METHOD FOR THE DETERMINATION OF DISSOLVED CHLORIDE, NITRATE, AND SULFATE IN NATURAL WATER USING ION CHROMATOGRAPHY

U.S. GEOLOGICAL SURVEY

Open-File Report 95-426A

METHOD FOR THE DETERMINATION OF DISSOLVED CHLORIDE, NITRATE, AND SULFATE IN NATURAL WATER USING ION CHROMATOGRAPHY

By Terry I. Brinton, Ronald C. Antweiler, and Howard E. Taylor

---

U.S. GEOLOGICAL SURVEY

Open-File Report 95-426A

Denver, Colorado
1996

U.S. DEPARTMENT OF THE INTERIOR

BRUCE BABBITT, Secretary

U.S. GEOLOGICAL SURVEY

Gordon P. Eaton, Director

For additional information write to:

Chief, Branch of Regional Research
U.S. Geological Survey
Box 25046, MS 418
Denver Federal Center
Denver, CO 80225

Copies of this report can be purchased from:

U.S. Geological Survey
Branch of Information Services
Box 25286
Denver, CO 80225

CONTENTS

FIGURES

TABLES

METHOD FOR THE DETERMINATION OF DISSOLVED CHLORIDE, NITRATE AND SULFATE IN NATURAL WATER USING ION CHROMATOGRAPHY

by Terry I. Brinton, Ronald C. Antweiler, and Howard E. Taylor

ABSTRACT

Ion chromatography was used for the determination of dissolved chloride, nitrate and sulfate in natural water where concentrations ranged from a detection limit of 0.02 milligrams per liter to 80 milligrams per liter for chloride, to 18 milligrams per liter for nitrate, and to 280 milligrams per liter for sulfate. Specific conductance was the mode of detection used. Three analytical sample size loops of 11, 61, and 250 microliters, were used to include the analytical ranges described. U.S. Geological Survey Standard Reference Water Samples were analyzed to test the precision and accuracy of the analyses.

INTRODUCTION

In order to evaluate the overall quality of natural water, it is necessary to determine the major anion concentration contributions. Ion chromatography has been shown to be an acceptable method for these determinations. Because anion concentrations in natural water vary with various hydrologic and seasonal conditions, a method was needed to accommodate these various concentrations. This report describes the method developed to meet this need for chloride, nitrate, and sulfate anions in natural water samples. The method is a modification of a previously described method (Hedley and Fishman, 1982).

The authors wish to thank John Garbarino and David Roth for their assistance with equipment modification. We also thank Heidi Hayes for her help with the analyses and Diane McKnight for the use of the ion chromatograph.

APPLICATION OF THE ANALYTICAL METHOD

Samples were analyzed by ion chromatography using a Dionex 2002i/SP series ion chromatograph (IC) fitted with a conductivity detector. Specific instrumentation is listed in Appendix 1. Concentrations greater than 80 mg/L for dissolved chloride, 18 mg/L for nitrate, and 280 mg/L for sulfate were diluted such that the values were within the calibration range used. All water samples were filtered through a 0.45-µm membrane filter prior to analysis to minimize particles obstructing the flow of the system and to insure only the dissolved phase of the analytes was determined. Three sample loops were used for sample introduction (flow injection): a small loop of 11-µL was used for higher concentration samples (greater than 7.2 mg/L for chloride and greater than 45 mg/L for sulfate, nitrate is not normally found in this concentration range); a medium size loop of 61-µL was used for chloride concentrations between 0.08 and 7.2 mg/L, nitrate concentrations between 0.2 and 18 mg/L, and sulfate concentrations between 0.5 and 45 mg/L; and a large loop of 250-µL was used for samples where the concentration was 0.02 to 1.6 mg/L for chloride, 0.02 to 4 mg/L for nitrate, and 0.02 to 10 mg/L for sulfate. The upper limits of concentration for chloride, nitrate, and sulfate were found the be limited by an arbitrary detector output of one million counts. The working concentration range may be modified by adjusting the sample loop size and the gain of the conductivity detector. For example, when using the 250 and 61-µL loops, an output range of 30 µS was generally used. To extend the concentration range, the detector range was changed to 100 µS when using the 11-µL sample loop. In general, the greater the mass of dissolved components passing through the column, the greater the load stress on the column, and hence the shorter its useful lifetime. On occasion dilutions were needed to bring the analyte or analytes of a sample or standard reference into the working calibration range of the loop size being used. The concentrations in tables 1 through 3 that are over the calibration range specified for each loop have been corrected for the dilution. For this reason some of the concentrations in these tables appear to be out of the working calibration range when in actuality they were analyzed with a dilution to within the calibration range.

Both IC eluant solutions and samples were at ambient temperature during analysis. The sample was delivered to the system using an ISCO model ISI autosampler coupled with a peristaltic pump. An exchange column and a pH-buffered eluant of carbonate/bicarbonate were used for anion separation. The system operating conditions are listed in Appendix 2. The presence of electrically conductive cations in the eluant will suppress the signal from the eluting analytes; therefore, a suppressor column is used for high-capacity suppression of cations. The acquisition of data requires the use of a computer with the application of proprietary chromatography automation software and a computer interface. An American Standard Code for Information Interchange (ASCII) file was created that stores information for each sample on all anion peaks detected, including (but not limited to) chloride, nitrate, and sulfate.

