USGS Water Science Center Laboratory, Troy, NY

Ion Chromatography

Standard Operating Procedure

1. Scope and Application

1.1 Analytes

Chloride, Nitrate, and Sulfate

1.2 Reporting Limit

2.0 μmol Cl^-/L
2.0 μmol NO_3^-/L
2.0 μmol SO_4^{2-}/L

1.3 Applicable Matrices

This method is used to determine the concentration of chloride, nitrate, and sulfate in precipitation, dilute surface waters and soil waters.

1.4 Dynamic Range

The analytical range for the determination of chloride is from 0.1 μmol Cl^-/L to 112.88 μmol Cl^-/L. The analytical range for the determination of nitrate is from 0.1 μmol NO_3^-/L to 64.512 μmol NO_3^-/L. The analytical range for the determination of sulfate is from 0.1 μmol SO_4^{2-}/L to 104.1 μmol SO_4^{2-}/L. Sample concentrations that exceed the ranges must be diluted and reanalyzed.

2. Summary of Procedure

Chloride, nitrate and sulfate are separated chromatographically after sample injection into an anion exchange column. Ions are separated on the basis of their affinity for the exchange sites of the resin. The separated anions are detected with an electrical conductivity cell. Anions are identified on the basis of their retention times.

3. Safety Issues

3.1 Chemical Hazards

A. All strong acids and bases should be mixed in a fume hood.
B. Gloves, safety glasses, and lab coats should be worn when preparing and performing this analysis.
C. For proper handling techniques for specific chemicals, consult the appropriate Material Safety Data Sheets (MSDS).

4. Sample Preservation, Containers, Processing and Analysis Times

4.1 Sample Preservation

Samples are filtered through a 0.4-µm polycarbonate filter and stored at 4°C.

4.2 Containers

Samples are stored in 30-mL polyethylene bottles. The bottles have been rinsed with DI water.

4.3 Processing and Analysis Times

Sample processing: one week
Lab analysis: one month
LIMS entry: one week

5. Reagents and Standards

5.1 Reagent General Information

All reagents are commercially purchased, reagent grade or better, and should be stored in the original container. Date the reagent bottles when received and when opened. Note expiration date, if any. No verification of the reagents is necessary.

5.2 Reagents

A. Eluent, 0.0015 M sodium bicarbonate/0.0016 M sodium carbonate
   1. Using a specially marked polyethylene bottle, fill to the 2-L line with Milli-Q water.
   2. Degas the Milli-Q water by sparging it with commercial grade helium for about 2 minutes.
   3. Add 0.25 g sodium bicarbonate ($NaHCO_3$) and 0.35 g sodium carbonate (Na_2CO_3) to the bottle and mix thoroughly.
   4. Prepare each day.

B. Nitrogen Gas

   Use standard-grade nitrogen gas, purchased commercially.

5.3 Standards

A. Mixed-Anion Standard Stock Solution, 1,000 mg Cl^-/L, 1,000 mg NO_3^-/L and 2,500 mg SO_4^{2-}/L.
   1. Dry about 5 g sodium chloride (NaCl), 5 g sodium nitrate ($NaNO_3$), and 7 g potassium sulfate (K_2SO_4) at 105°C for 2 hours and allow to cool in a dessicator.
   2. To a 1,000-mL volumetric flask containing about 500 mL of Milli-Q water, add the following:

NaCl	1.6484 g
$NaNO_3$	1.3707 g
K_2SO_4	4.5355 g

   3. Fill close to final volume with Milli-Q water, mix, then fill to final volume and mix again.

4. Store in polyethylene bottle at 4°C; label and date.
5. Prepare every 6 months.
6. To avoid contamination, aliquots of stock solution must not be withdrawn directly from the bottle.
7. This solution is not directly checked. One of the working standards prepared from this solution is compared to a working standard made from the old stock solution. The standard must be within 2% of the previously approved standard.

B. Mixed-Anion Working Standards
1. Pipet desired amount of mixed standard stock into a volumetric flask.
2. Fill close to final volume with Milli-Q water, mix, then fill to final volume and mix again.
3. Store Standards A - D in a polyethylene bottles at 4°C; label and date.
4. Prepare monthly.
5. Standard E is prepared daily from Milli-Q water.

