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DETERMINATION OF SELECTED ANIONS IN WATER BY ION
CHROMATOGRAPHY

U.S. GEOLOGICAL SURVEY

Water-Resources Investigations 79-101

REPORT DOCUMENTATION PAGE		1. REPORT NO.	2.	3. Recipient's Accession No.
4. Title and Subtitle DETERMINATION OF SELECTED ANIONS IN WATER BY ION CHROMATOGRAPHY				5. Report Date September 1979
7. Author(s) Marvin J. Fishman and Grace Pyen				6.
9. Performing Organization Name and Address U.S. Geological Survey, Water Resources Division, Box 25046, Denver Federal Center, Mail Stop 407 Lakewood, Colorado 80225				8. Performing Organization Rept. No. USGS/WRI 79-101
				10. Project/Task/Work Unit No. CR-145
				11. Contract(C) or Grant(G) No. (C) (G)
12. Sponsoring Organization Name and Address U.S. Geological Survey, Water Resources Division, Box 25046, Denver Federal Center, Mail Stop 407 Lakewood, Colorado 80225				13. Type of Report & Period Covered March 1978 - Final June 1979
15. Supplementary Notes Presented at 21st Rocky Mountain Conference on Analytical Chemistry, July 30, 1979.				14.
16. Abstract (Limit: 200 words) Ion chromatography is a rapid, sensitive, precise, and accurate method for the determination of major anions in rain water and surface waters. Simultaneous analyses of a single sample for bromide, chloride, fluoride, nitrate, nitrite, orthophosphate, and sulfate require approximately 20 minutes to obtain a chromatogram. Minimum detection limits range from 0.01 milligrams per liter for fluoride to 0.20 milligrams per liter for chloride and sulfate. Percent relative standard deviations were less than nine percent for all anions except nitrite in Standard Reference Water Samples. Only one reference sample contained nitrite and its concentration was near the minimum level of detection. Similar precision was found for chloride, nitrate, and sulfate at concentrations less than 5 milligrams per liter in rainfall samples. Precision for fluoride ranged from 12 to 22 percent, but is attributed to the low concentrations in these samples. The other anions were not detected. To determine accuracy of results, several samples were spiked with known concentrations of fluoride, chloride, nitrate, and sulfate; recoveries ranged from 96 to 103 percent. Known amounts of bromide and phosphate were added, separately, to several other waters, which contained bromide or phosphate. Recovery of added bromide and phosphate ranged from approximately 95 to 104 percent. No recovery data were obtained for nitrite. Chloride, nitrate, nitrite, orthophosphate, and sulfate, in several samples, were also determined independently by automated colorimetric procedures. An automated ion-selective electrode method was used to determine fluoride. Results are in agreement with results obtained by ion chromatography.				
17. Document Analysis a. Descriptors Water analysis, Chemical analysis, Laboratory test, Analytical technique, Anions: fluoride, chloride, nitrite, phosphate, bromide, nitrate, and sulfate				
b. Identifiers/Open-Ended Terms Analytical method				
c. COSATI Field/Group				
18. Availability Statement No restriction on distribution		19. Security Class (This Report) Unclassified		21. No. of Pages
		20. Security Class (This Page) Unclassified		22. Price

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September 1979

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DETERMINATION OF SELECTED ANIONS IN WATER BY ION CHROMATOGRAPHY

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ABSTRACT

Ion chromatography is a rapid, sensitive, precise, and accurate method for the determination of major anions in rain water and surface waters. Simultaneous analyses of a single sample for bromide, chloride, fluoride, nitrate, nitrite, orthophosphate, and sulfate require approximately 20 minutes to obtain a chromatogram.

Minimum detection limits range from 0.01 milligrams per liter for fluoride to 0.20 milligrams per liter for chloride and sulfate. Percent relative standard deviations were less than nine percent for all anions except nitrite in Standard Reference Water Samples. Only one reference sample contained nitrite and its concentration was near the minimum level of detection. Similar precision was found for chloride, nitrate, and sulfate at concentrations less than 5 milligrams per liter in rainfall samples. Precision for fluoride ranged from 12 to 22 percent, but is attributed to the low concentrations in these samples. The other anions were not detected.

To determine accuracy of results, several samples were spiked with known concentrations of fluoride, chloride, nitrate, and sulfate; recoveries ranged from 96 to 103 percent. Known amounts of bromide and phosphate were added, separately, to several other waters, which contained bromide or phosphate. Recovery of added bromide and phosphate ranged from approximately 95 to 104 percent. No recovery data were obtained for nitrite.

Chloride, nitrate, nitrite, orthophosphate, and sulfate, in several samples, were also determined independently by automated colorimetric procedures. An automated ion-selective electrode method was used to determine fluoride. Results are in agreement with results obtained by ion chromatography.

INTRODUCTION

Ion chromatography has been used since the early 1940's for separation of both organic and inorganic species. Analysis was relatively easy when the ion being eluted from an ion-exchange column had a directly measurable property, such as absorption in the ultraviolet or visible region of the spectrum, that could be distinguished from the background. Specific-conductance measurements were also used, but high background conductance of the electrolyte (eluent) usually overwhelmed the conductance of eluting ions. Small, Stevens, and Bauman, 1975, solved this detection problem by adding a suppressor column downstream from the separator column that suppressed or neutralized ions of the background electrolyte.

Ion chromatography is an extremely useful tool for anion determination in atmospheric precipitation and natural waters because detection limits for many of the anions are lower than by other techniques. Also several anions are determined sequentially on a small aliquot of filtered sample. One to two milliliters of sample is injected into the ion chromatograph, and 200 μL or other designated volume is loaded onto the column. The method described is suitable for determining dissolved bromide, chloride, fluoride, nitrate, nitrite, orthophosphate, and sulfate.

