

# Determination of Inorganic Cations and Ammonium in Environmental Waters Using a Compact, Integrated, High-Pressure Ion Chromatography System

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## ABSTRACT

**Purpose:** To determine inorganic cations and ammonium in environmental waters using a compact, high-pressure ion chromatography system with a 4- $\mu\text{m}$ -particle cation-exchange column to shorten analysis time

**Methods:** A cation exchange column was used to separate inorganic cations and ammonium, which were then detected by suppressed conductivity using the Thermo Scientific™ Dionex™ Integri™ HPIC™ system.

**Results:** Inorganic cations and ammonium in environmental waters and acidic soil extract samples were well resolved in less than 19 min using a 0.90 mL/min flow rate with low  $\mu\text{g/L}$  method detection limits.

## INTRODUCTION

In the U.S., the common alkali and alkaline earth cations are monitored as secondary drinking water contaminants. In contrast, alkali and alkaline earth cations are regulated in the European Union (EU) and Japan. Ammonium is routinely measured in the U.S. for wastewater discharge compliance monitoring and in the EU and Japan in both wastewater and drinking water.<sup>1</sup> Calcium and magnesium are also routinely measured to determine water hardness, an important parameter for corrosion control.<sup>2</sup> The present work describes the determination of dissolved alkali and alkaline earth cations and ammonium in drinking water and municipal wastewater using a compact, integrated, high-pressure ion chromatography system equipped with electrolytic eluent generation and suppressed conductivity and using 4- $\mu\text{m}$ -particle columns.

## MATERIALS AND METHODS

### Sample Preparation

Samples were filtered using 0.2  $\mu\text{m}$  syringe filters prior to analysis. Aqueous soil extracts were prepared by adding 30 mL of 30 mM methanesulfonic acid (MSA) to 3.0 g soil and sonicating in a bath sonicator for 30 min. Solutions were centrifuged to clear and then filtered as above.

### Ion Chromatography Conditions

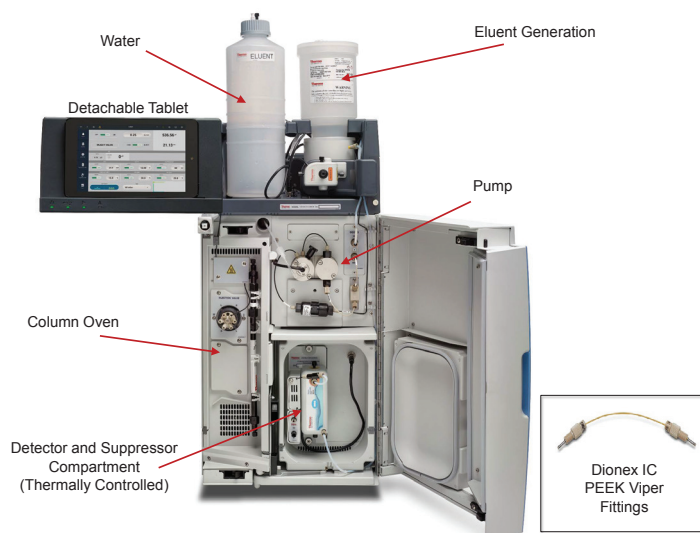
Columns	Thermo Scientific™ Dionex™ IonPac™ CS16-4 $\mu\text{m}$ column set, 4 mm
Eluent Source	Thermo Scientific™ Dionex™ EGC 500 MSA Eluent Generator Cartridge
Eluent Conc.	30 mM MSA
Flow Rate	0.9 mL/min
Column Temp.	40 °C
Inj. Volume	10 $\mu\text{L}$ (Full loop)
Detection	Suppressed conductivity
Detector Compart. Temp.	15 °C

Any variation from these conditions are indicated in the figures.

### Instrument

The Dionex Integri™ HPIC system, Reagent-Free™ IC (RFIC™) model (Figure 1) was configured for conductivity detection, which included automated eluent generation and Thermo Scientific™ Dionex™ IC PEEK Viper™ fittings (Figure 1 bottom right), for increased reproducibility and optimum performance.

Figure 1. Dionex Integri™ HPIC System.