Standard	Chloride Concentration	Nitrate Concentration	Sulfate Concentration	Mixed Standard Stock Added (mL)	Final Volume (mL)
A	112.88 μmol/L (4.0 mg/L)	64.512 μmol/L (4.0 mg/L)	104.1 μmol/L (10.0 mg/L)	2.0	500
B	56.44 μmol/L (2.0 mg/L)	32.256 μmol/L (2.0 mg/L)	52.05 μmol/L (5.0 mg/L)	1.0	500
C	14.11 μmol/L (0.5 mg/L)	8.064 μmol/L (0.5 mg/L)	13.01 μmol/L (1.25 mg/L)	0.5	1000
D	5.644 μmol/L (0.2 mg/L)	3.226 μmol/L (0.2 mg/L)	5.205 μmol/L (0.5 mg/L)	0.2	1000
E	2.24 μmol/L (0.08 mg/L)	1.29 μmol/L (0.08 mg/L)	2.08 μmol/L (0.2 mg/L)	2.0 ml "A"	100

C. Mixed-anion Quality-Control (QC) Stock Solution, 300 mg Cl^-/L, 300 mg NO_3^-/L and 800 mg SO_4^-/L.
1. Theses stocks must be from a manufacturer or lot different from the standard stocks.
2. Dry about 5 g sodium chloride (NaCl), 5 g sodium nitrate ($NaNO_3$), and 7 g potassium sulfate (K_2SO_4) at 105°C for 2 hours and allow to cool in a dessicator.
3. In a 1,000-mL volumetric flask containing about 500 mL of Milli-Q water, add the following:
   NaCl 0.4945 g
   $NaNO_3$ 0.4112 g
   K_2SO_4 1.4514 g
4. Fill close to final volume with Milli-Q water, mix, then fill to final volume and mix again.
5. Store in polyethylene bottle at 4°C; label and date.

6. Prepare every 3 months.
7. To avoid contamination, aliquots of stock solution must not be withdrawn directly from the bottle.

D. Mixed QC Samples
1. Pipet desired amount of mixed QC substock into a 500-mL volumetric flask.
2. Fill close to final volume with Milli-Q water, mix, then fill to final volume and mix again.
3. Store in a polyethylene bottle at 4°C; label and date.
4. Prepare monthly.

QC Sample	Chloride Concentration	Nitrate Concentration	Sulfate Concentration	Mixed QC Substock Added (mL)	Final Volume (mL)
High	84.66 μmol/L (3.0 mg/L)	48.384 μmol/L (3.0 mg/L)	83.28 μmol/L (8.0 mg/L)	5.0	500
Low	8.466 μmol/L (0.30 mg/L)	4.838 μmol/L (0.30 mg/L)	8.328 μmol/L (0.80 mg/L)	0.5	500

6. QC Procedure

A. The standard curve is a linear plot of standard concentration vs. peak height. The best-fit line is drawn and the curve is accepted if the correlation coefficient is 0.998 or greater.
B. Quality-control samples are analyzed at the start of a run, after every 10 samples during the run, and at the end of the run.
C. A quality-control sample is acceptable if the analyzed value is within 10 percent of the QC sample's known value.
D. If one of the QC samples fails the acceptance criteria, the run is stopped and the QC sample is re-run. If the QC sample fails again the run is stopped and the instrument is re-calibrated. Samples associated with the failed QC samples are re-analyzed.

7. Chemical Analysis Procedure

7.1 Instrumentation

Dionex ion chromatograph, Model *ICS-1000*
Chromeleon chromatography software v. 6.8
Dionex AS4A separator column and Dionex AG4A guard column

7.2 Start-Up

A. Take standard and QC sample bottles from the refrigerator and allow to warm to room temperature.
B. Empty eluent container on top of chromatography module and refill with fresh eluent.

C. Double Click on **Chromeleon** software icon. Click on **Instrument Panels**. Make certain the Connect box is green and says Connected.
D. Set eluent volume to 2 L.
E. Click **ON** located in pump section. The pump will turn on.
F. **SRS Mode** should be **ON.** Set **SRS Current** to 25 mA. Allow instrument to stabilize microsiemens readout, at least 2 hours.
G. Fill squeeze bottle with Milli-Q water daily.
H. Dump waste bucket.

7.3 Calibration

A. Fill sample vials with standards and QC samples and place in sample cartridges in the following order: Standard B (labeled Try and used to verify retention times), Standards E, D, C, B, A, QC-Low, QC-High, and Milli-Q water (used to test the instrument response).
B. Load cartridges onto autosampler, making sure that the white dot is to the right.
C. Autosampler should read Local. Push softkey labeled Hold/Run. Autosampler will go to Run and sample cartridges will slide into position.
D. On Chromeleon software screen, toggle **Ctrl** and **Tab** keys to get to Browser window. Scroll down left side to Sequence Template. Click **File** then **Save As** sequence date in the following format - mmddyyyy.
E. Toggle back to **Instrument Panels** screen. At top of window, click on **Batch**, then **Start**. The day's Sequence should appear in the window. If not, click **Add**, then select the day's Sequence. Click **Ready Check**. When Ready Check Was Successful comes up, click **Start**. Autosampler will respond and calibration will begin.
F. Toggle back to Browser screen. Click on the previous Sequence most recently run. At top of screen, click on **Anions.qnt**. Drag this to current Sequence. Click **Copy**, then **Yes to all**.
G. When the Try sample in the calibration has finished, click on it from the Sequence window. The chromatogram will appear. Check to see that all 3 peaks are visible and that the sulfate peak has had enough time to finish.
H. When the calibration has finished, check to see if it meets the criteria by clicking on **Calibration** at the bottom of the chromatogram window. If the calibration passes, continue the run. If the calibration fails, recalibrate.
I. Print the acceptable calibration. From the Sequence window, click on one of the samples (ex. qcl). At the bottom of the chromatogram, click the Calibration window. Under File, choose Print, scroll down to Calibration (Current Peak), then OK.