ANALYTICAL METHOD

1. Application

Ion chromatography may be used for determination of dissolved fluoride, chloride, nitrite, orthophosphate, bromide, nitrate, and sulfate in atmospheric precipitation and natural waters. Table 1 specifies upper and lower concentration limits. Samples containing anion concentrations greater than the upper concentration limit must be diluted before analysis because the analytical curve becomes nonlinear.

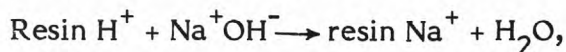
Table 1.--Analytical limits

Constituent	Minimum concentration	Maximum concentration
	(mg/L)	(mg/L)
F	0.01	50
Cl	.20	50
$\text{NO}_2\text{-N}$.02	70
$\text{PO}_4\text{-P}$.06	40
Br	.10	150
$\text{NO}_3\text{-N}$.05	150
SO_4	.20	100

2. Summary of method

All seven anions are determined on a single filtered and unacidified sample with an ion chromatograph.

In anion analysis the ions of interest elute through an anion-ion exchange separator column at different rates, depending upon the affinity of each with the ion-exchange resin. On entering a suppressor column, the eluting base, for example, NaOH, is removed by the acid resin:

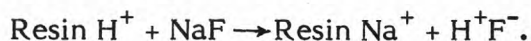
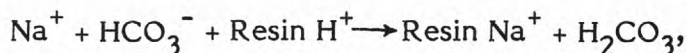
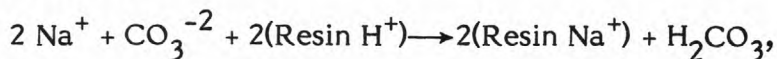


and the analyte anions (A^-) are converted to their acids:



which pass through the suppressor column and into a flow-through conductivity cell where they are detected. A system for anion analysis is shown in figure 1, which includes an eluent reservoir, pump, sample injection device, separator, and suppressor columns followed by a flow-through conductivity cell, meter, and recorder, and (or) integrator.

In the HCO_3^- - CO_3^{2-} system described in figure 1, the suppressor reactions are as follows:



A typical chromatogram for these seven anions is shown in figure 2.

3. Interferences

3.1 Depression of the baseline is a common problem in anion determinations. A small sharp dip prior to the fluoride peak is the void volume indication of the columns; however, this dip will not affect fluoride results.

3.2 A second broader depression is a "water dip" just before the chloride peak. The water dip may be the result of eluent dilution, elution of low concentration levels of hydroxide ion, or pure water. Dip interference is negligible when determining milligram per liter levels of fluoride and chloride.

Ion chromatography - anions

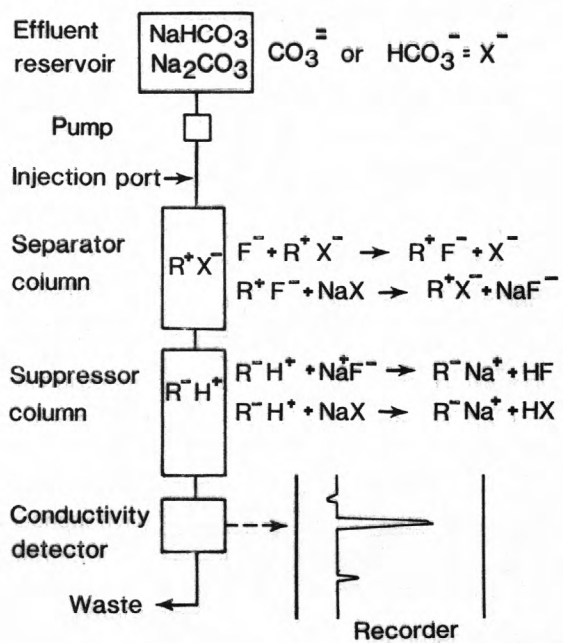


Figure 1.--Ion chromatography system for anions.

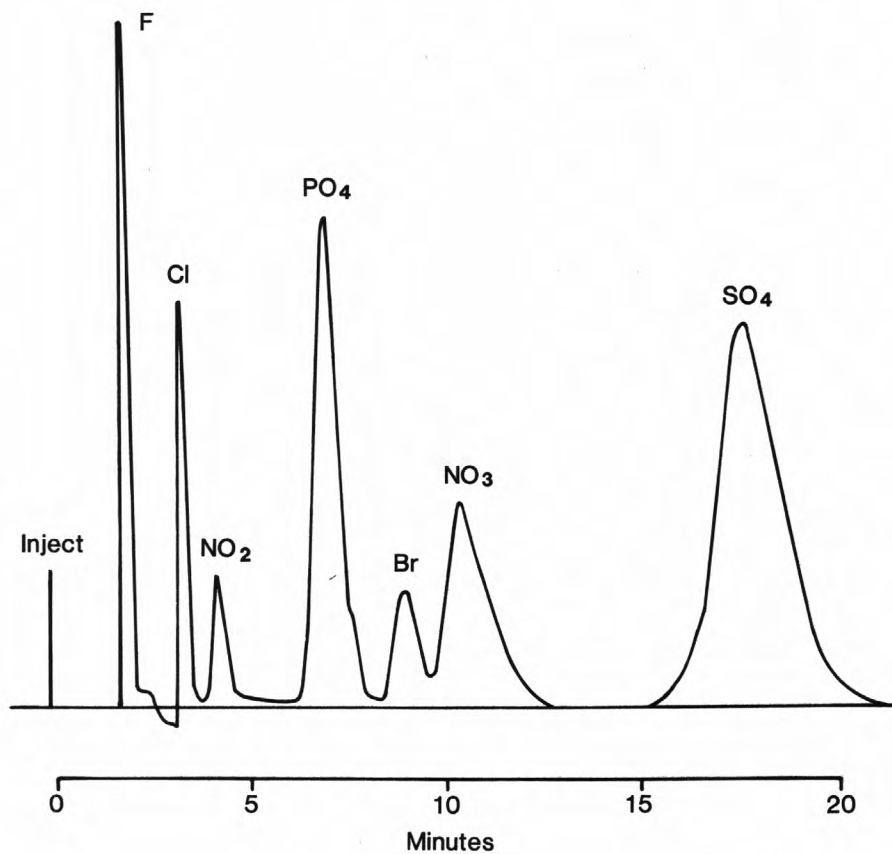


Figure 2.--A typical chromatogram for seven anions.