Appendix 3 gives the procedure used for the preparation of the calibration standards for the 11, 61, and 250 μL loops. The preparation of the eluant is described in Appendix 4. Appendix 5 describes the sample preparation. A troubleshooting guide is listed in Appendix 6.

DATA PROCESSING

After transferring raw data to a computer as an ASCII file, it is extensively processed within a commercial spreadsheet computer program. The specific peak heights of chloride, nitrate, and sulfate for each analyte are copied into a blank spreadsheet. Because totally resolved well-defined peaks are obtained in the analysis, peak heights instead of peak areas are used in all computations. The operator is responsible for ensuring that the chromatography software has identified the proper peaks; the spreadsheet macros assume the analyte peak is labeled correctly. The next step is to perform regression analysis on the working calibration standards. Calibration standards are used to delineate the range in which the concentrations of the analytes could be determined. A spreadsheet macro calculates a quadratic regression from these standards and reports regression diagnostic statistics. Typically, r^2 values for the three anions are greater than 0.999. Any significant departure from this r^2 value of 1.000 is cause for further investigation. The operator is required to override the macros if, for example, a linear regression is desired or if the expected concentration of one of the calibration standards deviates from an expected value.

The final step is organizing the data report. A spreadsheet macro sorts the data, converts peak height to concentration, and tabulates final results. If the concentrations are greater than those used to establish the working calibration curve, the sample is reanalyzed with a dilution or with a smaller sample loop.

QUALITY CONTROL

This section discusses the quality of the data: precision, accuracy, detection limits, and the statistical confidence of the reported analyte concentrations. Reporting concentration levels are dependent on the size of the sample loop.

Precision

The data precision refers to the expected reproducibility of the method when it is repeated on a homogeneous sample under controlled conditions, regardless of whether or not the observed values are widely displaced from the true value as a result of systematic or constant errors present throughout the measurements. Precision can be expressed as follows (American Public Health Association, 1985, p. 20):

$$P_s = SD_s \cdot t_{(n-1,0.99)}/(dh/dc) \qquad (1)$$

where P_s is the measurement precision of a standard s, and SD_s is the standard deviation of the peak heights of the standard for n replicates; $t_{(n-1,0.99)}$ is the student t statistic at the 99-percent confidence level for n-1 degrees of freedom; and dh/dc is the slope of the calibration curve (peak height versus concentration). Precision is dependent on analyte concentration. Low concentration standards will have lower precision than high standards. A measure that is relatively independent of concentration is the percent precision (%P), which is the precision (calculated from equation 1) divided by the concentration (C) of the standard, multiplied by 100 [%P = 100*P/C].

There are two approaches available for calculating the precision: (1) it can be calculated for a specific calibration standard on a specific day (daily precision), or (2) it can be calculated for a specified standard over a several month period of time (composite precision). In general, the daily precision is realistically a better estimate of the confidence in reported concentrations, because a set of analyses performed on any given day is internally consistent (that is, the precision stands by itself regardless of what happens on other days). The composite precision evaluates how the instrument is performing over a longer period of time, and the degree of confidence for large data sets. Both the composite and daily precision are listed in tables 1-3. The mean observed concentration is close to the reported concentration as indicated in tables 4-6. The daily percent precision for the large loop is usually much better than the composite percent. In general, the large loop allows more precise results than the small loop.

Accuracy

Accuracy refers to the agreement between the amount of an analyte measured by the test method and the amount actually present (American Public Health Association, 1985, p. 20). The Standard Reference Water Samples (SRWS) used have analyte concentrations that are within the calibration standards range of each specific loop size. For the 11-µL, 61-µL, and 250-µL loops, SRWS standards M6, M84, M86, M90, M96, M102, M104, M106 and M112; M106 and M6; and P11 and P12, respectively, were used to evaluate accuracy. The observed and reported values of the SRWS at the 95-percent confidence level are listed in table 4-6. In general, the observed values for the SRWS agree within 1 to 2 percent of the reported values. The observed values for a few of the SRWS analytes range as high as 7.2 percent. The observed values (11-µL loop) compared with the reported concentrations for chloride and sulfate over a wide concentration range indicate that over these ranges the accuracy is acceptable for normal water quality testing as demonstrated in figure 1. Nitrate concentrations in natural water have been found to be too low for analysis using the 11-µL loop.

Detection Limit

The detection limit is the smallest concentration of analyte that can be reliably discerned from background measurement noise. The detection limit has been defined (Skogerboe and Grant, 1970) as follows:

$$DL = SD_{blank} t_{(n-1,0.99)}/(dh/dc)$$

where DL is the detection limit in milligrams per liter; SD_{blank} is the standard deviation of the peak heights of the blank for n replicates; $t_{(n-1,0.99)}$ is the student t statistic at the 99-percent confidence level for n-1 degrees of freedom; and dh/dc is the slope of the calibration curve (peak height versus concentration). The detection limits for the 250-µL loop are listed in table 7; a detection limit is not specified for the 11-µL or 61-µL loops because they are not designed for the determination of low concentrations.

