

Anions, ion-exchange chromatographic, automated

Parameters and Codes:
Anions, dissolved, I-2057-85 (see below)

<u>Parameter</u>	<u>Code</u>	<u>Parameter</u>	<u>Code</u>
Bromide (mg/L as Br)	71870	Nitrite (mg/L as N)	00613
Chloride (mg/L as Cl)	00940	Orthophosphate (mg/L as P)	00671
Fluoride (mg/L as F)	00950	Sulfate (mg/L as SO ₄)	00945
Nitrate (mg/L as N)	00618		

1. Application

1.1 This method may be used only for the determination of dissolved bromide, chloride, fluoride, nitrate, nitrite, orthophosphate, and sulfate in natural water. Table 1 shows approximate lower and upper concentration limits. Actual limits depend on many factors including the column age, which affects column resolution, the relative concentrations of closely eluting species, and the volume of the sample injected. Samples containing anion concentrations high enough to overload the column resins or interfere with closely eluting species need to be diluted or a sample loop smaller than the 200- μ L sample loop specified in this method needs to be used. Sample dilution or use of smaller volumes will change the detection limits for all anions.

1.2 Analyses must be performed on filtered and unacidified samples.

1.3 The ion chromatographic (IC) technology is so new that instruments and associated data-processing equipment and software available on the commercial market are not standardized and operating conditions vary enormously. Until operating conditions of various manufacturers' instruments become more comparable and the equivalency of methods using those instruments is established by extensive testing, the IC method approved for U.S. Geological Survey use will specify instrument and associated software brands. This does not imply endorsement of one product over another, but rather, acknowledges that IC

Table 1.-Working ranges of anions by ion chromatography

Constituent	Minimum Concentration ¹ (mg/L)	Maximum concentration (mg/L)
Fluoride	0.01	50
Chloride	.20	50
Nitrite-nitrogen	.02	70
Orthophosphate-phosphorus	.06	40
Bromide	.10	150
Nitrate-Nitrogen	.05	150
Sulfate	.20	100

¹With a larger sample loop (for example, 600 μ L), minimum concentration levels can be lowered.

technology is rapidly changing and developing.

2. Summary of method

2.1 A sample is injected into an ion chromatograph and is pumped through three different ion-exchange columns into a specific-conductivity detector. The first two columns, a precolumn and separator column, are packed with low-capacity anion exchanger. Ions are separated based on their affinity for the exchange sites of the resin. The last column is a suppressor column that contains cation exchange resin in the hydrogen form. The suppressor column reduces the background conductivity of the eluent to a low or negligible level and converts the anions in the sample into their corresponding acids. The separated anions in their acid form are measured using an electrical conductivity cell. Anions are identified based on their retention

retention times compared with known standards. Quantitation is accomplished by measuring the peak height or area and by comparing it with an analytical curve generated from known standards.

2.2 During analysis, the suppressor column will slowly be exhausted and, therefore, will need to be regenerated. Other suppressors, such as the hollow fiber suppressor, which is continuously regenerated, may be used.

2.3 For additional information on ion chromatography, see Small and others (1975) and Fishman and Pyen (1979).

3. Interferences

3.1 Because bromide and nitrate elute very closely together, they potentially interfere with each other. Bromide-to-nitrate ratios should not exceed 1:10 or 10:1 if both ions are to be quantitated.

3.2 High levels of organic acids may be present in industrial and domestic wastes which may interfere with inorganic-anion analysis. Two common species, formate and acetate, elute between fluoride and chloride.

3.3 Water from the sample injection will cause a negative peak or dip in the chromatogram when it elutes, because its conductivity is less than that of the suppressed eluent. This dip usually occurs between F^{-1} and Cl^{-1} . Any peak of interest eluting near the water dip must be sufficiently resolved from the dip to be accurately quantitated. A method of eliminating the conductivity drop due to bicarbonate and carbonate is to introduce into the sample concentrations of bicarbonate and carbonate that closely approximate those of the eluent used for analysis. Adjustment of the sample background may be accomplished in two ways.

3.3.1 Dilute the sample with eluent if sample dilution is required prior to analysis.

3.3.2 A volume of 1.0 mL of a prepared eluent concentrate (a solution that is 100 times more concentrated than the eluent with respect to bicarbonate and carbonate ions) can be added per 100.0 mL of sample. CAUTION: Samples prepared in this manner have a pH of about 10 and will readily absorb carbon dioxide if left exposed to the atmosphere. The result will cause a positive-peak interference.