3.3 Samples containing high concentrations of chloride or other ions may cause unresolved 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.

4. Apparatus

4.1 Dionex Model 10 Ion Chromatograph with Dual Pen Recorder^{1/} (1 V and 100 mV) or equivalent, using the following operating conditions:

Sample loop.....200 μ L
Eluent flow rate.....138 mL/h
Specific conductance meter settings...10, 30, and 100 μ mho
Recorder chart speed.....0.5 cm/min

4.2 For any additional information, refer to the manufacturer's instruction manual.

5. Reagents

5.1 Anion Standard Solutions

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

5.1.2 Bromide standard solution II, 1.00 mL = 0.10 mg Br: Dilute 100 mL bromide standard solution I to 1,000 mL with demineralized water.

5.1.3 Bromide standard solution III, 1.00 mL = 0.01 mg Br: Dilute 100 mL bromide standard solution II to 1,000 mL with demineralized water.

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

5.1.5 Chloride standard solution II, 1.00 mL = 0.10 mg Cl: Dilute 100 mL chloride standard solution I to 1,000 mL with demineralized water.

^{1/} "The use of the brand name in this report is for identification purposes only and does not imply endorsement by the U.S. Geological Survey."

5.1.6 Chloride standard solution III, 1.00 mL = 0.01 mg Cl: Dilute 100 mL chloride standard solution II to 1,000 mL with demineralized water.

5.1.7 Fluoride standard solution I, 1.00 mL = 1.00 mg F: Dissolve 2.2100 g NaF in demineralized water and dilute to 1,000 mL.

5.1.8 Fluoride standard solution II, 1.00 mL = 0.10 mg F: Dilute 100 mL fluoride standard solution I to 1,000 mL with demineralized water.

5.1.9 Fluoride standard solution III, 1.00 mL = 0.01 mg F: Dilute 100 mL fluoride standard solution II to 1,000 mL with demineralized water.

5.1.10 Nitrate-nitrogen standard solution I, 1.00 mL = 1.00 mg $\text{NO}_3\text{-N}$: Dissolve 6.0714 g NaNO_3 in demineralized water and dilute to 1,000 mL.

5.1.11 Nitrate-nitrogen standard solution II, 1.00 mL = 0.10 mg $\text{NO}_3\text{-N}$: Dilute 100 mL nitrate-nitrogen standard solution I to 1,000 mL with demineralized water.

5.1.12 Nitrate-nitrogen standard solution III, 1.00 mL = 0.01 mg $\text{NO}_3\text{-N}$: Dilute 100 mL nitrate-nitrogen standard solution II to 1,000 mL with demineralized water.

5.1.13 Nitrite-nitrogen standard solution I, 1.00 mL = 1.00 mg $\text{NO}_2\text{-N}$: Dissolve 4.9286 g NaNO_2 in demineralized water and dilute to 1,000 mL.

5.1.14 Nitrite-nitrogen standard solution II, 1.00 mL = 0.10 mg $\text{NO}_2\text{-N}$: Dilute 100 mL nitrite-nitrogen standard solution I to 1,000 mL with demineralized water.

5.1.15 Nitrite-nitrogen standard solution III, 1.00 mL = 0.01 mg $\text{NO}_2\text{-N}$: Dilute 100 mL nitrite-nitrogen standard solution II to 1,000 mL with demineralized water.

5.1.16 Phosphorus standard solution I, 1.00 mL = 1.00 mg P: Dissolve 4.5806 g anhydrous Na_2HPO_4 in demineralized water and dilute to 1,000 mL.

5.1.17 Phosphorus standard solution II, 1.00 mL = 0.10 mg P: Dilute 100 mL phosphorus standard solution I to 1,000 mL with demineralized water.

5.1.18 Phosphorus standard solution III, 1.00 mL = 0.01 mg P: Dilute 100 mL phosphorus standard solution II to 1,000 mL with demineralized water.

5.1.19 Sulfate standard solution I, 1.00 mL = 1.00 mg SO_4 : Dissolve 1.8142 g K_2SO_4 in demineralized water and dilute to 1,000 mL.

5.1.20 Sulfate standard solution II, 1.00 mL = 0.10 mg SO_4 : Dilute 100 mL sulfate standard solution I to 1,000 mL with demineralized water.

5.1.21 Sulfate standard solution III, 1.00 mL = 0.01 mg SO_4 : Dilute 100 mL sulfate standard solution II to 1,000 mL with demineralized water.

5.2 Eluent, 0.003M NaHCO_3 /0.002M Na_2CO_3 (NOTE 1): Dissolve 1.008 g NaHCO_3 and 0.848 g Na_2CO_3 in demineralized water and dilute to 4 L.

NOTE 1. Eluent concentration may be varied slightly to obtain same retention times for each anion when a new separator column is used.

5.3 Mixed working-anion standard solution

5.3.1 Mixed standard solution I, 0.25 mg/L F, Cl, NO_2 -N, P, Br, NO_3 -N, SO_4 : Combine 25 mL of each anion standard solution III (0.01 mg/mL) and dilute to 1,000 mL with demineralized water.

