

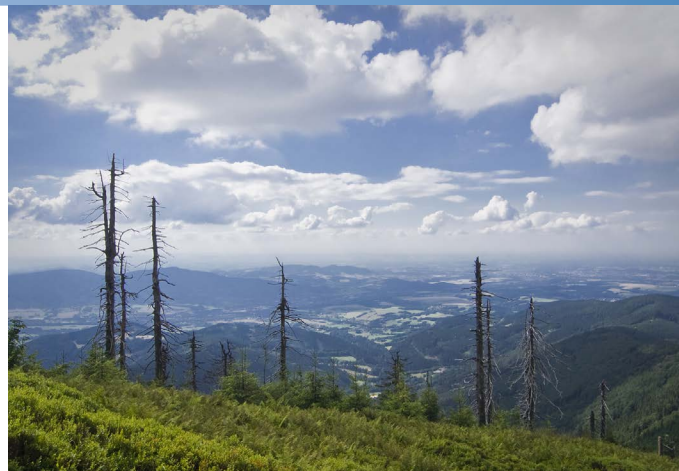
Determination of Anions in Acid Rain by Ion Chromatography

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Introduction

The increase in acidity of wet and dry atmospheric depositions has been attributed to the increase of SO₂ and NO₂ emissions from stationary and mobile pollution sources. The acid rain problem has reached dramatic proportions throughout many regions of the United States, Europe, Canada, and Japan. Monitoring air and rain is essential, not only for assessing the effects of pollutants on global ecology, but also for monitoring the progress of pollution control and abatement efforts.

Ion chromatography (IC) is a convenient and reliable technique for determining low concentrations of inorganic anions in acid rain. IC with suppressed conductivity detection offers excellent precision and accuracy for the measurement of such pollutants and has been specified by the U.S. Environmental Protection Agency (EPA) as the method of choice for determining inorganic anions in wet deposition samples.^{1,2} In this application update, we describe the use of automated eluent generation combined with a high-capacity, hydroxide-selective, anion-exchange column—the Thermo Scientific™ Dionex™ IonPac™ AS18 column—for the determination of inorganic anions in rainwater. This document updates Dionex (now part of Thermo Scientific) Application Note 31 by incorporating electrolytic eluent generation with the Dionex IonPac AS18 column to eliminate the need for manually preparing the eluents off-line, and thereby increasing the IC system's level of automation and ease of use. We evaluated the IC method with a simulated rainwater sample obtained from High-Purity Standards (HPS). The anion concentrations of this sample are traceable to the National Institute of Standards and Technology (NIST), Standard Reference Material No. 3100 series.



Equipment

A Thermo Scientific™ Dionex™ ICS-2000 Reagent-Free™ Ion Chromatography (RFIC™) system* was used in this work. The Dionex ICS-2000 system is an integrated ion chromatograph that consists of:

- Eluent Generator
- Column Heater
- Pump Degas
- Thermo Scientific Dionex EGC-KOH Cartridge
- Thermo Scientific Dionex CR-ATC Continuously Regenerated Anion Trap Column
- Thermo Scientific Dionex AS50 Autosampler
- Thermo Scientific™ Dionex™ Chromeleon™ 6.8 Chromatography Data System (CDS) Workstation

**Equivalent or improved results can be achieved using a Thermo Scientific™ Dionex™ ICS-2100 RFIC™ system or a Thermo Scientific™ Dionex™ ICS-5000+ RFIC™ system.*

Reagents and Standards

- Deionized water, Type I reagent-grade, 18 MΩ-cm specific resistance or better
- Sodium and potassium salts, ACS reagent-grade or better, for preparing anion standards
- Fluoride standard 1000 mg/L, 100 mL
- Chloride standard 1000 mg/L, 100 mL
- Sulfate standard 1000 mg/L, 100 mL
- Nitrate standard 1000 mg/L, 100 mL
- Phosphate standard 1000 mg/L, 100 mL
- Bromide standard 1000 mg/L, 100 mL

Conditions	
Columns:	Dionex IonPac AS18 Analytical, 4 × 250 mm Dionex IonPac AG18 Guard, 4 × 50 mm
Eluent:	38 mM potassium hydroxide
Eluent Source:	Dionex ICS-2000 system with Dionex CR-ATC column
Flow Rate:	1.0 mL/min
Temperature:	30 °C
Injection:	25 µL
Detection:	Suppressed conductivity, Thermo Scientific™ Dionex™ ASRS™ Ultra Anion Self-Regenerating suppressor ULTRA, 4 mm, AutoSuppression™ recycle mode 100 mA current
Background Conductance:	~1.4 µS
System Backpressure:	~2500 psi
Run Time:	10 min

Preparation of Solutions and Reagents

Stock Standard Solutions

Stock Anion Standard Solutions (1000 mg/L)

For several analytes of interest, 1000 mg/L standard solutions are available from Thermo Scientific and other commercial sources. When commercial standards are not available, 1000 mg/L standards can be prepared by dissolving the appropriate amounts of the corresponding mass in 1000 mL of deionized water according to Table 1. Standards are stable for at least one month when stored at 4 °C.