### Data Analysis

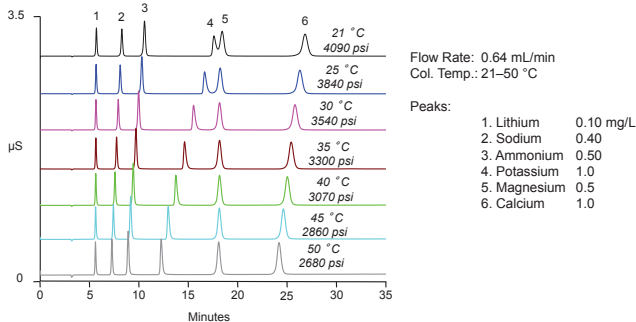
Thermo Scientific™ Dionex™ Chromeleon™ Chromatography Data System software version 7.2 SR4

## RESULTS

### Impact of Temperature on Cation Separation

On the Dionex IonPac CS16-4 $\mu$ m column, the cation retention time varies with temperature (Figure 2). Of the six cations analyzed, the retention time of potassium was the most sensitive to temperature. This retention time variability can be exploited to optimize selectivity among analytes, but a constant temperature should be maintained to ensure the best possible retention time reproducibility. Retention time variability may lead to misidentified peaks if the sample contains amines or other unknown compounds that elute near the standard cations.

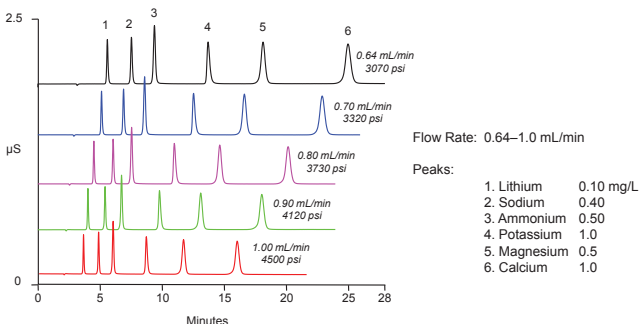
Figure 2. Comparison of cation retention times at different flow rates.



### Impact of Eluent Flow Rate on Run Time and Peak Resolution

To reduce the run time, flow was increased from 0.64 to 1 mL/min (Figure 3). Even at this maximum recommended flow rate, the cation standards were baseline resolved using a 4- $\mu$ m-particle column, which has greater peak efficiencies than standard, larger-particle-size columns. A flow rate of 0.9 mL/min was used for the remainder of the data shown here because it produced a relatively short run time while yielding sufficient resolution to quantify ammonium in the presence of a 10,000x ratio of sodium.

Figure 3. Comparison of cation retention times at different flow rates.



### Method Linear Calibration Ranges and Method Detection Limits

The calibration curves were linear over three orders of magnitude for all of the cations, except ammonium (Table 1). The nonlinear dependence of area on amount is common for analytes that form weak acids or weak bases in the suppressor. A quadratic curve-fitting function extends the calibration curve for ammonium to a concentration of 40 mg/L. Coefficients of determination ( $r^2$ ) ranged from 0.9996 to 1.000.

Table 1. Linear range and MDLs for cations and ammonium.

Cation	Range (mg/L)	Coefficient of Determination ( $r^2$ )	MDL Standard ( $\mu$ g/L)	Calculated MDL <sup>a</sup> ( $\mu$ g/L)
Li <sup>+</sup>	0.03–80	1.000	1	0.12
Na <sup>+</sup>	0.1–1000	0.9999	4	0.70
NH <sub>4</sub> <sup>+</sup> <sup>b</sup>	0.02–40	0.9996	5	0.89
K <sup>+</sup>	0.03–80	0.9999	10	1.12
Mg <sup>2+</sup>	0.03–80	1.000	5	0.75
Ca <sup>2+</sup>	0.03–80	0.9999	10	2.24