3.3.3 Standard solutions need to be prepared in the same manner as the samples. It is important

to prepare a blank using demineralized water at eluent strength in bicarbonate and carbonate to indicate any interferences that may have been introduced by the sample-preparation technique.

3.4 Samples containing high concentrations of chloride or other anions may prevent resolution of closely eluting peaks. For example, the peak for 0.1 mg of bromide per liter in the presence of greater than 1,000 mg of chloride per liter is swamped by the chloride peak. Bromide begins to elute before the chloride peak completely returns to the baseline.

3.5 Unexpected, late-eluting peaks are a potential source of interference. A peak eluting about two minutes after sulfate, believed to be oxalate, has been observed in some precipitation samples.

4. Apparatus

4.1 *Ion Chromatograph, Dionex Model 19 auto-sampler, Gilson; integrator (NOTE 1 V, Spectra Physics* using the following operating conditions:

Sample loop ----- 200 μ L

Eluent flow rate ----- 138 mL/h (30 percent of full capacity)

Sample pump flow rate -- 50 percent of full capacity

Specific conductance

meter settings ----10, 30, or 100 μ S

NOTE 1. A dual pen recorder (1 V and 100 mV) may replace an integrator. The recorder should be capable of full-scale response in two seconds or less. A typical chart speed is 0.5 cm/min.

4.1.1 *Precolumn*, 4 X 50-mm, fast-run, anion resin column (Dionex P/N 030831 or equivalent) placed before the separator column to protect the separator column from contamination by particulates or species strongly retained by the ionexchange resin.

4.1.2 *Separator column*, 4 X 250-mm, fast, run, anion-separator column packed with low capacity, pellicular, anion-exchange resin (Dionex P/N 030830 or equivalent) that is styrene divinylbenzene-based. This is suitable for resolving fluoride, chloride, nitrite, orthophosphate, bromide, nitrate, and sulfate.

4.1.3 *Suppressor column*, 6 X 250-mm, column-packed, with a high-capacity, column-exchange resin (Dowex 50W-X 16-H form resin or equivalent) that is capable of converting the eluent and

separated anions to their respective acid forms.

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

5. Reagents

5.1 *Eluent*, 0.003 M sodium bicarbonate 0.0024 M sodium carbonate: Dissolve 0.2520 g NaHCO₃ and 0.2544 g Na₂CO₃ in demineralized water and dilute to 1 L (NOTE 2).

NOTE 2: Eluent concentration may be varied slightly to obtain the same retention times for each anion when a new separator column is used. The NaHCO₃ is subject to thermal decomposition and must be weighed without prior drying.

5.2 *Suppressor regeneration solution*, 1N H₂SO₄: Cautiously add 111 mL concentrated H₂SO₄ (sp gr 1.84) to approx 600 mL demineralized water. Cool and dilute to 4 L with demineralized water.

5.3 *Standard anion solutions*: **Dry all** salts for 1 h at 105°C unless otherwise specified. Store each standard solution in TFE-fluorocarbon bottles.

5.3.1 *Bromide standard solution*, 1.00 mL = 1.00 mg Br: Dissolve 1.2877 g NaBr in demineralized water and dilute to 1,000 mL.

5.3.2 *Chloride standard solution*, 1.00 mL = 1.00 mg Cl: Dissolve 1.6484 g NaCl in demineralized water and dilute to 1,000 mL.

5.3.3 *Fluoride standard solution*, 1.00 mL = 1.00 mg F: Dissolve 2.2101 g NaF in demineralized water and dilute to 1,000 mL.

5.3.4 *Nitrate-nitrogen standard solution*, 1.00 mL = 1.00 mg NO₃-N: Dissolve 6.0681 g NaNO₃ in demineralized water and dilute to 1,000 mL.

5.3.5 *Nitrite-nitrogen standard solution*, 1.00 mL = 1.00 mg NO₂-N: Dissolve 4.9259 g NaNO₂ in demineralized water and dilute to 1,000 mL.

5.3.6 *Phosphorus standard solution*, 1.00 mL = 1.00 mg P: Dissolve 4.3936 g anhydrous KH₂PO₄ in demineralized water and dilute to 1,000 mL.

5.3.7 *Sulfate standard solution*, 1.00 mL = 1.00 mg SO₄: Dissolve 1.8140 g K₂SO₄ in demineralized water and dilute to 1,000 mL.

5.4 *Mixed stock solution*: Prepare 1,000 mL mixed stock solution by appropriate quantitative dilution of each standard solution (NOTES 3 and 4).

