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# Determination of Anions in Acid Rain by Ion Chromatography

## INTRODUCTION

The increase in the acidity of wet and dry depositions has been attributed to the increase of SO<sub>2</sub> and NO<sub>2</sub> emissions from stationary and mobile sources. The problem of acid rain has reached dramatic proportions throughout many regions of the United States, Canada, Europe, and Japan. Monitoring of air and rain are essential for assessing the effects of pollutants on global ecology.

Ion chromatography (IC) offers the analyst the unique advantage of selective and rapid determination of low concentrations of anions in acid rain. The trend toward decreasing anion concentrations in wet deposition for certain areas of the United States<sup>1</sup> emphasizes the need for the improved sensitivity that IC can provide over other analytical methods. Chemically suppressed IC has secured a place in acid rain monitoring because of its high degree of accuracy and reliability, and has been specified by the United States Environmental Protection Agency (EPA) as the method of choice for the determination of chloride, phosphate, nitrate, and sulfate (Cl<sup>-</sup>, PO<sub>4</sub><sup>3-</sup>, NO<sub>3</sub><sup>-</sup>, SO<sub>4</sub><sup>2-</sup>) in wet deposition samples.<sup>2-4</sup> Several studies employing IC have been conducted to date.<sup>5-7</sup>

This application note describes the established ion chromatographic method for the determination of anions in rainwater samples extended to the use of microbore columns and accessories. A rainwater standard from the National Institute of Standards and Technology (NIST) was analyzed, verifying the accuracy of the method.

## EQUIPMENT

Any Dionex chromatographic system including:  
High Performance Pump  
Conductivity Detector  
Dionex AI-450 Chromatography Workstation

## REAGENTS AND STANDARDS

Dionex AS4A Eluent Concentrate (P/N 39513)  
(Sodium carbonate and sodium bicarbonate may also be used)  
Sodium chloride  
Potassium dihydrogen phosphate  
Sodium nitrate  
Potassium sulfate  
Sodium fluoride, sodium nitrite, and sodium bromide (optional)  
18-MΩ Deionized water

## CONDITIONS

Columns:	IonPac® AS4A-SC 2-mm analytical and AG4A-SC 2-mm guard (Alternatively, 4-mm analytical and guard columns may be used; changes in experimental conditions are noted below in parentheses.)
Eluent:	1.8 mM Sodium carbonate / 1.7 mM Sodium bicarbonate
Flow Rate:	0.5 mL/min (2.0 mL/min for 4-mm columns)
Inj. Vol.:	5.0 µL (20 µL for 4-mm columns)
Detection:	Suppressed conductivity
Suppressor:	ASRS, 2 mm (or 4 mm), AutoSuppression mode; or AMMS, 2 mm (or 4 mm)
Regenerant:	50 mN Sulfuric acid with AMMS
Regenerant Flow:	5–7 mL/min for AMMS

## PREPARATION OF SOLUTIONS AND REAGENTS

Eluent: 1.8 mM Sodium Carbonate /  
1.7 mM Sodium Bicarbonate

Dilute 10 mL of AS4A eluent concentrate to 1.0 L with DI water.

### Stock Standard Solutions

Prepare 1000 mg/L (1000 ppm) stock anion standard solutions by dissolving the amount of each salt (anhydrous) listed in Table 1 in deionized water and diluting to 1.000 L.

**Table 1 Preparation of Stock Standard Solutions**

Anion	Salt	Amount (g)
Fluoride	Sodium fluoride (NaF)	2.210
Chloride	Sodium chloride (NaCl)	1.648
Nitrite	Sodium nitrite (NaNO <sub>2</sub> )	1.499
Bromide	Sodium bromide (NaBr)	1.288
Nitrate	Sodium nitrate (NaNO <sub>3</sub> )	1.371
Phosphate	Potassium dihydrogen phosphate (KH <sub>2</sub> PO <sub>4</sub> )	1.433
Sulfate	Potassium sulfate (K <sub>2</sub> SO <sub>4</sub> )	1.814

### Calibration Standards

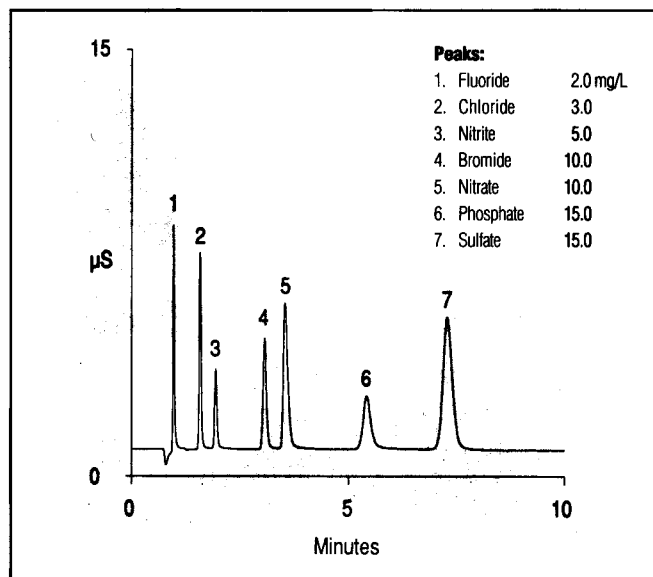
Calibration standards are prepared by diluting stock standard solutions containing 1000 mg/L (1000 ppm) of each anion, either directly or using a series of dilutions. The anions can be combined to prepare a single set of calibration solutions.