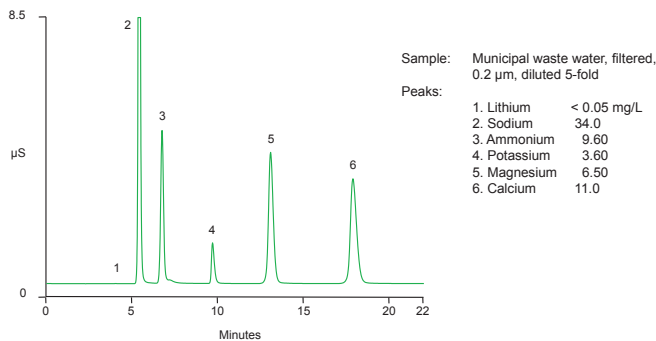
<sup>a</sup> MDL = (t)  $\times$  (S) where t = Student's t value for a 99% confidence level and a standard deviation estimate with n-1 degrees of freedom (t = 3.14 for seven replicates of the MDL Standard), and S = standard deviation of the replicate analysis

<sup>b</sup> Quadratic fit

### Cations in Environmental Water

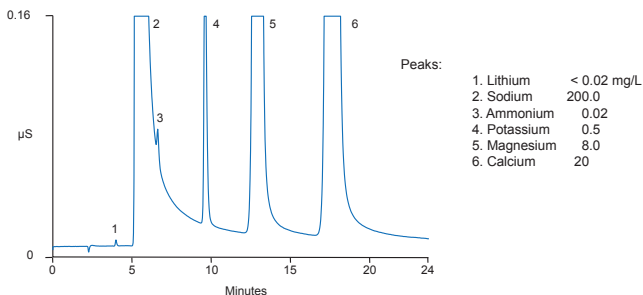
The Dionex IonPac CS16-4 $\mu$ m column is a high-capacity column, therefore, environmental samples, such as municipal wastewater, which can have a wide range of ionic strength, can be analyzed without interference from the matrix (Figure 4).

Figure 4. Determination of inorganic cations and ammonium in municipal wastewater.



The Dionex IonPac CS16-4 $\mu$ m column is ideal for the determination of low concentrations of ammonium in environmental waters. This column offers improved resolution of sodium from ammonium and alkanolamines compared to larger-particle-size columns, even for samples high in ionic strength. Figure 5 illustrates the determination of trace-level ammonium in the presence of high sodium (1:10,000).

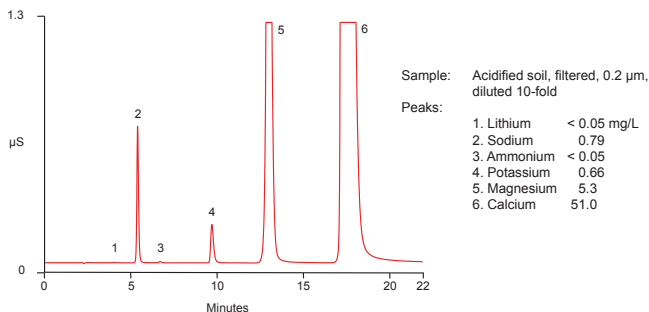
Figure 5. Determination of trace ammonium in the presence of high sodium (1:10,000).



### Cations in Acidic Soil Extracts

The Dionex IonPac CS16-4 $\mu$ m column packing is compatible with acidic eluents and samples. Acid digests, acid-preserved samples, or acidic soil extracts that contain up to 100 mM hydronium ion in a volume of 25  $\mu$ L can be injected without pH adjustment (Figure 6).

Figure 6. Determination of inorganic cations and ammonium in acidic soil extract.



## CONCLUSIONS

Ion chromatography that paired the high-pressure capability of the Dionex Integriion HPLC system with the Dionex IonPac CS16-4µm column enabled:

- A flow rate of 0.9 mL/min to be used, reducing the total run time to less than 24 min
- Determination of inorganic cations and ammonium at concentrations ranging from 0.1–80 mg/L
- Resolution of trace ammonium in the presence of a 10,000-fold higher concentration of sodium
- Analysis of a wide range of environmental waters and acidic soil extract

## REFERENCES

1. Jackson, P.E., Ion Chromatography in Environmental Analysis, Encyclopedia of Analytical Chemistry; Meyers, R.A., Ed; John Wiley & Sons, Chichester, U.K., 2000, 2779–2801.
2. World Health Organization. Hardness in Drinking-water. Background document for development of WHO Guidelines for Drinking-water Quality. Geneva, Switzerland, 2011.

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