INTERFERENCES

There are no known naturally occurring interferences in the determination of chloride, nitrate, or sulfate using this methodology. In terms of non-natural substances, the only common interference is the chlorate ion, which co-elutes with nitrate. Chlorate is rare in natural water and is considered to be an insignificant problem. There are no known anions that co-elute with chloride and sulfate using the operating conditions described.

The presence of metal cyanide complexes and large aliphatic organic compounds, such as surfactants or humic acids, will degrade column performance (Dionex Corporation, 1983). Removal of these substances from the column, even with manufacturer's recommended cleaning procedures, may be difficult, requiring column replacement. To minimize this problem, a guard column is inserted ahead of the separator column to remove these unwanted substances.

Because chloride and sulfate are ubiquitous, contamination of samples and standards is a common problem. Clean handling procedures are necessary to minimize contamination. These procedures require the use of gloves and the dedication of clean glassware for standards and sample solutions. Ultrapure (18 Megohm) water was used to prepare all standards and solutions, sample dilutions, and for rinsing all items that come into contact with the sample.

SUMMARY

The method described in this report has been shown effective for the determination of dissolved chloride, nitrate and sulfate in natural water having concentration ranges of 0.02 to 80 mg/L for chloride, 0.02 to 18 mg/L for nitrate and 0.02 to 280 mg/L for sulfate. Generally, all raw data are processed using a quadratic regression fit of the calibration standards and for the calculation of the concentrations of the samples. It is the final responsibility of the operator the verify the data for accuracy and precision.

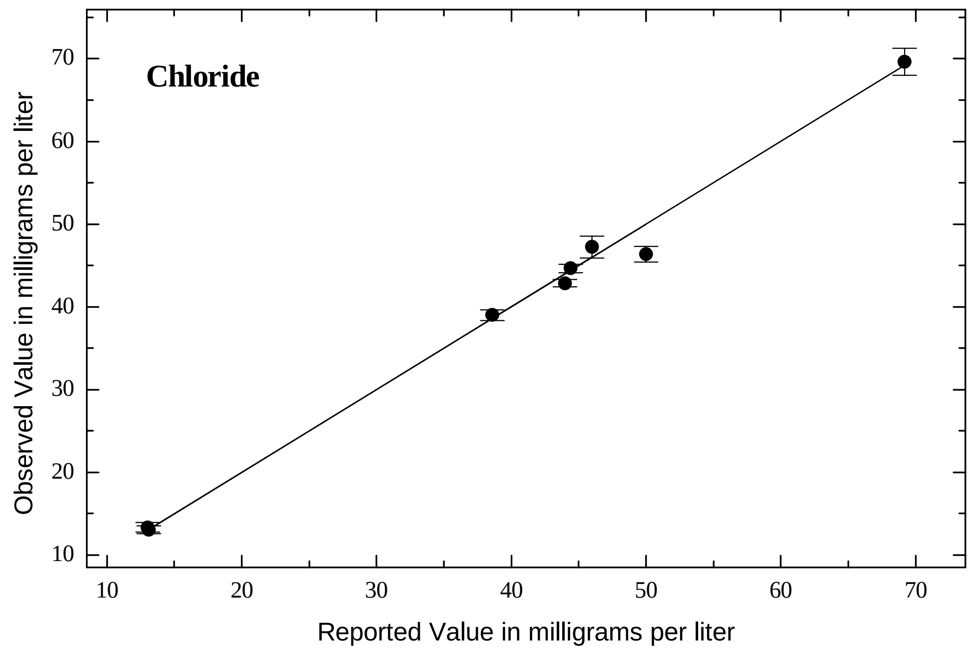
REFERENCES CITED

American Public Health Association and others, 1985, Precision, accuracy, and correctness of analyses, Standard Methods for the Examination of Water and Wastewater, [16th ed.]: Washington, D.C., American Public Health Association, p. 20-25.

Dionex Corporation, 1983, Chromatography training course manual, Methods Development: Sunneyvale, Calif., 35 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, 38 p.

Skogerboe R.K., and Grant C.L. 1970, Comments on the definitions of the terms sensitivity and detection limit: *Spectroscopic Letters*, v. 3, nos. 8 and 9, p. 215-220.



