL/min and turn it on.

10.2.5. Turn the system back on using the following procedure:

Wait till the pump pressure at 0.15 mL/min is stable. Turn the EG on at 17 mM for AS18 method or at 20 mM for AS19 method. Immediately turn the CR-TC on after turning the EG on. Turn the suppressor on at 57 mA for AS18 method or at 71 mA for AS19 method. Turn the pump up to 0.20 mL/min. Wait for the pressure to stabilize. Repeat at 0.25 mL/min → 0.30 mL/min → 0.35 mL/min → 0.38 mL/min.

10.2.6. Prime the AS-AP:

10.2.6.1. Priming the AS-AP normally.

Ensure there are no bubbles in the syringe. Click the "Sampler" tab. Then "Prime Syringe" for 10 cycles. Then "Wash Needle and Fluidics" for 1000 µL. Then "Wash Sample Loop" with 1000 µL. Check there are no bubbles in the syringe afterwards. If so, manually prime the syringe.

10.2.6.2. To manually prime the syringe:

Go to the Sampler tab. Click "Wellness" then "Start Change." Once the syringe has stopped moving, unscrew the mounting bolt first and then the syringe.
Using DI water in a beaker, manually prime the syringe until all the bubbles have been expelled. Ensure that there is a white o-ring in the syringe valve. While holding the syringe vertically, push a small amount of DI water out of the top.
Screw in the syringe and then the mounting bolt finger tight. Click "Finish Change," close out the Wellness window, and then click the "OK" at the top of the screen to finish changing the syringe and return it to home position. Go through the normal priming steps (10.2.6.1) after manually priming the syringe.

10.2.6. Click "Monitor Baseline" and wait for a stable baseline.

10.3. Daily maintenance for ongoing runs. Perform the following maintenance for every day in a calendar week after the first day that the instrument continues to run:

10.3.1 Top off DI water reservoirs. The system must not run out of DI water, have air go through it, or run dry. **This may damage instrument**

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components. The DI water used for this purpose must be sonicated for 30 min prior to use.

10.3.2. Check for leaks or unusually low pressure.

10.3.3. Check for air bubbles in syringe. If there are air bubbles, manually prime the syringe (10.2.6.2.)

10.3.4. Click "Monitor Baseline" and watch for a stable baseline.

10.4. Routine replacement of parts:

10.4.1. The Eluent Generator Cartridge and Regenerating Anion Trap Column (CR-ATC 500) should be replaced when EGC % remaining is low.

10.4.2. The analytical column should be replaced when the pressure gets close to the maximum (5000 psi) or the peak resolution and baseline is too poor to continue use.

10.4.3. Aging suppressor will have reduced capacity for converting eluent to the less conductive water. Problems with baseline and changes in peak areas can result.

10.4.3. The suppressor or carbonate removal device (CRD) deterioration can cause an unstable baseline or a baseline that doesn't recover well after a peak has gone through. This can be seen by tailing and extra peaks in the peak tail.

10.5. If any significant changes are made to the system, such as a new column, check the analytes' retention time and any interfering anion retention times by running the interference check standard. All peaks should be clearly resolved and well within the established retention time windows. If necessary, the method isocratic window times may need to be adjusted (see 6.1.6.)

10.6. Record in the maintenance log any maintenance carried out. Write down the serial numbers of all parts removed from or installed on the system. Also, place all service visit receipts in the maintenance log.

11. SAFETY/HAZARDOUS WASTE MANAGEMENT/POLLUTION PREVENTION

11.1. Review the Laboratory Health and Safety Plan (accessible on the intranet at https://www.fldepnet.org/content/dear/bureau-laboratories-safety-documents).

11.2. Safety glasses, gloves and lab coats should be worn at all times while handling samples and reagents.

11.3. Read the MSDS information for safe reagent and sample handling.

11.4. The IC analysis does not normally generate hazardous waste, so the eluent and sample waste can go down the drain. The Dionex may be set up to flush waste directly into a sink, or the waste can be directed into a plastic carboy that is emptied as needed.

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12. REFERENCES/DEFINITIONS

For definitions see section 3 of the FDEP Quality Manual. All abbreviations used throughout the document are defined at least once in the document usually at the first time of use.

12.1. Dionex AS-AP Autosampler Operator's Manual, Thermo Fisher Scientific Inc, 2012. Document No. 065361.

12.2. Dionex IonPac AS18-4µm Column Product Manual, Thermo Fisher Scientific Inc, 2014. Document No. 065499-02.

12.3. Dionex IonPac AS19-4µm Column Product Manual, Thermo Fisher Scientific Inc, 2014. Document No. 065532-03.

12.4. Dionex DRS 600 Suppressor, Thermo Fisher Scientific Inc, 2018. Document No. 031956-13.

12.5. Chromeleon Manuals:

12.5.1. Chromeleon 7.2 Operator Training: Level 1, Thermo Fisher Scientific Inc, 2015. Document CM 7.2 Level 1.

12.5.2. Chromeleon 7.2 Operator Training: Level 2, Thermo Fisher Scientific Inc, 2015. Document CM 7.2 Level 2.

12.6. EPA Method 300.0 Rev. 2.1 (1993).

12.7. DEP SOP NU-033, Summary of Sample Analysis Procedures for the General Chemistry and Nutrients workgroups.

12.8. DEP SOP NU-038, Nutrients and General Chemistry: Quality Assurance and Quality Control.

12.9. DEP SOP NU-041, Reagent Preparation Procedure.

12.10. DEP SOP NU-042, Standard Preparation Procedure.

12.11. DEP SOP NU-043, Nutrients and General Chemistry Quality Assurance and Data Authorization Guidelines

12.12. DEP SOP CM-018, Laboratory Policy Regarding Manual Chromatographic Peak Integration.

12.13. DEP SOP LB-006, Standard Operating Procedure for Records Maintenance and Storage.

12.14. Quality Manual, Bureau of Laboratories, FDEP.

12.15. Laboratory Health and Safety Plan.

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APPENDIX OF SIGNIFICANT CHANGES

07/06/2018	Introduced the AS19 column method for the determination of chloride, sulfate, and bromide on Dionex IC 2. Elevated PQLs for chloride (0.6 mg/L), sulfate (0.6 mg/L), and nitrate (0.15 mg/L) to comply with the 2016 TNI standard. The MDL for bromide on the Dionex AS19 column is0.013 mg/L. Added bromide information to the standard preparation procedures. Clarified standard preparation descriptions. Added a note on the optional carbonate standard. Revised CHCK1, INT STD preparation table. Removed references to CHCK5 standard. Added new guidelines for reporting matrix spike recoveries. Edited Instrument Methods table, added notes on changes to eluent program and suppressor current. Clarified Preparing a Sample Queue section. Changed location for the storage of the Certificates of Analysis for standards. Clarified explanations of data review, printing reports, assembling the report folder, and data archival. Expanded maintenance section. Clarified running over multiple days and Shutdown procedures. Moved system startup information from Sample Analysis section to Maintenance section. Added notes on chromatogram reviews.
02/06/2019	Revised Reagents and Standards chapter and removed references to use of MDL standard. Added reference to validation data. Added clarifications to Sample Analysis and Quantitation. Removed all references to sediment analysis of chloride, sulfate and nitrate.
01/03/2020	Changed PQL levels for Cl and SO4 to 0.5 ppm.
02/11/2020	Added control limits for the calibration points below PQL. Added requirement that DI water used for AS-AP and eluent is sonicated. Added clarifications to chapter 7.

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