J. Check the QC-low and QC-high values. If they are within acceptable limits, continue the run. If not, re-run the QCs.

7.4 Analysis

A. Load 10 samples on cartridges, then QC-low and QC-high. Go to the Browser screen and type in **Sample Serial Numbers** plus **qcl** and **qch**. Click **Save**.
B. Check QC-low and QC-high values after every 10 samples. Re-run if necessary, or load 10 more samples.
C. Review the sample peaks and analysis data as the run progresses.
D. If the instrument is to run overnight, go to Browser screen and scroll down to the last sample listed. On the next line, under the heading Program, click **Install Program,** then choose Stop from the drop-down menu. Click **Save**.
E. Still in Browser, click **File**, then **Print Sequence**.

7.5 Shut Down

A. Toggle to **Instrument Panels**, then click Off for pump. The pump will shut off and the SRS Current should go to 0 mA.
B. Remove caps from sample vials and soak in DI water.

7.6 Maintenance

A. Install a new AG4A guard column if system pressure goes above 2500 psi and/or peak retention times are significantly shortened.
B. Install a new AS4A separator column if peak retention times are significantly shortened.

7.7 Data Processing and LIMS Entry

A. Click the computer's green **Start** box, go to My Recent Documents, then scroll down to Anion Template.csv.
B. In chromatogram window of Chromeleon, select QCs and samples to be imported by highlighting them, click **Edit**, then **Copy**.
C. Go back to Anion Template.csv and Paste under heading Sample Name.
D. Go back to chromatogram window of Chromeleon, select the first Chloride peak. Under column headed Amount umol/L Chloride select values by highlighting, go to **Edit**, then **Copy**.
E. Go back to Anion Template.csv**.** and Paste under heading Chloride.
F. Repeat for Nitrate and Sulfate values.
G. Click **Save As**, then **Other Formats.** Go up to My Computer,then Local Disk (C:), then Anion Data, then appropriate year folder.
H. In File name, type name of file in the following format: mmddyyyy.csv.
I. Print the file then close Excel. Write the filename on the copy.

J. Note dilutions.
K. Double click **Watershed LIMS** icon.
L. Click **Custom**, then **Import Data**.
M. Under the Import drop down, click on **Anion data**.
N. Choose and open the desired file.
O. Choose Client, Units, type in Test Date, and choose Analyst.
P. Exclude and/or edit any data necessary.
Q. Click **Client ID to Sample No**.
R. Click **Check Analysis**.
S. Click **Set Data**.
T. Investigate problems for data that did not transfer or are duplicated.

8. Archiving

8.1 Data

Data files are backed-up daily by an automatic back-up program. Hard copies of the runs are filed and kept indefinitely. The laboratory LIMS system is backed up daily by an automatic back-up program.

8.2 Samples

Samples are stored at 4°C until data can be verified. Sample bottles are cleaned and reused for new samples.

9. References

Fishman, M.J., ed., 1993, Methods of analysis by the U.S. Geological Survey National Water Quality Laboratory – Determination of inorganic and organic constituents in water and fluvial sediments: U.S. Geological Survey Open-File Report 93-125, 217 p.

Fishman, M.J., and Friedman, L.C., eds., 1989, Methods for determination of inorganic substances in water and fluvial sediments: U.S. Geological Survey Techniques of Water-Resources Investigations book 5, chap. 1, 545 p.

Peden, M.E., and others, 1986, Methods for collection and analysis of precipitation: Champaign, Ill., Illinois State Water Survey Contract Report 381 (variously paged).

U.S. Environmental Protection Agency, 1987, Handbook of methods for acid deposition studies – laboratory analysis for surface water chemistry: Washington, D.C., U.S. Environmental Protection Agency, EPA 600/4-87/026 (variously paged).

10. Key Words

Ion chromatography, chloride, nitrate, sulfate, water, soil water

Author: Debra Horan-Ross *Approved by: Greg Lawrence* *Reviewed by: Ken Pearsall*