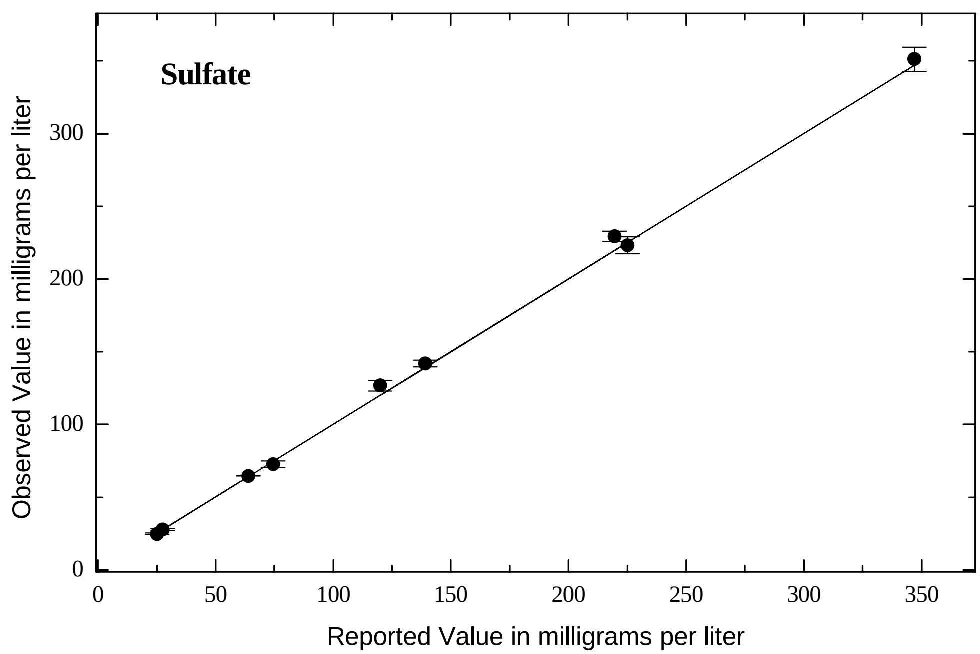


Figure 1.-- Relation between observed and reported concentrations of chloride and sulfate for U.S. Geological Survey Standard Reference Water Samples using a 11-microliter sample loop. Errors are 1 standard deviation of the mean concentrations.

Table 1.-- Precision data for chloride

[Precision (P) and percent precision (%P) of chloride for a variety of calibration standards and for U.S. Geological Survey Standard Reference Water samples using the 250-microliter, the 61-microliter, and the 11-microliter sample loops. The composite P and %P are from determinations averaged over a 7-month period. The precision and %P are determined at the 99-percent confidence level; n is the number of replicates]

Standard	Type	Concentration (milligrams per liter)	Loop size (microliters)	n	Precision	Percent precision
Calibration standard 1	Composite	0.04	250	19	0.006	15
Calibration standard 2	Composite	0.1	250	19	0.016	16
Calibration standard 3	Composite	0.2	250	19	0.02	10
Calibration standard 4	Composite	0.3	250	18	0.021	7
Calibration standard 5	Composite	0.4	250	19	0.04	10
Calibration standard 6	Composite	1	250	19	0.093	9.3
P12	Composite	0.66	250	81	0.062	9.4
P12	Daily	0.66	250	5	0.028	4.2
P12	Daily	0.66	250	7	0.108	16.4
P12	Daily	0.66	250	8	0.018	2.8
P12	Daily	0.66	250	8	0.024	3.6
P12	Daily	0.66	250	9	0.035	5.3
P12	Daily	0.66	250	5	0.01	1.5
Calibration standard 1	Composite	0.35	61	3	0.16	44.5
Calibration standard 2	Composite	1.6	61	3	0.94	58.8
Calibration standard 3	Composite	5.25	61	3	0.49	9.4
Calibration standard 4	Composite	7.9	61	3	0.28	3.5
M106	Composite	13.1	61	10	1.19	9.1
M6	Composite	13	61	10	0.82	6.3
M106	Daily	13.1	61	7	0.15	1.1
M106	Daily	13.1	61	3	1.10	8.4
M6	Daily	13	61	7	0.23	1.8
M6	Daily	13	61	3	0.85	6.5
Calibration standard 1	Composite	10	11	28	1.8	17.5
Calibration standard 1	Daily	10	11	5	0.8	8.3
Calibration standard 2	Composite	20	11	30	2.6	13.1
Calibration standard 2	Daily	20	11	5	2.4	11.9
Calibration standard 2	Daily	20	11	5	2.8	13.8
Calibration standard 2	Daily	20	11	5	0.9	4.3
Calibration standard 3	Composite	30	11	8	1.9	6.3
Calibration standard 3	Daily	30	11	5	3	9.9
Calibration standard 3	Composite	30	11	12	2.2	6.3
Calibration standard 4	Composite	40	11	12	3.2	8
Calibration standard 4	Daily	40	11	5	3.5	8.7
Calibration standard 5	Composite	50	11	29	5.2	10.5
Calibration standard 5	Daily	50	11	10	5.2	10.4
Calibration standard 5	Daily	50	11	5	4.4	8.8
Calibration standard 6	Composite	60	11	16	3.6	6
Calibration standard 6	Daily	60	11	4	8.6	14.3
Calibration standard 6	Daily	60	11	5	4	6.7
Calibration standard 7	Composite	70	11	25	8.1	11.6
Calibration standard 7	Daily	70	11	5	1.1	1.6
Calibration standard 8	Composite	80	11	14	4	5
Calibration standard 8	Daily	80	11	5	6.1	7.7
Calibration standard 8	Composite	85	11	6	6.6	7.7
Calibration standard 9	Daily	90	11	5	7.4	8.2
Calibration standard 9	Daily	90	11	4	4.5	5
M6	Composite	13.1	11	57	1.1	8.1
M6	Daily	13.1	11	6	1	7.8