5.3.2 Mixed standard solution II, 0.50 mg/L F, Cl, NO_2 -N, P, Br, NO_3 -N, SO_4 : Combine 50 mL of each anion standard solution III (0.01 mg/mL) and dilute to 1,000 mL with demineralized water.

5.3.3 Mixed standard solution III, 1.0 mg/L F, Cl, NO_2 -N, P, Br, NO_3 -N, SO_4 : Combine 10 mL of each anion standard solution II (0.10 mg/mL) and dilute to 1,000 mL with demineralized water.

5.3.4 Mixed standard solution IV, 5.0 mg/L F, Cl, NO_2 -N, P, Br, NO_3 -N, SO_4 : Combine 5 mL of each anion standard solution I (1.0 mg/mL) and dilute to 1,000 mL with demineralized water.

5.3.5 Mixed standard solution V, 10.0 mg/L F, Cl, NO_2 -N, P, Br, NO_3 -N, SO_4 : Combine 10 mL of each anion standard solution I (1.0 mg/mL) and dilute to 1,000 mL with demineralized water.

5.3.6 Mixed standard solution VI, maximum concentration of each constituent listed in Table 1. Prepare by appropriate dilution of individual anion standard solution I.

5.4 Precleaning column, 3 X 150 mm: Dionex pellicular anion resin or equivalent.

5.5 Regeneration solution, 1N H_2SO_4 : Add 111 mL concentrated H_2SO_4 to demineralized water. Cool and dilute to 4 L with demineralized water.

5.6 Separator column, 3 X 500 mm: Dionex pellicular anion resin or equivalent.

5.7 Suppressor column, 6 X 250 mm: Dowex 50 W-X 16-H form resin.

6. Procedure

6.1 Set up instrument with operating parameters described under apparatus. Elute columns with 0.003M Na_2CO_3 /0.002M Na_2CO_3 until baseline stabilizes (NOTE 2). Allow approximately 30 min for equilibration and begin analysis.

NOTE 2. Baseline will drift if room temperature fluctuates.

6.2 For mixed standard solutions I, II, and III set full-scale setting at 10 μmho . For mixed standard solutions III, IV, and V set full-scale setting at 30 μmho . For mixed standard solutions IV, V, VI set full-scale setting at 100 μmho (for P and SO_4 use 30 μmho).

6.3 Inject 2 mL of each mixed standard solution (I thru V) and record peak heights of each of the seven anions at specified scale setting given (NOTE 2). The retention time of each anion is shown in table 2.

Table 2.--Approximate retention time of anions

Constituent	Time (min)
F	2.2
Cl	3.8
NO_2	4.8
PO_4	7.4
Br	10.0
NO_3	11.8
SO_4	17.4

NOTE 3. The analytical curves for each of these anions are reproducible; therefore, the five mixed standard solutions are analyzed only once a week. Analyze only one mixed standard solution each day prior to analysis of samples.

6.4 Inject approximately 2 mL of each sample solution and record peak heights of each anion found.

6.5 Regenerate the suppressor column at the end of 8 to 10 h of operation.

7. Calculation

7.1 Prepare the two analytical curves by plotting the heights of each standard peak versus its respective anion concentration.

7.2 Identify each anion in each sample by comparison of retention times with those of standard solutions.

7.3 Compute the concentration of each anion in each sample by comparing its peak-height to the analytical curve.

DISCUSSION OF RESULTS

Retention times

Retention time of each anion shown previously in table 2 will vary slightly from one separator column to another. Eluent concentration may be varied slightly to obtain same retention times for each anion when a new separator column is used. Until there is a loss in resolution, which is an indication of a spent column, retention times will not vary. During this study, the separator column was replaced after about one year of continuous operation because of poor resolution between bromide and nitrate.

Precision

A number of U.S. Geological Survey Standard Reference Water Samples (SRWS) and rainfall samples were used to determine the precision of the ion chromatography technique. Table 3 shows precision data for fluoride, chloride, nitrate-nitrogen, and sulfate on five precipitation samples, using ion chromatography. Ten replicate analyses were performed on each sample over a period of several days. Percent relative standard deviation for fluoride is high, averaging about 19 percent, but is attributed to the low concentration of fluoride in these precipitation samples, as well as others. Precision for chloride, nitrate-nitrogen, and sulfate is good for the concentrations encountered in these samples. Additional data on precision were obtained on

Table 3.--Precision of ion chromatography on precipitation samples

Constituent	Mean ^{1/} (mg/L)	Standard deviation (mg/L)	Percent relative standard deviation
F	0.018	0.004	22.2
	.022	.004	18.2
	.031	.007	22.6
	.033	.007	21.2
	.080	.010	12.5
Cl	0.72	0.04	5.6
	.81	.09	11.1
	1.77	.02	1.1
	2.72	.24	8.8
	5.84	.19	3.2
NO ₃ -N	0.12	0.01	8.3
	.21	.01	4.8
	.42	.05	11.9
	.70	.08	11.4
	1.27	.05	3.9
SO ₄	1.68	0.05	3.0
	1.83	.08	4.4
	2.60	.05	1.9
	3.04	.02	0.7
	3.88	.10	2.6

^{1/}Values based on 10 replicate determinations.

five SRWS. These data are listed by sample number in table 4. In addition to fluoride, chloride, nitrate-nitrogen, and sulfate, orthophosphate as phosphorus occurs in two of the SRWS (Nos. 60 and 62). Bromide is present in SRWS No. 62, and nitrite is present in SRWS No. 58. Percent relative standard deviation is less than 8.3 percent for all anions except nitrite-nitrogen, which is 33.3 percent; however, the concentration of nitrite-nitrogen is extremely low and is near its minimum level of detection.

