Standard Operating Procedure for the Analysis of Chloride, Bromide and Sulfate in Fresh Waters by Ion Chromatography

CCAL 50B.2

Cooperative Chemical Analytical Laboratory
College of Forestry
Oregon State University
321 Richardson Hall
Corvallis, Oregon

Prepared by Kathryn Motter
And Cameron Jones

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Table of Contents

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1.0 Scope and Application

1.1 This method is applicable to the sequential measurement of anions in surface, ground, drinking and waste waters by ion chromatography. Measurement is direct on a single instrument after sample filtration. Currently, CCAL quantifies chloride, bromide, sulfate and fluoride exclusively; nitrate and phosphate may also be determined simultaneously. Detection limits of 0.01 mg Cl/L, 0.01 mg Br/L, 0.01 mg SO4/L and 0.01 mg F/L have been determined for this method using a 300 uL sample loop and SRS current of 43 mA.

2.0 Summary of Method

2.1 Samples are injected into a stream of carbonate/bicarbonate eluent, passed through a series of ion exchange columns and into a conductivity detector. The first column, a guard column, protects the analytical column by removing particulate and organic matter. The analytical column separates anions by their relative affinities for a low-capacity, strongly basic anion exchanger. The suppressor (between the analytical column and the conductivity detector) provides continuous suppression of background conductivity of the eluent and enhances response of the target analytes by acidification. The separated anions in their acidified form are measured by conductivity. The anions are identified based on retention times and quantified by conductivity relative to standard response.

3.0 Definitions

3.1 DI water: Water that has been through a deionization system to produce water similar to ASTM Type I reagent with 16.7 Mohms resistivity (ASTM) (Reference 16.3).

3.2 Method Detection Limit (MDL): The minimum concentration of an analyte that can be measured and reported with 99% confidence, based on a one-sided 99% confidence interval (*t*-value at a significance level of 0.01

and *n-1* degrees of freedom) from at least seven repeated measurements of a low concentration standard measured within an analysis run.

MDL = *ts*

Where,
t = Student's *t* value at a significance level of 0.01 and *n-1* degrees of freedom
s = standard deviation of at least seven repeated measurements of a low level standard

4.0 Interferences

4.1 Any substance with a retention time similar to that of an anion of interest, that produces a detector response, will interfere. A high concentration of a component with similar elution times may also interfere with resolution, and sometimes retention, of other analytes. Peak separation may be achieved by sample dilution, reduced eluent concentration or change in instrument parameters (eg sample size, flow rate or suppressor current).

4.2 Introduction of contaminants may lead to spurious peaks or elevated baseline.

4.3 Samples should be pre-filtered to prevent damage to columns and flow system.

5.0 Safety

5.1 The toxicity or carcinogenicity of each reagent has not been precisely determined; however, each chemical should be regarded as a potential health hazard. Exposure to these chemicals should be reduced to the lowest possible level. Cautions are included for known extremely hazardous materials.

5.2 The following chemicals have the potential to be highly toxic or hazardous. For detailed explanations, consult the MSDS.

5.2.1 Sulfuric acid (used in regeneration of the suppressor)
5.2.2 Oxalic acid (used in regeneration of the suppressor)
5.2.3 Methanol (cleaning agent)

6.0 Equipment and Supplies

Note: *Brand names, suppliers and part numbers are for illustrative purposes only. No endorsement is implied. Equivalent performance may be achieved using apparatus and materials other than those specified here, but demonstration of equivalent performance that meets the requirements of this method is the responsibility of the laboratory.*

6.1 Dionex ICS-1500 Chromatography System

6.1.1 Dionex AS-40 Autosampler
6.1.2 Instrument Controller
6.1.3 Data Collection Software (Chromeleon)
6.1.4 Anion Guard Column (AG14A-7um, 4 x 50 mm)
6.1.5 Anion Analytical Column (AS14A-7um, 4 x 250 mm)
6.1.6 Self-Regenerating Suppressor (AERS 500, 4-mm)
6.1.7 Eluent reservoirs

6.2 Nitrogen gas and regulator

6.3 Dionex 5 mL sample vials and filter caps

6.4 Laboratory glassware and pipettes

6.5 Balance

6.6 Safety glasses

6.7 Nitrile gloves

6.8 Lab coat or apron

6.9 Laboratory exhaust fume hood

6.10 High Density Polyethylene (HDPE) bottles

7.0 Reagents and Standards

7.1 Preparation of Reagents

7.1.1 *Sodium Carbonate/Bicarbonate Eluent Concentrate ($0.8\ M\ Na_2CO_3/0.1\ M\ NaHCO_3$)*
Dissolve 84.79 g sodium carbonate (Na_2CO_3, FW 105.99) and 8.40 g sodium bicarbonate ($NaHCO_3$, FW 84.01) in 700 mL DI water in a 1 L volumetric flask. When dissolution is complete, bring up to

1000 mL with DI water. Final concentration; 0.8 M Na_2CO_3/0.1 M $NaHCO_3$.