Table 1.-- Precision data for chloride--Continued

Standard	Type	Concentration (milligrams per liter)	Loop size (microliters)	n	Precision	Percent precision
M6	Daily	13.1	11	10	1	8
M6	Daily	13.1	11	8	0.9	6.9
M6	Daily	13.1	11	9	1.4	10.6
M6	Daily	13.1	11	9	0.8	5.8
M6	Daily	13.1	11	7	1.1	8.7
M6	Daily	13.1	11	5	0.7	5.5
M84	Daily	50	11	6	3.5	6.9
M84	Daily	50	11	6	3.4	6.8
M86	Daily	44.4	11	6	1.4	3.2
M86	Daily	44.4	11	5	3	6.7
M86	Daily	44.4	11	5	1.9	4.4
M96	Daily	38.6	11	5	3.1	8.1
M96	Daily	38.6	11	4	1.9	5
M102	Daily	44	11	4	2.3	5.3
M104	Daily	69.2	11	6	2.3	3.4
M104	Daily	69.2	11	6	5.3	7.7
M104	Daily	69.2	11	10	5.7	8.3
M104	Daily	69.2	11	5	4.9	7
M106	Daily	13	11	7	2.1	15.8
M106	Daily	13	11	6	0.3	2.6
M106	Daily	13	11	5	1.1	8.6
M106	Daily	13	11	5	0.8	6.1
M112	Daily	46	11	7	4.2	9.2
M112	Daily	46	11	6	4.2	9.1
M112	Daily	46	11	5	3.8	8.2
M112	Daily	46	11	5	2.9	6.2

Table 2.-- Precision data for nitrate

[Precision (P) and percent precision (%P) of nitrate for a variety of calibration standards and U.S. Geological Survey Standard Reference Water samples using the 250-microliter and the 61-microliter sample loops. The composite P and %P are from determinations averaged over a 7-month period. P and %P are determined at the 99-percent confidence level; n is the number of replicates]

Standard	Type	Concentration (milligrams per liter)	Loop size (microliters)	n	Precision	Percent precision
Calibration standard 1	Composite	0.04	250	23	0.008	20
Calibration standard 2	Composite	0.1	250	21	0.010	10
Calibration standard 3	Composite	0.2	250	21	0.013	6.5
Calibration standard 4	Composite	0.3	250	20	0.028	9.3
Calibration standard 5	Composite	0.4	250	21	0.033	8.2
Calibration standard 6	Composite	1	250	21	0.089	8.9
Calibration standard 7	Composite	2	250	21	0.187	9.4
P11	Composite	1.28	250	97	0.113	8.8
P11	Daily	1.28	250	5	0.056	4.4
P11	Daily	1.28	250	7	0.060	4.7
P11	Daily	1.28	250	8	0.283	28.3
P11	Daily	1.28	250	8	0.054	4.2
P11	Daily	1.28	250	9	0.069	5.4
P11	Daily	1.28	250	5	0.014	1.1
Calibration standard 1	Composite	1.5	61	3	0.07	5.0
Calibration standard 2	Composite	7.5	61	3	0.23	3.1
Calibration standard 3	Composite	22.5	61	3	0.72	3.2
Calibration standard 4	Composite	33.8	61	3	0.48	1.4
M106	Composite	1.9	61	12	0.19	9.9
M6	Composite	5.5	61	13	0.44	8.1
M106	Daily	1.9	61	8	0.10	5.0
M106	Daily	1.9	61	4	0.25	13.3
M6	Daily	5.5	61	7	0.15	2.8
M6	Daily	5.5	61	4	0.43	7.8

Table 3.-- Precision data for sulfate

[Precision (P) and percent precision (%P) of sulfate for a variety of calibration standards and U.S. Geological Survey Standard Reference Water Samples using the 250-microliter, the 61-microliter, and the 11-microliter sample loops. The composite P and %P are from determination averaged over a 7-month period. P and %P are determined at the 99-percent confidence level; n is the number of replicates]

