Determination of inorganic cations and ammonium in environmental waters by ion chromatography with a high-capacity cation-exchange column

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Abstract

While alkali and alkaline earth cations are commonly determined by using spectrometric techniques such as atomic absorption spectrometry or inductively coupled plasma, ammonium cation in the same sample must be measured separately by a wet chemical technique such as colorimetry, titrimetry, or ammonia-selective electrode. In a single 25-min run ion chromatography can determine all of the important inorganic cations including lithium, sodium, ammonium, potassium, magnesium and calcium. In this paper, we describe the use of ion chromatography with a new high-capacity cation-exchange column (the IonPac CS16), an electrolytically-generated methanesulfonic acid eluent and suppressed conductivity detection to determine dissolved alkali and alkaline earth cations and ammonium in drinking water, wastewater and aqueous soil extracts. The IonPac CS16 is a high-capacity cation-exchange column that incorporates recent advances in polymer chemistry to enable trace-level determinations of cations even in high-ionic-strength matrices. We discuss the linear range, method detection limits, and analyte recoveries obtained with this column, and evaluate the effect of potential interferences on method performance during the analysis of typical environmental samples. © 2002 Elsevier Science B.V. All rights reserved.

Keywords: Water analysis; Soil; Environmental analysis; Inorganic cations; Alkali cations; Alkali-earth cations; Ammonium

1. Introduction

The common alkali and alkaline earth cations, though not considered primary drinking water contaminants in the USA, are monitored and reported by many public water suppliers and are regulated in the European Union and Japan. Calcium and magnesium are also routinely measured to determine water hardness, an important parameter for corrosion control [1].

Ammonia is a colorless, pungent gas. Highly soluble in water, ammonia exists in equilibrium between a molecular form associated with water and the ammonium cation, NH_4^+. The extent of its toxicity to aquatic life depends upon the extent of dissociation, which in turn depends upon temperature and pH. Ammonia can enter environmental waters as a product of anaerobic decomposition of nitrogen-containing compounds or from waste streams containing ammonia [2]. Ammonium cation is routinely measured in the USA for National Pollutant Discharge Elimination System (NPDES) compliance monitoring, and in the European Union and Japan in drinking water [1].

Alkali and alkaline earth cations are commonly determined by using spectrometric techniques such as atomic absorption spectrometry or inductively

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coupled plasma, but the ammonium cation in the same sample must be measured separately by a wet chemical technique such as titrimetry, colorimetry (Nesslerization, Phenate or Automated Phenate methods), or ammonia-selective electrode [3]. Furthermore, the latter two methods may require a separate distillation step before ammonia can be determined in wastewater. Ion chromatography (IC) in a single run can determine ammonium plus all of the important inorganic cations including lithium, sodium, potassium, magnesium and calcium.

This paper describes the use of IC with an IonPac CS16 cation-exchange column, an electrolytically-generated methanesulfonic acid eluent and suppressed conductivity detection to determine dissolved alkali and alkaline earth cations and ammonium in drinking water, wastewater and aqueous soil extracts. The IonPac CS16 is a high-capacity cation-exchange column with 100% solvent compatibility and medium hydrophobicity. The high capacity of 8400 μequiv./column is achieved by using a smaller bead diameter (5 μm), a higher density of grafted carboxylic acid cation-exchange groups, and a larger column format. The higher capacity improves performance for trace-level determinations of cations in high-ionic-strength matrices by extending the linear range and allowing resolution of higher concentration ratios of sodium and ammonium [4].

We discuss the linear range, method detection limits, and analyte recoveries obtained with this column, and evaluate the effect of potential interferences on method performance during the analysis of typical environmental samples.

2. Experimental

2.1. Chemicals

All solutions were prepared from analytical-reagent grade chemicals in reagent water [deionized water obtained from a Labconco Water Pro PS purification system (Kansas City, MO, USA) with a specific resistance >17.8 MΩ cm]. Stock solutions of sodium, potassium, ammonium, magnesium and calcium were prepared from their analytical reagent grade chloride salts. Lithium chloride, sodium chloride, and calcium chloride dihydrate were purchased from Fisher Scientific (Pittsburgh, PA, USA), am-

monium chloride and potassium chloride were from Sigma (St. Louis, MO, USA), and magnesium chloride hexahydrate from Aldrich (Milwaukee, WI, USA). A Combined Six Cation Standard-II solution is available from Dionex (Sunnyvale, CA, USA) and individual cation standard solutions are available from Ultra Scientific through VWR Scientific Products (Brisbane, CA, USA). Stock standards stored at 4 °C are stable for at least 1 month. Working standards were prepared fresh daily.

2.2. Instrumentation

The IC system used for this work was a Dionex (Sunnyvale, CA, USA) DX-600 system consisting of a GP50 gradient pump with vacuum degas option, AS50 automated sampler with thermal compartment, EG40 eluent generator with EGC-MSA cartridge, an ED50A electrochemical detector with conductivity cell, DS3 detector stabilizer and a Dionex CSRS-ULTRA 4 mm operating in the recycle mode. A Dionex PeakNet Chromatography Workstation was used for system control and data collection.

