Anions, ion-exchange chromatographic, low ionic-strength water, automated

Parameters and Codes:
Anions, dissolved, I-2058-85 (see below)

Parameter	Code	Parameter	Code
Bromide (mg/L as Br)	71870	Nitrate (mg/L as N)	00618
Chloride (mg/L as CI)	00940	Orthophosphate (mg/L as P)	00671
Fluoride (mg/L as F)	00950	Sulfate (mg/L as So_4)	00945

1. Application

1.1 This method may be used only for the determination of dissolved bromide, chloride, fluoride, nitrate, orthophosphate, and sulfate in water with a specific conductance of approx 100 µS/cm or less. Table 14 specifies the lower and upper concentration limits using a 200-µL sample loop. Samples containing anion concentrations greater than the upper concentration limits must be diluted or the conductivity meter must be changed to a less sensitive setting before analysis.

1.2 Analyses must be performed on a filtered (rinsed 0.45-µm membrane filter) or particulate-free, unacidified sample.

2. Summary of method

2.1 All six anions are determined on a single filtered or particulate-free, unacidified sample with an ion chromatograph.

2.2 In anion analysis, the ions of interest elute through an anion-ion exchange separator column at different rates, depending upon the affinity of each anion for the ion- exchange resin. Then the ions elute through a fiber suppressor, which consists of a semi-permeable membrane in the interior of the suppressor's outer shell. The membrane is wrapped around the interior of the fiber, which is packed with inert beads. A suppressor regenerant solution flows countercurrent to the eluent intrained samples and surrounds the outside of the semi-permeable fiber. The regenerant is continuously fed by gravity through the suppressor's interior. This latter process operates continuously.

Table 14.-Analytical ranges used in the determination of the six anions

Constituent	Minimum concentration (mg/L)	Maximum concentration (mg/L)
Fluoride	0.01	0.5
Chloride	.01	3.0
Orthophosphate-phosphorus	.01	.6
Bromide	.01	.6
Nitrate-nitrogen	.01	.6
Sulfate	.01	10.0

2.3 For additional information on ion chromatography, see Small and others (1975).

3. Interferences

3.1 A negative peak or dip, which is caused by a combination of water and carbonate, is seen in the chromatogram using a fiber suppressor. This interference is eliminated by adding concentrated eluent to the sample.

3.2 Because low ionic-strength samples contain low concentrations of these six anions, there will be no unresolved peaks and, therefore, no interferences.

3.3 Oxalate, acetate, or formate may interfere if present.

4. Apparatus

4.1 *Ion Chromatograph, Dionex Model 2120i* (NOTE 1) or equivalent, using the following operating conditions:

Eluent-pump flow rate 2.0 mL/min
Sample loop --------------- 200 μL
Specific-conductance
meter settings ---- 1,3,10,30 μS

NOTE 1. Concentration limits and operating conditions may vary according to model of instrument.

4.2 *Pump, LDC/Milton Roy mini Metric I* (NOTE 2) or equivalent that gives pulse-free flow of liquid. These pumps are used to eliminate "water and carbonate dip" by adding a volume of concentrated eluent (10x) to each sample.

Sample pump flow rate 2.4 mL/min
Concentrated eluent
pump flow rate --- 0.23 mL/min
(NOTE 3)

NOTE 2. Deactivate the Reset switch to bypass the low-pressure-limit adjustment.

NOTE 3. These flow rates will vary slightly depending on the eluent concentration. Adjust flow rates of pumps by injecting a blank until "water and carbonate dip" disappears.

4.2.1 Sample and concentrated eluent pumps are connected to the ion chromatographic Relays 3 and 4, respectively, and are controlled by Auto Ion 100 Controller program.

4.3 *Integrator, Spectra Physics; auto sampler*, *Gilson* or their equivalents, connected to the ion chromatograph's Relays 1 and 2, respectively.

4.4 *Proportioning pump, Technicon*, or equivalent, provides demineralized water into the wash receptacle of the sampler.

4.5 *Precolumn*, HPIC AS-4 Dionex pellicular anion-resin or equivalent.