Standard	Type	Concentration (milligrams per liter)	Loop size (microliters)	n	Precision	Percent precision
Calibration standard 1	Composite	0.04	250	19	0.011	27.5
Calibration standard 2	Composite	0.1	250	19	0.007	7
Calibration standard 3	Composite	0.2	250	19	0.018	9
Calibration standard 4	Composite	0.3	250	21	0.028	9.3
Calibration standard 5	Composite	0.4	250	23	0.039	9.8
Calibration standard 6	Composite	1	250	23	0.103	10.3
Calibration standard 7	Composite	2	250	23	0.226	11.3
P12	Composite	0.65	250	108	0.067	9.9
P12	Daily	0.65	250	5	0.033	4.9
P12	Daily	0.65	250	7	0.01	1.5
P12	Daily	0.65	250	8	0.007	1.1
P12	Daily	0.65	250	8	0.014	2
P12	Daily	0.65	250	9	0.034	5
P12	Daily	0.65	250	5	0.008	1.2
Calibration standard 1	Composite	2.1	61	3	1.40	67
Calibration standard 2	Composite	9.4	61	3	2.20	23
Calibration standard 3	Composite	30	61	3	0.60	2
Calibration standard 4	Composite	45	61	3	0.27	1
M106	Composite	27.6	61	14	1.06	4
M6	Composite	74.5	61	11	7.03	9
M106	Daily	27.6	61	8	1.14	4
M106	Daily	27.6	61	4	0.57	2
M6	Daily	74.5	61	7	3.01	4
M6	Daily	74.5	61	4	1.43	2
Calibration standard 1	Composite	10	11	27	1.3	13.2
Calibration standard 1	Daily	10	11	5	1.1	10.5
Calibration standard 2	Composite	40	11	24	3.3	8.2
Calibration standard 2	Daily	40	11	5	4.1	10.3
Calibration standard 2	Daily	40	11	5	4.3	10.8
Calibration standard 2	Daily	40	11	5	1.4	3.5
Calibration standard 3	Composite	80	11	18	7.4	9.2
Calibration standard 3	Daily	80	11	5	7.5	9.3
Calibration standard 4	Composite	120	11	23	17.7	14.7
Calibration standard 4	Daily	120	11	6	12.8	10.7
Calibration standard 4	Daily	120	11	5	12.3	10.3
Calibration standard 5	Composite	160	11	16	8.1	5.1
Calibration standard 5	Daily	160	11	4	36.3	22.7
Calibration standard 5	Daily	160	11	5	14.9	9.3
Calibration standard 6	Composite	200	11	21	19.8	9.9
Calibration standard 6	Daily	200	11	5	5.2	2.6
Calibration standard 7	Composite	240	11	13	11	4.6
Calibration standard 7	Daily	240	11	5	5.4	2.2
Calibration standard 8	Composite	280	11	17	21	7.5
Calibration standard 8	Daily	280	11	5	30.6	10.9
Calibration standard 8	Daily	280	11	4	42.4	15.1
Calibration standard 8	Daily	280	11	5	18.8	6.7
M6	Composite	74.5	11	66	7.6	10.3
M6	Daily	74.5	11	6	3.8	5.1
M6	Daily	74.5	11	10	7.8	10.5

Table 3.-- Precision data for sulfate--Continued

Standard	Type	Concentration (milligrams per liter)	Loop size (microliters)	n	Precision	Percent precision
M6	Daily	74.5	11	8	6.9	9.2
M6	Daily	74.5	11	9	3.4	4.6
M6	Daily	74.5	11	7	6.5	8.7
M6	Daily	74.5	11	5	3.8	5.2
M6	Daily	74.5	11	9	6.9	9.3
M86	Daily	219.7	11	6	7.3	3.3
M86	Daily	219.7	11	5	18	8.2
M86	Daily	219.7	11	5	11.8	5.4
M90	Daily	120	11	6	8.3	6.9
M90	Daily	120	11	5	10.1	8.4
M96	Daily	139	11	5	11.8	8.5
M96	Daily	139	11	4	11.2	8
M104	Daily	225	11	6	10.7	4.8
M104	Daily	225	11	6	15.7	7
M104	Daily	225	11	10	15.6	6.9
M104	Daily	225	11	5	16.2	7.2
M106	Daily	27.6	11	7	3.8	13.8
M106	Daily	27.6	11	6	0.6	2.3
M106	Daily	27.6	11	5	1.4	5
M106	Daily	27.6	11	5	1.6	6
M112	Daily	25	11	7	2.5	10.1
M112	Daily	25	11	6	1.4	5.5
M112	Daily	25	11	5	2.2	8.8
M112	Daily	25	11	5	2	8.1

Table 4.-- Comparison between the observed and the reported concentrations of chloride for U.S. Geological Survey Standard Reference Water Samples

Reference standard	Concentration (milligrams per liter)		Number of replicates	Concentration (milligrams per liter)	
	Observed concentration	Standard deviation		Reported concentration	Standard deviation
P12	0.70	0.03	101	0.66	0.02
M6	13.1	0.5	66	13.1	0.2
M84	46.4	0.9	15	50	0.5
M86	44.7	0.5	27	44.4	0.4
M96	39.0	0.7	11	38.6	0.4
M102	42.9	0.4	4	44	0
M104	69.6	1.6	34	69.2	0.7
M106	13.4	0.6	45	13	0
M112	47.2	1.3	43	46	3.1

Table 5.-- Comparison between the observed and the reported concentration of nitrate for the U.S. Geological Survey Standard Reference Water Sample P11

Reference standard	Concentration (milligrams per liter)		Number of replicates	Concentration (milligrams per liter)	
	Observed Concentration	Standard deviation		Reported concentration	Standard deviation
P11	1.27	0.03	85	1.28	0.13

Table 6.--Comparison between the observed and the reported concentration of sulfate for U.S. Geological Survey Standard Reference Water Samples

Reference standard	Concentration (milligrams per liter)		Number of replicates	Concentration (milligrams per liter)	
	Observed Concentration	Standard deviation		Reported concentration	Standard deviation
P12	0.65	0.02	101	0.66	0.02
M6	72.7	2.2	66	74.5	0.9
M86	229.4	3.4	27	219.7	2.8
M90	126.8	3.6	17	120	2
M96	141.9	2.4	11	139	2
M104	222.3	5.8	35	225	4
M106	27.8	0.8	45	27.6	0.4
M110	64.7	0.2	2	64	1
M112	24.9	0.6	43	25.0	1.5