Table 1. Preparation of stock standard solutions.

Anion	Compound	Amount (g)
Fluoride	Sodium fluoride (NaF)	2.210
Chloride	Sodium chloride (NaCl)	1.648
Nitrite	Sodium nitrite (NaNO ₂)	1.499
Bromide	Sodium bromide (NaBr)	1.288
Nitrate	Sodium nitrate (NaNO ₃)	1.378
Phosphate	Potassium phosphate, monobasic (KH ₂ PO ₄)	1.433
Sulfate	Sodium sulfate (Na ₂ SO ₄)	1.479

Working Standard Solutions

Composite working standard solutions at lower analyte concentrations are prepared from the 1000 mg/L standards described above. Working standards containing less than 100 mg/L anions should be prepared daily. Five levels of calibration standards were used in this study to cover the expected concentrations found in rainwater samples. Table 2 shows the linear concentration range, method detection limits (MDLs), and the concentrations used to determine the MDLs for each inorganic anion investigated.

Table 2. Linear concentration ranges and MDLs^a.

Analyte ^b	Range (mg/L)	Linearity (r ²)	Calculated MDL (µg/L)	MDL Standard (µg/L)
Fluoride	0.025–2.5	0.9997	2.5	10
Chloride	0.020–2.0	0.9994	2.8	10
Nitrate	0.10–10	0.9999	6.2	20
Sulfate	0.20–20	0.9999	4.8	15

^a MDL = (t) × (S) where t = Student's t value for a 99% confidence level and a standard deviation estimate with n – 1 degrees of freedom (t = 3.14 for seven replicates of the MDL Standard), and S = standard deviation of the replicate analysis.

^b A 25 µL injection volume was used.

Simulated Rainwater Sample, SR-II

The simulated rainwater sample, SR-II, was obtained from HPS and analyzed without further treatment by direct injection.

Results and Discussion

The Dionex IonPac AS18 column is a latex agglomerated column with a 7.5 µm diameter macroporous resin bead consisting of ethylvinylbenzene (EVB) cross-linked with 55% divinylbenzene (DVB), which makes the column solvent compatible with reversed-phase solvents. The outer layer consists of 65 nm latex functionalized with alkanol quaternary ammonium groups. The net result is a resin that has high capacity, high peak efficiencies, and a high selectivity toward hydroxide eluents (i.e., hydroxide-selective). The Dionex IonPac AS18 column is ideal for use with isocratic hydroxide eluents for fast separations (e.g., <10 min) of common inorganic anions in relatively simple matrices, such as rainwater.

An anion analysis of rainwater requires the determination of fluoride, chloride, nitrate, and sulfate. IC is ideal for this analysis because it can also be used to determine nitrite, bromide, and phosphate. Figure 1 shows a chromatogram of seven common inorganic anions separated in less than 10 min on the Dionex IonPac AS18 column. The Dionex IonPac AS18 column has a different selectivity than conventional anion-exchange columns that use carbonate eluents. Using the eluent conditions described in this application update, sulfate elutes before bromide, nitrate, and phosphate. However, if samples contain high amounts of dissolved CO₂, then a gradient hydroxide separation should be used to improve the resolution between chloride and carbonate.³

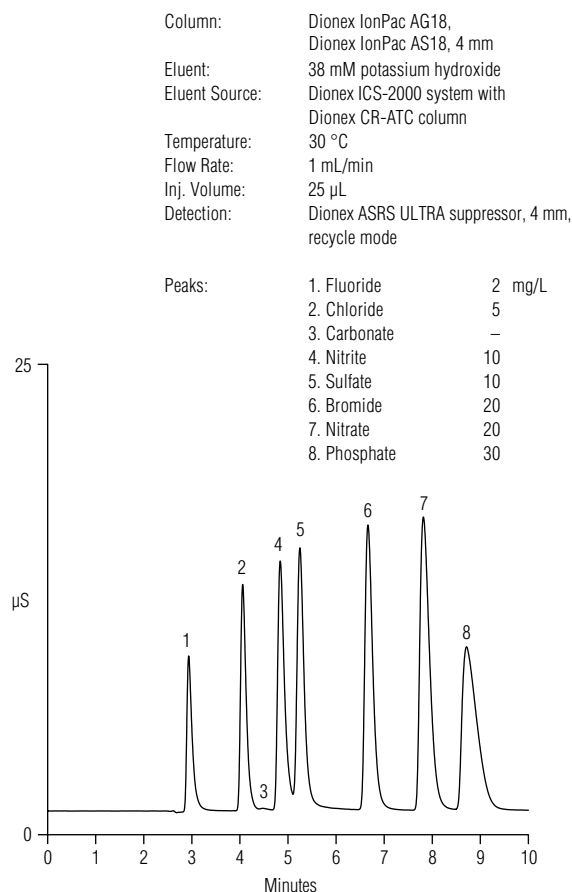


Figure 1. Separation of common inorganic anions using the Dionex IonPac AS18 column.