### Simulated Rainwater Sample, SRM 2694-II

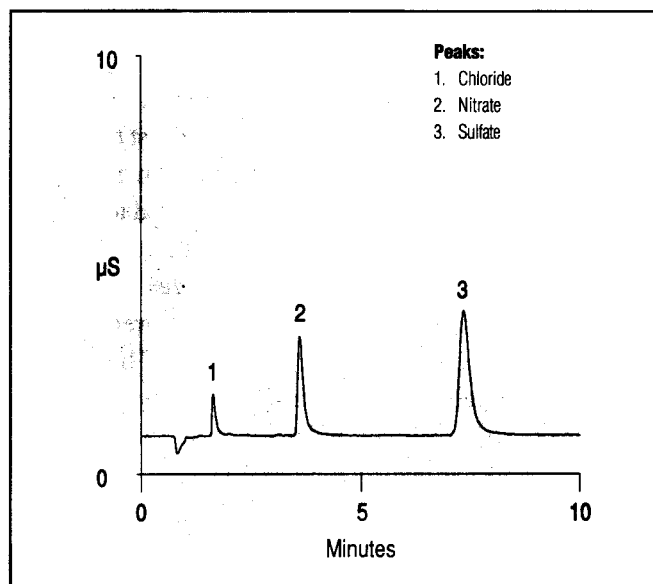
The simulated rainwater sample, SRM 2694-II, was obtained from the Office of Standard Reference Materials, National Institute of Standards and Technology, Gaithersburg, Maryland 20899, USA.

## RESULTS AND DISCUSSION

The ion chromatographic analysis of wet deposition usually involves the determination of chloride, nitrate, phosphate, and sulfate; however, the method may be applied to fluoride, nitrite, and bromide as well. A chromatogram of standards of these seven anions is illustrated in Figure 1. Figure 2 illustrates the application of this



**Figure 1** Common inorganic anions resolved using the IonPac AS4A-SC (2 mm) column



**Figure 2** Analysis of simulated rainwater, SRM 2694-II

**Table 2 Analysis of Simulated Rainwater, SRM 2694-II**

Anion	Concentration - Found (mg/L)	Concentration - NIST Value (mg/L)
Chloride	1.00 ± 0.02	0.94*
Nitrate	7.09 ± 0.04	7.19 ± 0.16
Sulfate	10.6 ± 0.1	10.6 ± 0.1

\*Standard deviation was not supplied.

**Table 3 MDLs and RSDs**

Anion	MDL* (µg/L)	RSD (%)**		Median Conc. (µg/L)
		Low Conc.	High Conc.	
Chloride	3	7.4	2.1	100
Nitrate	4	3.8	2.1	1000
Phosphate	17	5.0	1.8	20
Sulfate	5	3.6	1.4	1500

\*Determined at "3 x noise". Similar detection limits were obtained by "SD x t<sub>s</sub>".  
 \*\*Low concentrations were: chloride, 15 µg/L; nitrate, 40 µg/L; phosphate, 110 µg/L; sulfate, 50 µg/L. High concentrations were 3 mg/L for each anion.

**Table 4 Linearity Coefficients and Concentration Ranges**

Anion	Over 2 Decades Conc. Range (mg/L)	Over 4 Decades Conc. Range (mg/L)		
		r <sup>2</sup>	Conc. Range (mg/L)	r <sup>2</sup>
Chloride	0.015–1.5	0.9999	0.015–150	0.9999
Nitrate	0.040–4.0	1.0000	0.040–400	0.9999
Phosphate	0.10–10	1.0000	0.10–1000	0.9999
Sulfate	0.050–5.0	0.9998	0.050–500	0.9997

method to a simulated rainwater sample from the NIST. Phosphate was not detected in this sample. Results of the analysis are in Table 2.


Method detection limits (MDLs) and relative standard deviations (RSDs) for chloride, nitrate, phosphate, and sulfate are listed in Table 3, along with the median concentrations of these anions in wet deposition samples. Linear coefficients of determination (r<sup>2</sup>) and the concentration ranges over which they were determined are presented in Table 4.

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