7.1.2 *Working Carbonate Eluent Solution* *(8 mM Na_2CO_3/1 mM $NaHCO_3$)*
Pipette 10.0 mL of eluent concentrate into a 1 L volumetric flask and bring to volume with DI water. Exclude particulates from the system with Dionex 0.2 um end-line filter.

7.1.3 *Supressor Regenerant*
Dilute solutions of sulfuric or oxalic acid may be required to clean away build-up over time. See the suppressor manual for concentration specific to application.

7.2 Preparation of Standards

7.2.1 *Calibration Standards:*
Standards are prepared by dilution of a mixed standards purchased from a vendor that provide traceability to NIST standards. A mixed standard of concentration 100 mg/L of each chloride, bromide, fluoride and sulfate is used to prepare working standards in the table below.

	mg Cl/L	mg Br/L	mg SO_4/L	mg F/L
1	0.20	0.20	0.20	0.20
2	0.50	0.50	0.50	0.50
3	1.00	1.00	1.00	1.00
4	2.00	2.00	2.00	2.00
5	5.00	5.00	5.00	5.00

7.2.2 *Second Source Check Standard:*
Standard prepared by dilution of mixed element standard purchased from a vendor that provide traceability to NIST standards, this from a source other than that of the calibration standards. Check standard concentration should be mid-calibration range; currently 1.00 mg/L for each chloride, bromide, fluoride and sulfate.

8.0 Sample Handling and Storage

8.1 If required, unfiltered samples are filtered upon receipt through glass fiber filters into clean HDPE bottles and stored at 4°C in the dark. If samples must be held longer than 28 days prior to analysis, they are stored frozen at -18ºC unless otherwise requested.

9.0 Quality Control

9.1 Preparation of stock standards is recorded on worksheets and documented by weight of standard added to a given flask before dilution to volume with DI water. All records of certification are kept on file at CCAL Laboratory.

9.2 Blank: DI water run before and after the calibration, and after every check standard.

9.3 Second Source Check Standard: Run every ten samples to monitor drift and column efficiency.

9.4 Method Detection Limit (MDL): Established for each analyte. Based on a one-sided 99% confidence interval (t-value) from at least seven repeated measurements of a low concentration standard. The t-distribution value is multiplied by the standard deviation of the population (n-1) to obtain the MDL.

9.5 Analytical Duplicate: Separate analysis from the same sample aliquot. One per ten samples.

9.6 A bulk surface water Quality Control Check Standard is used to generate control charts and is tracked over time to monitor overall performance.

9.7 Samples with concentration greater than the highest calibration standard are diluted and reanalyzed.

10.0 Calibration and Standardization

10.1 Balances: calibrated yearly by external vendor.

10.2 Pipette delivery checked by weight to within 1% of theoretical weight of aliquot volume.

10.3 The IC is calibrated every analysis run. The Chromeleon software is setup to use quadratic curve fit of six working standards (see section 7.2). The r^2 value of each calibration curve should be greater than 0.995.

10.4 Check standard recovery must be within 10% of theoretical value.

11.0 Procedure

11.1 Dionex ICS-1500 Instrument Operating Parameters

Nitrogen Gas Pressure:	
tank regulator	40 psi
eluent regulator	6 psi
Flow Rate	1.0 mL/min
Sample Loop Size	300 uL
Aquisition Time	15.00
Pressure Limit	200 - 3000 psi
Injection Duration	60 sec
Cell T	30ºC
Column T	30ºC
Data Collection Rate	5 Hz
Supressor current	43 mA

11.2 Procedure

11.2.1 Prime the pumps
11.2.2 Allow instrument to equilibrate at normal operating parameters until baseline is stable. Normal baseline conductivity is approximately 25 uS/cm. Normal operating pressure approximately 1700 psi. Values vary with column life.