Accuracy

An indication of accuracy of ion chromatography also can be seen from results shown in table 4. Listed in the table are values obtained by interlaboratory analysis. Results by ion chromatography are in good agreement with the interlaboratory mean, and all results fall within, at least, one standard deviation of the interlaboratory mean value.

Recovery by ion chromatography - To further determine the accuracy of results obtained by ion chromatography, 10 precipitation samples and 10 surface-water samples were spiked with known concentrations of fluoride, chloride, nitrate, and sulfate. These results are shown in tables 5 and 6, respectively. Recoveries for fluoride, chloride, and sulfate on precipitation samples, which are shown in table 5, ranged from 96 to 103 percent, and for nitrate from 96 to 102 percent. Recoveries for fluoride, chloride, and sulfate on surface waters, which are shown in table 6, ranged from 97 to 103 percent, and for nitrate from 96 to 103 percent. Bromide was not found in any of the above samples; however, several ground-water samples, containing bromide, were spiked and recoveries ranged from 93 to 103 percent (table 7). Additional indication of accuracy is shown in the analysis of spiked samples which is described in a subsequent section.

Table 4.—Precision of ion chromatography on Standard Reference Water Samples (SRWS)
(Results in mg/L except for column relating to percent relative standard deviation).

Sample No.	Constituent	Ion chromatography data ^{1/}			Interlaboratory SRWS program data	
		Mean	Standard deviation	Percent relative standard deviation	Mean	Standard deviation
50	F	2.02	0.15	7.4	2.11	0.26
	Cl	119	1.2	1.0	122	5
	NO ₃ -N	1.08	.09	8.3	1.08	.10
	SO ₄	100	1.4	1.4	99.9	4.0
51	F	0.92	0.01	1.1	0.92	0.13
	Cl	9.76	.19	2.0	8.69	1.10
	NO ₃ -N	.53	.01	1.9	.46	.11
	SO ₄	68.1	.60	.9	68.9	2.6
58	F	0.91	0.03	3.3	0.92	0.07
	Cl	1.71	.06	3.5	1.71	.70
	NO ₂ -N	.03	.01	33.3	—	—
	SO ₄	15.1	.80	5.3	13.5	2.2
60	F	0.79	0.02	2.5	0.84	0.10
	Cl	58.6	.7	1.2	58.0	1.7
	PO ₄ -P	1.45	.01	.7	1.48	.09
	NO ₃ -N	5.26	.14	2.7	4.86	.52
	SO ₄	146	3	2.0	144	8
62	F	0.78	0.03	3.8	0.80	0.06
	Cl	9.90	.39	3.9	8.76	2.22
	PO ₄ -P	.273	.010	3.7	.344	.032
	Br	.295	.020	6.8	.550	.312
	SO ₄	62.1	.9	1.4	59.7	4.2

^{1/} Values based on 10 replicate determinations of SRWS.

Table 5.--Recovery data on precipitation samples (results in milligrams per liter)

Sample No.	Constituent	Present	Added	Found	Percent recovery
1	F	0.038	0.04	0.08	102
	Cl	.294	.3	.61	103
	NO ₃ -N	.56	.6	1.14	98
	SO ₄	10.54	10.0	19.7	96
2	F	0.052	0.05	0.105	103
	Cl	.385	.4	.77	98
	NO ₃ -N	.618	.6	1.21	99
	SO ₄	6.74	7.0	14.2	103
3	F	0.043	0.04	0.08	96
	Cl	.304	.3	.62	103
	NO ₃ -N	.475	.5	.95	97
	SO ₄	5.70	6.0	11.2	96
4	F	0.063	0.06	0.125	102
	Cl	.945	1.0	1.99	102
	PO ₄ -P	.057	.06	.12	102
	NO ₃ -N	1.39	1.5	2.95	102
	SO ₄	7.60	7.0	15.1	103
5	F	0.030	0.027	0.057	100
	Cl	.95	1.0	2.0	102
	NO ₃ -N	.428	.4	.81	98
	SO ₄	3.52	3.73	7.2	99

Table 5.--Recovery data on precipitation samples (results in milligrams per liter)
(Continued)

Sample No.	Constituent	Present	Added	Found	Percent recovery
6	F	0.057	0.053	0.11	100
	Cl	.55	.53	1.04	96
	NO ₃ -N	1.76	1.75	3.45	98
	SO ₄	9.12	9.33	18.0	98
7	F	0.029	0.04	0.07	101
	Cl	.51	.5	.98	97
	NO ₃ -N	1.31	1.5	2.81	100
	SO ₄	7.98	7.0	15.5	103
8	F	0.024	0.025	0.05	102
	Cl	.314	.3	.60	98
	NO ₃ -N	.88	1.0	1.8	96
	SO ₄	7.32	7.0	14.4	100
9	F	0.074	0.07	0.143	99
	Cl	.332	.5	.82	98
	NO ₃ -N	.76	.75	1.48	98
	SO ₄	8.3	7.0	15.8	103
10	F	0.057	0.06	0.115	98
	Cl	.446	.5	.95	100
	NO ₃ -N	.774	.75	1.48	97
	SO ₄	11.3	7.0	18.8	103

Table 6.--Recovery in surface water samples (results in milligrams per liter).