Table 7.--Detection limits for chloride, nitrate, and sulfate using the 250-microliter sample loop

[Blanks are averaged for 6 months. The detection limit is formally defined in the text]

Analyte	Number of samples	Detection limit (milligrams per liter)
Chloride	23	0.02
Nitrate	31	0.02
Sulfate	23	0.02

APPENDIX 1. INSTRUMENTATION

Dionex 2002i S/P ion chromatograph	
Analytical column	(IonPac AS4A)
Guard column	(AG4A)
Dionex Al-450 chromatography automation software	
Dionex Anion self-regenerating suppressor	
Dionex advanced computer interface	
Dionex controlled air module	
ISCO ISI autosampler	
Relay switch box	
HP-110 portable computer	
Computer with an RS-232 port	

APPENDIX 2. OPERATING CONDITIONS

Sample loop volume	11-µL (Cl 5-80 mg/L; SO_4 30-280 mg/L)
and working range	61-µL (Cl 1.6 to 7.2 mg/L; NO_3 4 to 18 mg/L; SO_4 10 to 45 mg/L)
	250-µL (Cl 0.02 to 1.6 mg/L; NO_3 0.02 to 4.0 mg/L; SO_4 0.02 to 10 mg/L)
Suppressor	Dionex Anion self-regenerating suppressor
Eluant	1.8mM Na_2CO_3/1.7mM $NaHCO_3$
Deionized Water	18 Megohm, degassed
Eluant flow	2 mL/min
Regenerant flow	3 mL/min
Conductivity(background)	15 to 20 µS
Sample volume	5 mL
System pressure	800 to 1300 lb/in^2
Switching valve pressure	80-100 lb/in^2
Output range	30 µS (for 250 and 61-µL loop)
	100 µS (for 11-µL loop)
Temperature compensation	1.7
Automation interface remote	On

APPENDIX 3. PREPARATION OF CALIBRATION STANDARDS

High purity standard solutions of 1,000 milligrams per liter of chloride and nitrate and 2,000 milligrams per liter of sulfate are used to prepare the working standards described below. All solutions prepared are brought to volume using deionized water that has been degassed**.** All calibration standards are stored in dedicated 1-L Teflon bottles.

Multielement calibration standards for the 11-microliter sample loop

	Primary standard	Dilution (mL/mL)		Calibration standard
1	1,000 mg/L chloride	(5/1,000)	=	5 mg/L Cl
	2,000 mg/L sulfate	(15/1,000)	=	30 mg/L SO_4
2	1,000 mg/L chloride	(10/1,000)	=	10 mg/L Cl
	2,000 mg/L sulfate	(30/1,000)	=	60 mg/L SO_4
3	1,000 mg/L chloride	(30/1,000)	=	30 mg/L Cl
	2,000 mg/L sulfate	(60/1,000)	=	120 mg/L SO_4
4	1,000 mg/L chloride	(50/1,000)	=	50 mg/L Cl
	2,000 mg/L sulfate	(90/1,000)	=	180 mg/L SO_4
5	1,000 mg/L chloride	(80/1,000)	=	80 mg/L Cl
	2,000 mg/L sulfate	(140/1,000)	=	280 mg/L SO_4

Multielement secondary standards for the 61 and 250-microliter sample loops

Primary standard	Dilution (mL/mL)		Secondary standard
1,000 mg/L chloride	(32/1,000)	=	32 mg/L Cl
1,000 mg/L nitrate	(80/1,000)	=	80 mg/L NO_3
2,000 mg/L sulfate	(100/1,000)	=	200 mg/L SO_4

Multielement calibration standards for the 61-microliter sample loop

	Secondary Standard	Dilution (mL/mL)		Concentration
1	32 mg/L chloride	(2.5/1,000)	=	0.08 mg/L Cl
	80 mg/L nitrate	(2.5/1,000)	=	0.20 mg/L NO_3
	200 mg/L sulfate	(2.5/1,000)	=	0.50 mg/L SO_4
2	32 mg/L chloride	(10/1,000)	=	0.32 mg/L Cl
	80 mg/L nitrate	(10/1,000)	=	0.80 mg/L NO_3
	200 mg/L sulfate	(10/1,000)	=	2.0 mg/L SO_4
3	32 mg/L chloride	(50/1,000)	=	1.6 mg/L Cl
	80 mg/L nitrate	(50/1,000)	=	4.0 mg/L NO_3
	200 mg/L sulfate	(50/1,000)	=	10 mg/L SO_4
4	32 mg/L chloride	(150/1,000)	=	4.8 mg/L Cl
	80 mg/L nitrate	(150/1,000)	=	12 mg/L NO_3
	200 mg/L sulfate	(150/1,000)	=	30 mg/L SO_4
5	32 mg/L chloride	(225/1,000)	=	7.2 mg/L Cl
	80 mg/L nitrate	(225/1,000)	=	18 mg/L NO_3
	200 mg/L sulfate	(225/1,000)	=	45 mg/L SO_4