11.3 System Notes

11.3.1 Yearly preventative maintenance as suggested by the manufacturer is required for optimum performance.
11.3.2 Column and suppressor must be maintained or replaced as needed to retain peak separation.
11.3.3 Peak separation for individual sample matrices may be achieved by sample dilution, reduced eluent concentration or change in instrument parameters (eg sample size, flow rate or suppressor current).

12.0 Data Analysis and Calculations

12.1 The Chromeleon software prepares a standard curve by plotting standard response against known concentration. Sample response is compared to the standard curve to determine concentration.

12.2 Samples with concentration greater than the highest calibration standard are diluted and reanalyzed.

13.0 Method Performance

13.1 This method was validated through inter-laboratory studies. The CCAL Water Analysis Laboratory participates in the USGS Standard Reference Water QA program and the National Water Research Institute's (NWRI) Environment Canada Proficiency Testing (PT) Program.

14.0 Pollution Prevention

14.1 The chemicals used in this method pose little threat to the environment when properly managed.

14.2 All standards and reagents should be prepared in volumes consistent with laboratory use to minimize the volume of disposable waste.

14.3 For further information on pollution prevention consult *Less is better: Laboratory Chemical Management for Waste Reduction*, available from the American Chemical Society's Department of Government Relations and Science Policy, 1155 16th Street NW, Washington D.C. 20036, (202) 872-4477.

15.0 Waste Management

15.1 It is the laboratory's responsibility to comply with all federal, state and local regulations governing waste management, and to protect the environment by minimizing and controlling all releases from fume hoods and bench operations. Compliance with all sewage discharge permits and regulations is required.

15.2 For further information on waste management, consult "The Waste Management Manual for Laboratory Personnel", and "Less is Better: Laboratory Chemical Management for Waste Reduction", both available from the American Chemical Society's Department of Government Relations and Science Policy, 1155 16th Street NW, Washington DC, 20036.

16.0 References

16.1 Standard Methods For The Examination of Water and Wastewater, Method 4110 B; Ion Chromatography with Chemical Suppression of Eluent Conductivity. American Public Health Association. 21st Edition, 2005.

16.2 Code of Federal Regulations. Protection of Environment. Section 40, Appendix B to Part 136. Definition and procedure for the determination of the method detection limit. Revision 1.11. Revised July 1, 1990. Office of the Federal Register, National Archives and Records.

16.3 ASTM. American Society for Testing and Materials. Standard Specifications for Reagent Water. D1193-77 (Reapproved 1983). Annual Book of ASTM Standards, Vol. 11.01. ASTM: Philadelphia, PA, 1991.

16.4 Dionex Instrument, Software and Accessory manuals. Dionex Corporation; Sunnyvale, California.

16.5 Pfaff, J.D., Hautman, D.P. and Munch, D.J., 1997. EPA Method 300.1, Revision 1.0. "Determination of Inorganic Anions in Drinking Water by Ion Chromatography", US EPA NERL, ORD, Cincinnati, Ohio.

16.6 US EPA, 1994. "Determination of Inorganic Anions by Ion Chromatography", Method 9056, SW-846, US Environmental Protection Agency, Office of Solid Wate and Emergency Response, Washington, DC.

17.0 Tables, Diagrams, Flowcharts, and Validation Data

17.1 NA

18.0 Document Revision History

Original Document: April 2006
Version: 50A.0
Title: Standard Operating Procedure for the Analysis of Chloride and Sulfate in Fresh Waters by Ion Chromatography

Edit Date: May 2008
New Version: 50B.0
Title and documentation changed to include bromide
Section 1.1: change from 250 to 300 uL sample loop

Section 7.2.1 and 7.2.2: change concentrations of calibration and check standards. Change from serial dilution to dilution. Change from individual standards to mixed standards.

Edit Date: February 2010
New Version: 50B.1
Address update
Section 1.1: change sulfate detection limit to 0.01 mg SO4/L
Section 11.1: change sample loop size to 300 uL
Section 11.2.2: change baseline conductivity to 25 uS/cm
Section 13.1: add Environment Canada Proficiency Testing Program participation.

Edit Date: May 2015
New Version: 50B.2
Section 1.1 & 7.2: add fluoride to routine analyses
Section 5.2: add methanol
Section 6.1: update suppressor information
Section 8.1: add hold time
Section 9.6: edit performance standard
General edits throughout