Sample No.	Constituent	Present	Added	Found	Percent recovery
1	F	0.125	0.1	0.23	102
	Cl	6.94	.75	7.80	101
	NO ₃ -N	.142	.1	.24	99
	SO ₄	22.4	2.5	25.2	101
2	F	0.20	0.2	0.4	100
	Cl	1.16	1	2.2	102
	NO ₃ -N	.077	.1	.18	102
	SO ₄	42.9	3	45.6	99
3	F	0.432	0.4	0.82	99
	Cl	4.70	.7	5.55	103
	NO ₃ -N	.432	.5	.925	99
	SO ₄	32.3	5	36.0	97
4	F	0.46	0.4	0.85	99
	Cl	3.12	.5	3.72	103
	NO ₃ -N	.091	.1	.197	103
	SO ₄	39.0	3	41.5	99
5	F	0.51	0.4	0.94	103
	Cl	3.12	2	55.2	102
	NO ₃ -N	.154	.1	.26	102
	SO ₄	36.1	5	41.6	101

Table 6.--Recovery in surface water samples (results in milligrams per liter).
(Continued)

Sample No.	Constituent	Present	Added	Found	Percent recovery
6	F	1.06	0.2	1.27	101
	Cl	2.30	2	4.25	99
	NO ₃ -N	.125	.1	.215	96
	SO ₄	2.17	1	3.20	101
7	F	1.06	0.2	1.25	99
	Cl	3.12	.5	3.63	100
	NO ₃ -N	.106	.5	.605	100
	SO ₄	2.94	3	6.12	103
8	F	0.17	0.2	.37	100
	Cl	2.35	2	4.2	97
	NO ₃ -N	.139	.6	.710	96
	SO ₄	1.79	1	2.78	100
9	F	0.115	0.07	0.18	97
	Cl	3.26	1.5	4.78	100
	NO ₃ -N	.269	.1	.378	102
	SO ₄	3.59	.3	3.9	100
10	F	0.086	0.07	0.16	103
	Cl	1.34	1.5	2.9	102
	NO ₃ N	.067	.05	.120	103
	SO ₄	2.90	2	4.95	101

Table 7.—Recovery of bromide on ground-water samples
(results in milligrams per liter).

Sample No.	Present	Added	Found	Percent recovery
1	0.88	0.50	1.38	100
	.44	.38	.80	98
2	1.67	1.50	3.10	98
	.83	.75	1.60	101
3	2.29	2.50	4.87	102
	1.14	1.13	2.22	98
4	6.35	6.00	12.7	103
	3.18	3.00	6.30	102
5	0.29	0.25	0.53	98
	.14	.15	.27	93

Comparison of methods - To determine the accuracy of the ion chromatographic technique, a number of precipitation and surface waters analyzed by ion chromatography were also analyzed by other techniques. These methods are as follows:

Chloride: Automated colorimetric ferric thiocyanate;

Nitrate: Automated colorimetric cadmium reduction-diazotization;

Fluoride: Automated electrometric ion-selective electrode;

Nitrite: Automated colorimetric diazotization;

Phosphate: Automated colorimetric phosphomolybdate;

Sulfate: Automated colorimetric complexometric methylthymol blue.

These methods appear in Techniques of Water-Resources Investigations (TWRI), book 5, chapter A1, "The Determination of Inorganic Substances in Water and Fluvial Sediment" (Skougstad and others, 1979).

Results on precipitation waters for fluoride, chloride, nitrate, and sulfate are shown in table 8. The concentrations of fluoride ranged from 0.01 to 0.10 mg/L, and therefore were too low to be detected by the ion-selective electrode method. Chloride concentrations in precipitation samples were extremely low, and there is bias. Results by ion chromatography are greater than those by the automated colorimetric method; however, in most instances, results are greater by only 0.1 mg/L, which is usually not significant. The correlation coefficient between methods is 0.977. No bias occurs in results for nitrate in the precipitation samples; the correlation coefficient is 0.977. Sulfate results show a positive bias by ion chromatography; however, the method is more sensitive than by automated colorimetry. Even with this bias, the correlation coefficient is 0.997. At 13 mg/L, the percent relative standard deviation for the automated colorimetric method is 13 as reported by Skougstad and others, 1979. In tables 3 and 4, the percent relative standard deviation for sulfate by ion chromatography ranged from 0.7 to 5.3 over a concentration range of 1.68 to 146 mg/L. It appears that ion chromatography gives better results at sulfate levels below 10 mg/L.

Table 8.--Comparison between ion chromatographic (IC) and colorimetric (AC) methods on precipitation samples (results in milligrams per liter).

Sample No.	Cl		NO ₃ N		SO ₄	
	IC	AC	IC	AC	IC	AC
1	1.2	1.3	1.46	1.50	8.70	9.2
2	.2	.2	.53	.56	7.45	6.8
3	.2	.2	.62	.69	11.0	10.0
4	.2	.2	.55	.69	5.90	5.9
5	.2	.3	.87	.82	8.55	8.7
6	.2	.1	.61	.63	8.35	8.3
7	.4	.3	1.49	1.45	8.00	7.8
8	.5	.4	.74	.71	7.50	7.4
9	.2	.2	.45	.45	4.40	4.7
10	.6	.7	1.60	1.50	8.05	8.6
11	.1	.1	.5	.56	5.90	5.3
12	.9	.8	1.61	1.70	8.00	7.7
13	.2	.2	.90	.93	8.50	7.6
14	1.0	.9	.52	.50	3.65	3.1
15	.4	.2	1.02	.93	7.00	6.6
16	.1	.2	.51	.59	3.90	4.1
17	.6	.6	.91	.93	12.1	12.0
18	1.0	1.1	.29	.33	2.50	2.9
19	.1	.2	.77	.78	9.45	9.2
20	.5	.5	.87	.86	9.45	9.6
21	.2	.2	.70	.75	7.50	7.6

Table 8.--Comparison between ion chromatographic (IC) and colorimetric (AC) methods on precipitation samples (results in milligrams per liter).
(Continued)