4.6 *Separator column*, HPIC AS-4 Dionex pellicular anion-resin or equivalent.

4.7 *Suppressor*, Dionex anion fiber suppressor, No. 35350.

4.8 For additional information, refer to the manufacturers' instruction manuals.

5. Reagents

5.1 *Anion stock solutions I*, 1.00 mL = 1.00 mg: Prepare six individual anion stock solutions I by dissolving indicated amount of reagent grade chemicals, dried to a constant weight at 105°C, in demineralized water and dilute to 1,000 mL and store in Teflon bottles.

Anion	Salt	g/L
Br	NaBr	1.2877
Cl	NaCl	1.6484
F	NaF	2.2101
NO_3-N	$NaNO_3$	6.0681
PO_4 -P	KH_2PO_4	4.3936
SO_4	K_2SO_4	1.8140

5.2 *Anion Stock Solutions II*, 1.00 mL = 0.10 mg: Prepare chloride and sulfate stock solutions by diluting 100 mL each of chloride and sulfate stock solutions I to 1,000 mL with demineralized water and store in Teflon bottles.

5.3 *Concentrated eluent*, 0.0280*M* sodium bicarbonate-0.0225*M* sodium carbonate: Dissolve 9.408 g $NaHCO_3$ and 9.540 g Na_2CO_3 in demineralized water and dilute to 4 L.

5.4 *Demineralized water*: Pass water through a post column (millipore or equivalent) with 0.2-μm pore size filter which is placed after laboratory demineralized water system.

5.5 *Eluent*, 0.00280*M* sodium bicarbonate 0.00225*M* sodium carbonate (NOTE 4): Dissolve 5.410 g $NaHCO_3$ and 5.486 g Na_2CO_3 in demineralized water and diulute to 23 L.

NOTE 4. Eluent concentration may be varied slightly to obtain the same retention times for each anion when a new separator column is used.

5.6 *Mixed-anion standard solution I*: Prepare 1,000 mL by appropriate quantitative dilution of anion stock solutions I with demineralized water.

Anion	Concentration (mg/L)	Volume (m/L)
Br	10	10.0
CI	250	250
F	10	10.0
NO_3- N	30	30.0
PO_4-P	10	10.0
SO_4	300	300

5.7 *Mixed-anion standard solution II*: Dilute 10.0 mL mixed anion standard solution I to 1,000 mL with demineralized water.

Anion	Concentration (mg/L)
Br	0.1
Cl	2.5
F	0.1
NO_3- N	0.3
PO_4-P	0.1
SO_4	3.0

5.8 *Mixed-anion standard solution III*: Prepare 1,000 mL by appropriate dilution of anion stock solutions II.

Anion	Concentration (mg/L)	Volume (mL)
Cl	0.2	2.0
SO_4	0.2	2.0

5.9 *Suppressor-regeneration solution*, 0.025*N* H_2SO_4: Cautiously add 2.8 mL concentrated H_2SO_4 (sp gr 1.84) to demineralized water, cool, and dilute to 4L with demineralized water.

6. Procedure

6.1 Operate instrument according to parameters described in paragraph 4.1. Supply continuously by gravity-feeding suppressor-regeneration solution for fiber supressor (0.025*N* H_2SO_4) at a flow rate of 2.4 mL/min. Equilibrate the columns with 0.00280*M* $NaHCO_3$-0.00225*M* Na_2CO_3 eluent until baseline stabilizes. Allow approximately 30 min for equilibration.

6.2 Enter appropriate program into the Auto Ion 100 Controller of ion chromatograph according to manufacturer's instructions. This controls autosampler, integrator, sample pump, and concentrated eluent pump. This program is best suited for most of the precipitation samples. Set the OutPut Range of the conductivity meter similar to the expected concentration of samples.

6.3 Press the PT EVAL (peak threshold evaluation) key for integrator to evaluate the detector signal for noise and drift.

6.4 Create the information file through a "dialog" with the integrator.

Select calculation of the best straight-line fit using method 5 (external standard method) (NOTE 5).