Anion	Concentration (mg/L)	Volume (mL)
F	5.00	5
Cl	50.00	50
NO ₂ -N	5.0	5
PO ₄ P	5.0	55
Br	5.0	5
NO ₃ -N	50.00	50
SO ₄	50.00	50

NOTE 3. If nitrite is omitted from the mixed stock solution, the solution is stable for at least 1 month when stored and refrigerated in a clean TFE-fluorocarbon bottle. If nitrite is included in the mixed-stock solution, the solution needs to be prepared fresh daily.

NOTE 4. The above is only an example of a mixed-stock solution. Other appropriate concentrations can be prepared.

5.5 *Mixed standard solutions*: Prepare at least three mixed standard solutions by appropriate dilution of the mixed stock solution. The solutions should bracket the concentration range of interest.

6. Procedure

6.1 Set up the ion chromatograph according to the operating parameters described in 4.1. Equilibrate the columns with eluent until a stable baseline is obtained. Allow approximately 30 min for equilibration.

6.2 Set the full-scale conductivity to 10, 30, or 100 µS as is appropriate for the expected sample-anion concentrations. The higher settings are required for higher sample-anion concentrations.

6.3 Level the integrator at 10 mV (a display of 1000 with no signal). Adjust the ion chromatograph's offset to approximately 11 mV (a display of 1100). This ensures that the ion chromatograph's signal will not fall below 10 mV during the course of the analyses. The baseline signal tends to drift in a negative direction over a long period of time. Each chromatogram can be started at a signal level of 10 mV using the integrator's automatic-zero control.

6.4 Enter an appropriate program into the main program controller of the ion chromatograph according to the manufacturer's instruction manual. The system is configured so that the ion chromatograph controls the autosampler and starts the integrator at the beginning of each sample injection (NOTE 5).

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

6.5 Place the mixed standard solutions in the first positions of the sample tray followed by a standard reference material and then the samples. Place a standard reference material in every twentieth position of the remainder of the sample tray.

6.6 Create an information file in the integrator by pressing the DIALOG key. Through this information file, various integrator functions can be enabled or disabled during the recording of a chromatogram. The only necessary function is ER (end run). It terminates the chromatogram at the appropriate time as determined by the operator's setting of the ion chromatograph's controller, which actuates the sampler and causes the injection of a new sample.

6.7 Press the integrator's PT EVAL key before starting a series of analyses. The integrator will take about 50 s to store the baseline signal so that a peak can be distinguished from baseline noise. The baseline noise can be evaluated before each chromatogram, using the integrator's ET function.

6.8 Set the ion chromatograph's PGM/AUTO/MANUAL switch from MANUAL to AUTO and press Start/Step to begin the analyses.

7. Calculation

7.1 The integrator automatically computes the concentration of each anion in each sample by comparing its peak height or area to the analytical curve. Retention times for the seven anions are given in table 12.

8. Report

8.1 Report bromide (71870), chloride (00940), fluoride (00950), nitrate-nitrogen (00618), nitrite-nitrogen (00613), orthophosphate-phosphorus (00660), and sulfate (00945), dissolved, concentrations as follows: less than 1 mg/L, nearest 0.01 mg/L; 1 mg/L and above, two significant figures.

9. Precision

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 13.

Table 12.-Approximate retention times of anions by ion Chromatography

Constituent	Time (min)
Fluoride	2.2
Chloride	3.3
Nitrate-nitrogen	4.0
Orthophosphate-phosphorus	4.9
Bromide	6.5
Nitrate-nitrogen	7.5
Sulfate	8.6

Table 13.-Precision for ion chromatographic determination of anions

Constituent	Mean (mg/L)	Standard deviation (mg/L)	Relative standard deviation (percent)
Bromide	0.295	.020	6.8
Chloride	.72	.04	5.6
Do.	1.71	.06	3.5
Do.	2.72	.24	8.8
Do.	5.84	.19	3.2
Do.	9.90	.39	3.9
Do.	58.6	.7	1.2
Do.	119	1.2	1.0
Fluoride	.018	.004	22.2
Do.	.080	.010	12.5
Do.	.79	.02	2.5
Do.	.92	.01	1.1
Do.	2.02	.15	7.4
Nitrate-Nitrogen	.12	.01	8.3
Do.	.42	.051	1.9
Do.	.70	.081	1.4
Do.	1.27	.05	3.9
Do.	5.26	.14	2.7
Nitrite-nitrogen	.03	.01	33.3
Orthophosphate-phosphorus	.273	.010	3.7
Sulfate	1.68	.05	3.0
Do.	3.88	.10	2.6
Do.	15.1	.80	5.3
Do.	62.1	.9	1.4
Do.	100	1.4	1.4
Do.	146	3	2.0

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.
- Hadley, 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.