Sample No.	Cl		NO ₃ N		SO ₄	
	IC	AC	IC	AC	IC	AC
22	5.9	4.7	1.24	1.26	3.08	2.4
23	.4	.1	.69	.52	2.10	2.1
24	.2	.0	.94	.61	1.75	1.6
25	.4	.3	.46	.45	1.75	1.3
26	.3	.0	.43	.42	2.55	2.3
27	.4	.0	.73	.80	1.95	1.4
28	.8	.5	.70	.64	1.97	2.0
29	.4	.2	.32	.33	1.50	1.4
30	1.8	1.6	.12	.11	1.62	1.1
31	2.7	2.2	.19	.19	1.77	1.4
32	.7	.1	.36	.44	3.80	3.4
33	.2	.1	.37	.46	1.13	0.9
34	.2	.2	.35	.32	1.27	0.9
35	.3	.0	.20	.20	1.60	1.0
36	.5	.1	.37	.33	2.47	2.0
37	.9	.3	.74	.66	2.60	2.1
38	.4	.3	.65	.61	1.95	2.0

Table 9 shows a comparison of results on surface waters for the same constituents, and also includes orthophosphate, at higher levels than those found in precipitation waters. Again a positive bias occurs for chloride; however, the correlation is good (0.995). For sulfate, the bias is reversed from results found in the precipitation samples. The correlation is not quite as good (0.978); however, results for most samples compare favorably. It will be pointed out later that chloride and sulfate recovery on spiked samples is superior by ion chromatography. Only 13 of the samples contained orthophosphate; although a negative bias occurs, results are in good agreement, with a correlation of 0.995. No bias occurs for nitrate, and the correlation coefficient is 0.996. The correlation of fluoride results using ion chromatography vs. an automated ion-selective electrode method appears to be poor (0.848). It must be pointed out, however, that results by ion-selective electrode are reported only to one significant figure, as specified in the reporting procedure. The ion chromatographic technique is more sensitive, and it is possible to report results to the nearest 0.01 mg/L.

Table 10 gives results for nitrite on a few surface water samples by both ion-chromatographic and automated-colorimetric methods. The concentrations of nitrite found were low, but results compared favorably, even though results by ion chromatography were obtained on a different day than results obtained by the colorimetric method. No samples available at the time of this study contained higher levels of nitrite.

Because of the limited volume of water, no comparison was made for bromide. The conventional titrimetric, hypochlorite oxidation method (Skougstad and others, 1979) for bromide requires a comparatively large sample volume, which was not available.

Comparison of methods (recovery) - Ten surface-water samples were analyzed for fluoride, chloride, nitrate, and sulfate by techniques previously discussed. These samples were then spiked with known concentrations of the above-mentioned anions. Data obtained are shown in table 11. Percent recovery of chloride, nitrate, and sulfate by automated colorimetry is generally higher than percent recovery by ion chromatography. The percent recovery ranged as follows:

	Ion chromatography	Automated colorimetry
Cl	97-103	97-134
NO ₃	96-105	90-121
SO ₄	97-103	90-108

Recovery for nitrate in sample No. 10 was 233 percent.

Table 9.--Comparison between ion chromatograph (IC), and ion-selective electrode (ISE) and colorimetric (AC) methods on surface water samples (results in milligrams per liter).

Sample No.	F		Cl		PO ₄ -P		NO ₃ -N		SO ₄	
	IC	ISE	IC	AC	IC	AC	IC	AC	IC	AC
1	0.50	0.1	2.3	2.0	0.00	0.01	0.12	0.04	3.1	2.1
2	.72	.7	645.	410.	2.84	2.84	2.03	2.01	133.	140.
3	.48	.5	415.	300.	1.60	1.77	3.28	3.23	102.	90.
4	.78	.7	460.	320.	.25	.44	.31	.35	330.	250.
5.	.81	.8	72.	55.	1.42	1.63	5.50	5.50	117.	115.
6.	.75	.9	72.	58.	1.50	1.72	5.50	5.60	117.	131.
7	.44	.1	11.4	13.	.00	.01	2.40	2.49	7.5	12.
8	.47	.8	72.	59.	1.45	1.50	5.45	5.00	117.	136.
9	.15	.2	41.	47.	.09	.16	.00	.01	.36	1.0
10	.78	.8	78.	61.	1.48	1.72	5.70	5.07	125.	136.
11	.28	.3	7.5	6.3	.30	.31	3.05	2.90	17.	19.
12	.41	.5	6.8	5.6	.24	.25	3.60	3.10	17.	18.

Table 9.--Comparison between ion chromatograph (IC), and ion-selective electrode (ISE) and colorimetric (AC) methods on surface water samples (results in milligrams per liter). (Continued)

Sample No.	F		Cl		PO ₄ -P		NO ₃ -N		SO ₄	
	IC	ISE	IC	AC	IC	AC	IC	AC	IC	AC
13	0.32	0.3	2.1	1.8	0.11	0.12	0.87	0.52	7.1	7.2
14	.22	.2	8.4	7.0			.05	.08	9.2	11.
15	.23	.3	15.	15.			4.2	4.10	13.3	13.
16	.12	.1	20.	21.			2.93	2.97	11.4	12.
17	.22	.2	103.	110.			.04	.04	13.3	16.
18	.23	.2	3.5	2.2			.09	.14	38.	39.
19	.23	.2	2.3	2.0			.09	.01	34.	35.
20	.55	.5	8.0	7.6			.15	.21	148.	122.
21	.50	.6	10.8	7.7			.15	.30	116.	97.
22	.23	.3	19.6	16.5			.17	.23	36.	37.
23	.07	.1	8.7	8.0			1.47	1.43	15.	15.
24	.14	.2	29.	31.			.00	.01	1.5	1.8

Table 10.--Comparison of nitrite (as nitrogen) between ion chromatographic (IC) and colorimetric (AC) on on surface water samples (results in milligrams per liter).