NOTE 5. For additional information on computerized data reduction, see Hedley and Fishman (1982).

6.5 Run a demineralized water blank through the system to ensure that flow rates of sample and concentrated-eluent pumps are in correct proportion to eliminate the "water and carbonate dip."

6.6 Place mixed-anion standard solutions III and II at the beginning of the sample holder followed by standard reference materials and samples. Place a standard reference material in every tenth position of the remainder of this sample holder.

6.7 Turn on the proportioning pump to deliver demineralized water into the wash receptacle of the sampler.

6.8 Press START on the OPERATION-SELECT of AutoIon 100 Controller to begin the analysis.

7. Calculations

7.1 The integrator automatically computes the concentrations of six anions in each sample by comparing their peak heights to the analytical curve. Approximate retention times for the six anions are given in table 15.

8. Report

8.1 Report bromide (71870), chloride (00940), fluoride (00950), nitrate-nitrogen (00618), orthophosphate-phosphorus (00660), and sulfate (00945), dissolved, concentrations as follows: less than 1 mg/L, nearest 0.01 mg/L; 1.0 mg/L and above, nearest 0.1 mg/L.

9. Precision and Bias

9.1 Analysis of a number of test samples 10 times each by one operator resulted in mean values, standard deviations, and percent relative standard deviations as shown in table 16.

Table 15.-Approximate retention times of anions

Constituent	Time (min)
Fluoride	1.4
Chloride	2.2
Orthophosphate-phosphorus	3.4
Bromide	4.8
Nitrate-nitrogen	5.6
Sulfate	7.6

Table 16.-Precision and bias for ion chromatography on simulated precipitation samples

Standard reference water sample number	Constituent	Ion chromatography data[1]			Interlaboratory standard reference water sample data	
		Mean (mg/L)	Standard deviation (mg/L)	Relative standard deviation (percent)	Mean (mg/L)	Standard deviation[2] (mg/L)
70 (1:10)	F	0.09	0.01	8.1	0.089	0.06
	Cl	.23	.01	4.3	.271	.84
	NO_3-N	.06	.005	7.7	.069	.065
	SO_4	2.60	.07	2.6	2.62	1.4
72 (1:10)	F	.10	.01	9.3	.09	0.06
	Cl	4.89	.14	2.8	4.50	1.4
	PO_4-P	.05	.004	8.8	.059	.048
	NO_3-N	.30	.01	4.4	.302	.29
	SO_4	10.6	.34	3.2	11.1	10
P-1	Cl	.40	.01	2.3	.44	.045
	NO_3-N	.13	.003	2.3	.12	.016
	SO_4	1.14	.03	2.5	1.18	.09
P-2	F	.10	.01	7.8	.10	.00
	Cl	.47	.01	1.8	.60	.33
	NO_3-N	.04	.002	6.0	.074	.068
	SO_4	2.96	.06	1.9	3.24	1.43
80 (1:10)	F	.11	.01	9.4	.114	.07
	Cl	3.20	.09	3.0	3.15	1.5
	PO_4-P	.06	.005	9.6	.073	.063
	NO_3-N	.06	.004	7.3	.055	.070
	SO_4	7.08	.16	2.3	7.24	5.15

[1] Values based on 10 replicate determinations of SRWS.
[2] Standard deviations for undiluted SRWS.

References

Fishman, M. J., and Pyen, G. S., 1979, Determination of selected anions in water by ion chromatography: U.S. Geological Survey Water-Resources Investigations, 79-101, 30 p.

Hedley, A. G., and Fishman, M. J., 1982, Automation of an ion chromatograph for precipitation analysis with computerized data reduction: U.S. Geological Survey Water Resources Investigations, 81-78, 33 p.

Small, H., Stevens, T.S., Bauman, W.C., 1975, Novel ion exchange chromatographic method using conductimetric detection: Analytical Chemistry, v. 47, p. 1801-9.

Stevens, T.S., Davis J.C., Small, H., 1981, Hollow fiber ion-exchange suppressor for ion chromatography: Analytical Chemistry, V. 53, p. 1488-92.