The Dionex ICS-2000 system was calibrated to cover the expected concentrations found in rainwater samples. Table 2 shows the linear concentration ranges investigated, the coefficients of determination (r^2), and typical calculated method detection limits (MDLs) for each anion separated on the Dionex IonPac AS18 column. The response of each anion was linear, over the concentrations reported in Table 2, with r^2 values >0.999. The MDLs were determined by performing seven replicate injections of the MDL standard shown in Table 2 and calculating the MDL values based on the standard deviation of the mean multiplied by 3.143 (Student's t value for a 99% confidence for $n = 7$).

Simulated rainwater samples were analyzed and the results were compared with the values reported by HPS (Table 3). The results were well within the standard deviation ranges certified by HPS. Figure 2 illustrates the application of this method to a simulated rainwater sample. Table 4 shows typical retention time and peak area precision data for 20 replicate injections of the simulated rainwater sample. The excellent retention time stability and peak area precision can be attributed to the consistent generation of high-purity potassium hydroxide by the Dionex ICS-2000 system.

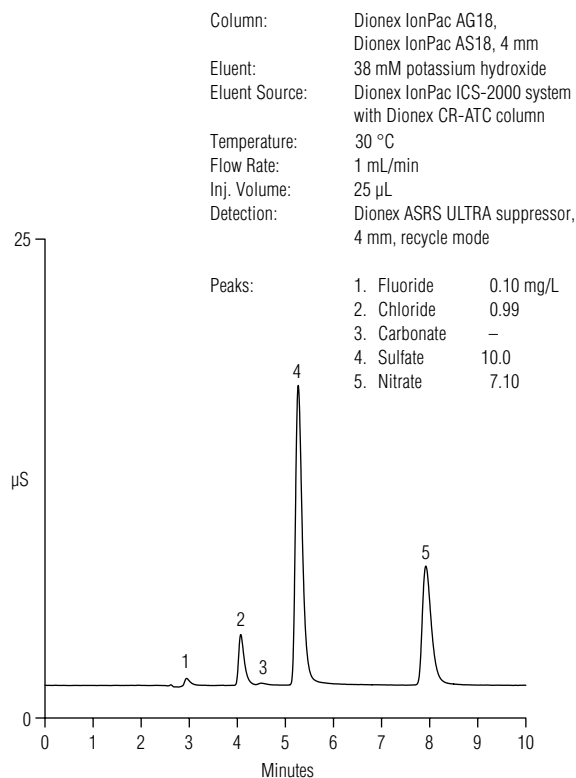


Figure 2. Analysis of simulated rainwater.

Table 3. Analysis of simulated rainwater, SR-II.

Analyte	Concentration Found (mg/L)	HPS Certified Value (mg/L)
Fluoride	0.10 ± 0.002 ^a	0.10 ± 0.01
Chloride	0.99 ± 0.02	0.98 ± 0.03
Nitrate	7.10 ± 0.04	7.00 ± 0.20
Sulfate	10.0 ± 0.03	10.1 ± 0.3

^a The standard deviations were calculated from twenty replicate injections ($n = 20$).

The data presented in Table 4 are typical results that can be expected when using the Dionex IonPac AS18 column for environmental analyses, such as rainwater samples. The routine use of hydroxide eluents can further improve the performance of existing IC methods where carbonate/bicarbonate eluents have commonly been used. The advantages of using hydroxide eluents for IC are improved linearity, lower background conductivity, and improved method detection limits when compared to “conventional” IC columns using carbonate/bicarbonate eluents. Electrolytic generation of potassium hydroxide further enhances the level of instrument automation by requiring the analyst to merely add water to the system. Using only water, the system automatically prepares the eluent, cleans the trap column, and suppresses the eluent for conductivity detection.

Table 4. Precision of the retention times and peak areas for anions in simulated rainwater.

Analyte	Retention Time RSD ^a (%)	Peak Area RSD ^a
Fluoride	0.053	1.98
Chloride	0.043	2.43
Nitrate	0.024	0.49
Sulfate	0.035	0.30

^a The relative standard deviations (RSDs) were calculated from twenty replicate injections ($n = 20$).

Summary

The use of IC with an Dionex IonPac AS18 column and electrolytic eluent generation provides a rapid, isocratic analysis for the determination of inorganic anions in rainwater. The results obtained from the simulated rainwater samples were comparable to the values reported by HPS and were well within the certified standard deviation ranges. In addition, electrolytic generation of potassium hydroxide eliminates the need to manually prepare eluents, increasing the IC system's level of automation, ease of use, and analytical performance. This approach also improves retention time precision and quantitation reliability, and allows easy method transfer between different operators and laboratories.

References

1. *Chloride, Orthophosphate, Nitrate, and Sulfate in Wet Deposition by Chemically Suppressed Ion Chromatography*, EPA Method 300.6; U.S. Environmental Protection Agency, 1986.
2. *Standard Test Method for the Determination of Chloride, Nitrate, and Sulfate in Atmospheric Wet Deposition by Chemically Suppressed Conductivity*. Method D5085-90; Vol. 11.03; American Society for Testing and Materials: West Conshohocken, PA, 2003.
3. Dionex (now part of Thermo Scientific) Application Note 154: Determination of Inorganic Anions in Environmental Waters Using a Hydroxide-Selective Column. Sunnyvale, CA, 2003.

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