Sample No.	IC	AC
1	0.05	0.15
2	.13	.12
3	.12	.20
4	.15	.13
5	.15	.15
6	.15	.16
7	.22	.11
8	.08	.11
9	.15	.13

Table 11.--Comparison and recovery data between ion chromatographic (IC) and colorimetric (AC) methods. Fluoride determined by ion-selective methods. Results in milligrams per liter.

Sample No.	Constituent	Present		Added	Found		Percent Recovery	
		IC	AC		IC	AC	IC	AC
1	F	0.12	0.10	0.10	0.23	0.25	105	125
	Cl	6.94	4.66	.75	7.80	5.76	101	106
	NO ₃ -N	.14	.15	.10	.24	.27	100	108
	SO ₄	22.4	22.8	2.5	25.2	23.0	101	91
2	F	0.20	0.19	0.20	0.40	0.50	100	128
	Cl	1.16	1.16	1.0	2.20	2.65	102	118
	NO ₃ -N	.08	.11	.10	.18	.21	100	100
	SO ₄	42.9	35.5	3.0	45.6	41.0	99	106
3	F	0.43	0.38	0.40	0.82	0.98	99	126
	Cl	4.70	4.90	.70	5.55	6.03	103	108
	NO ₃ -N	.43	.39	.50	.92	1.00	99	112
	SO ₄	32.3	30.7	5.0	36.0	35.0	97	98
4	F	0.46	0.43	0.40	0.85	1.00	99	120
	Cl	3.12	3.26	.50	3.72	3.84	103	102
	NO ₃ -N	.09	.11	10	.20	.25	105	121
	SO ₄	39.0	36.0	3.0	41.5	39.0	99	100
5	F	0.51	0.43	0.40	0.94	1.00	103	120
	Cl	3.12	3.22	2.0	5.20	5.74	102	110
	NO ₃ -N	.15	.20	.10	.26	.27	104	90
	SO ₄	36.1	33.6	5.0	41.6	38.0	101	98

Table 11.--Comparison and recovery data between ion chromatographic (IC) and colorimetric (AC) methods. Fluoride determined by ion-selective methods. Results in milligrams per liter. (Continued)

Sample No.	Constituent	Present		Added	Found		Percent recovery	
		IC	AC		IC	AC	IC	AC
6	F	1.06	0.92	0.20	1.27	1.30	101	116
	Cl	2.30	2.25	2.0	4.25	4.10	99	97
	NO ₃ -N	.12	.13	.10	.22	.25	96	110
	SO ₄	2.17	2.25	1.0	3.20	3.50	101	108
7	F	1.06	0.92	0.20	1.25	1.21	99	108
	Cl	3.12	2.94	.50	3.63	4.60	100	134
	NO ₃ -N	.11	.12	.50	.60	.65	98	105
	SO ₄	2.94	2.94	3.0	6.12	5.40	103	91
8	F	0.17	0.16	0.20	0.37	0.48	100	133
	Cl	2.35	2.16	2.0	4.2	4.70	97	113
	NO ₃ -N	.14	.14	.60	.71	.77	96	104
	SO ₄	1.79	1.76	1.0	2.78	2.9	100	105
9	F	0.12	0.10	0.07	0.18	0.21	95	124
	Cl	3.26	3.82	1.5	4.78	5.95	100	112
	NO ₃ -N	.27	.33	.10	.38	.42	103	98
	SO ₄	3.59	3.72	.30	3.9	3.6	100	90
10	F	0.09	0.10	0.07	0.16	0.17	100	100
	Cl	1.34	1.47	1.5	2.9	3.22	102	108
	NO ₃ -N	.07	.01	.05	.12	.14	100	233
	SO ₄	2.90	3.53	2.0	4.95	5.0	101	90

Table 12 presents comparison and recovery data for orthophosphate on surface-water samples by both ion chromatographic and automated-colorimetric methods. These samples contained high concentrations of phosphate, and the recovery study was done in two ways. One set was diluted 1:1, and the other set was spiked with similar concentrations of phosphate originally present in samples. Again, the recovery data by automated colorimetry (97-122 percent) showed generally higher values than found by ion chromatography (95-104 percent).

Table 12.--Comparison and recovery data for orthophosphate (as P) between ion chromatographic (IC) and colorimetric (AC) methods.
Results in milligrams per liter.

Sample No.	Present		Diluted	Added	Found		Percent recovery	
	IC	AC			IC	AC	IC	AC
1	2.63	2.5	1:1		1.26	1.5	95	120
	2.50	2.4		2.5	5.15	5.0	103	102
2	2.40	2.3	1:1		1.16	1.4	97	122
	2.28	2.2		2.0	4.20	4.6	98	110
3	2.95	2.9	1:1		1.50	1.6	101	110
	2.80	2.8		3.0	6.0	6.0	103	103
4	2.20	2.0	1:1		1.08	1.2	98	120
	2.09	1.9		1.0	3.10	3.5	100	121
5	1.98	2.0	1:1		0.97	1.1	98	110
	1.88	1.9		2.0	4.02	4.2	104	108
6	3.65	3.8	1:1		1.76	1.9	96	100
	3.47	3.6		3.0	6.40	6.6	99	97

CONCLUSIONS

From the data presented, ion chromatography is a superior technique for determining bromide, chloride, fluoride, nitrate, nitrite, orthophosphate, and sulfate in atmospheric precipitation. The method is more sensitive, accurate, and precise than other current standard methods. The method is suitable for other types of natural waters, although speed of analysis is much faster by other techniques. It would be ideally suited for turbid and colored samples.

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