APPENDIX 3. PREPARATION OF CALIBRATION STANDARDS--CONTINUED

Multielement calibration standards for the 250-microliter sample loop

	Secondary standard	Dilution (mL/mL)		Concentration
1	32 mg/L chloride	(0.5/1,000)	=	0.02 mg/L Cl
	80 mg/L nitrate	(0.5/1,000)	=	0.04 mg/L SO_4
	200 mg/L sulfate	(0.5/1,000)	=	0.1 mg/L NO_3
2	32 mg/L chloride	(1.25/1,000)	=	0.04 mg/L Cl
	80 mg/L nitrate	(1.25/1,000)	=	0.1 mg/L NO_3
	200 mg/L sulfate	(1.25/1,000)	=	0.25 mg/L SO_4
3	32 mg/L chloride	(2.5/1,000)	=	0.08 mg/L Cl
	80 mg/L sulfate	(2.5/1,000)	=	0.2 mg/L NO_3
	200 mg/L nitrate	(2.5/1,000)	=	0.5 mg/L SO_4
4	32 mg/L chloride	(5/1,000)	=	0.16 mg/L Cl
	80 mg/L nitrate	(5/1,000)	=	0.4 mg/L NO_3
	200 mg/L sulfate	(5/1,000)	=	1.0 mg/L SO_4
5	32 mg/L chloride	(12.5/1,000)	=	0.4 mg/L Cl
	80 mg/L nitrate	(12.5/1,000)	=	1.0 mg/L NO_3
	200 mg/L sulfate	(12.5/1,000)	=	2.5 mg/L SO_4
6	32 mg/L chloride	(25/1,000)		0.8 mg/L Cl
	80 mg/L nitrate	(25/1,000)		2.0 mg/L SO_4
	200 mg/L sulfate	(25/1,000)		5.0 mg/L NO_3
7	32 mg/L chloride	(37.5/1,000)	=	1.2 mg/L Cl
	80 mg/L nitrate	(37.5/1,000)	=	3.0 mg/L NO_3
	200 mg/L sulfate	(37.5/1,000)	=	7.5 mg/L SO_4
8	32 mg/L chloride	(50/1,000)	=	1.6 mg/L Cl
	80 mg/L nitrate	(50/1,000)	=	4.0 mg/L NO_3
	200 mg/L sulfate	(50/1,000)	=	10 mg/L NO_3

APPENDIX 4. PREPARATION OF ELUANT

1. Concentrate preparation [100x]: (19.08 g Na_2CO_3 +14.28 g $NaHCO_3$)/L.
2. Using a dedicated 2-L glass volumetric flask, make a 20/2000 dilution with deionized waterof the eluant from the concentrate prepared above.
3. Transfer solution to the eluant delivery carboy.
4. Cap carboy loosely to obtain equilibration with atmospheric pressure.

APPENDIX 5. PREPARATION OF SAMPLES

All samples are filtered through a 0.45-µm polysulfone membrane in a Luer-lock filter assembly. Samples are prepared as follows:

1. Rinse a dedicated 10-mL or larger syringe with DI.
2. Attach Luer lock filter and filter >5-mL of DI and discard.
3. Rinse syringe with sample and discard.
4. Filter and collect sample discarding the first 5-mL.
5. Rinse the collection vessel (17x100-mm polystyrene test tubes) with ~5-mL aliquot of sample and discard.
6. Collect remaining sample for analysis.
7. Load the autosampler as follows:

Position Number	Sample identification	Comment
1	Standard 1	
2	Standard 2	
3	Standard 3	
4	Standard 4	
5	Standard 5	(Stop here if using the 61-µl or the 11-µl loop)
6	Standard 6	
7	Standard 7	
8	Standard 8	
9	DI blank	
10	SRWS #1	(Always run after every six samples.)
11	SRWS #2	(Vary with other SRWS throughout run.)
12-17	Samples	
18	SRWS #1	
19	SRWS #3	
20-25	Samples	
26	SRWS #1	
27	SRWS #4	
28-31	Standards 1,3,5,7	
32	DI blank	
33+		Repeat sequence from position 10 through 33 standards 2,4,6,8

APPENDIX 6. TROUBLESHOOTING

Troubleshooting

There are many problems that may develop when using the ion chromatograph. The following are some of the most common problems and some suggested remedies.

Symptom	Cause	Remedy
System pressure too high, >1300 lb/in^2	Crimped gripper	Replace gripper
	Clogged bed supports	Replace supports
	Air in the column	Pump eluant until pressure decreases.
	Biological growth	Change columns, the guard, or analytical column.
System pressure too low,	Eluant leak	Isolate the leak and repair <800 lb/in^2
Baseline off scale	Detector offset incorrect	Set offset to zero
Output is offset	Attenuation incorrect Range is offset	Set to 1024 Set output range to 30-µS for the 250-µL loop and the 61-µL loops. Set to 100-µS for the 11-µL loop
Integrator not responding to run	Cable from the automation interface not connected	Connect cable
	Detector leads not connected	Connect leads
	Automation interface remote off	Remote on