2.3. Columns

A Dionex IonPac CS16 250 mm×5 mm analytical column and a CG16 50 mm×5 mm guard column were used for separations. The CS16 stationary phase is composed of 55% crosslinked ethylvinylbenzene (EVB)–divinylbenzene polymer particles with a grafted ion-exchange layer of carboxylic acid groups. The macroporous particles have an average diameter of 5.5 μm and pore size of 150 Å. Experiments were performed at ambient temperature or with the columns kept at a constant at 30 °C.

2.4. Mobile phase

The eluent of 26 mM methanesulfonic acid (MSA) was generated on-line from reagent water with an EG40 eluent generator and EGC-MSA cartridge. Alternatively, 26 mM MSA can be prepared by diluting 65 ml of 0.4 M methanesulfonic acid eluent concentrate (Dionex) to 1.0 l with reagent water. Manually prepared eluents should be degassed by

sonicating under vacuum for 10 min or by sparging with helium, and stored in plastic labware.

2.5. Sample preparation

Water samples were collected in 1-l plastic bottles and kept refrigerated at 4 °C. The drinking water sample was taken from a faucet, and the domestic wastewater sample from a septic tank, in Sunnyvale, CA, USA. The spring surface water sample was taken from a reservoir near Concord, CA, USA. The ASTM wastewater was prepared according to an ASTM specification [10]. All water samples were filtered through Gelman 0.45 μm IC syringe filters (Ann Arbor, MI, USA) prior to injection. The soil extracts were prepared by placing 10 g of dried soil in a 250-ml beaker and adding reagent water or 26 mM MSA to a total volume of 100 ml. The samples were extracted for 30 min in an ultrasonic bath, allowed to settle and filtered through a 0.45 μm IC syringe filter before injection.

3. Results and discussion

3.1. Selection of conditions

During the development process, the IonPac CS16 column selectivity was optimized for a 40 °C operating temperature to maximize peak efficiencies. In order to develop a method for inorganic cation and ammonium analysis with the broadest applicability for environmental monitoring, we began by demonstrating that acceptable selectivity and run times could be obtained by using a 26 mM MSA eluent, 1.5 ml/min flow-rate, and no column temperature control. If run at ambient temperature, these conditions will provide good selectivity between the cations, as shown in Fig. 1A. In Fig. 1A, a low-mg/l level cation standard was run once at ambient temperature, and then two more times as the temperature was increased to 27 °C to simulate typical variations in a laboratory's ambient temperature. On the CS16 column, the retention time of cations does vary somewhat with temperature. The retention time of potassium is especially variable, at 1.5% RSD for the three runs shown. This variability can be exploited to optimize selectivity among analytes, but could lead to misidentified peaks if the sample
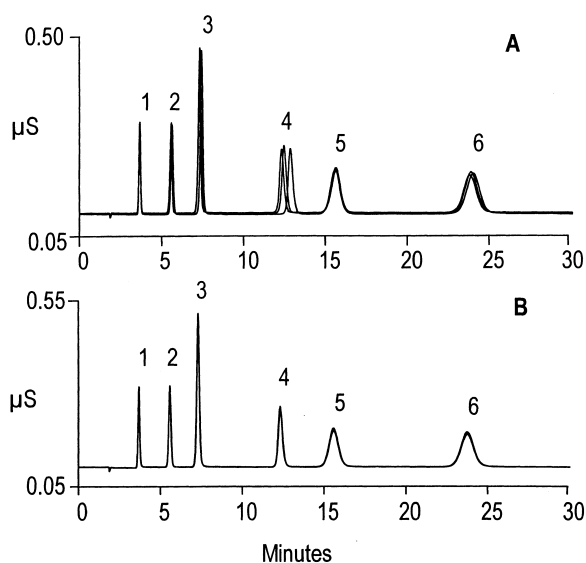

Fig. 1. Separation of inorganic cations and ammonium, (A) at ambient temperature to 27 °C, (B) at 30 °C. Other conditions: column, IonPac CS16; eluent, 26 mM methanesulfonic acid; flow-rate, 1.5 ml/min; detection, CSRS-ULTRA operated at 100 mA in recycle mode; injection volume, 25 μl. Solutes: 1=lithium, 2=sodium, 3=ammonium, 4=potassium, 5=magnesium, 6=calcium.

contains amines or other unknown compounds that elute near the standard cations.

We then compared the results without temperature control to those obtained at a constant temperature. Three chromatograms of the same cation standard run at a constant temperature of 30 °C are overlayed in Fig. 1B, demonstrating that good retention time reproducibility results from temperature control (<0.1% RSD for potassium). For the purposes of this work, we chose to use a constant temperature to ensure the best possible reproducibility. Under these conditions, lithium, sodium, ammonium, potassium, magnesium and calcium are baseline resolved within 25 min.

3.2. Performance evaluation

We evaluated this method by examining several criteria of performance. First we determined method linearity for inorganic cations and ammonium over a seven-point calibration range. Then we determined the method detection limit (MDL), defined as the minimum concentration of an analyte that can be

identified, measured and reported with 99% confidence that the analyte concentration is greater than zero. The MDL for each analyte was determined as in US Environmental Protection Agency (EPA) Method 300.0 [5] by calculating the standard deviation of seven replicates of reagent water fortified with each analyte at a concentration of three to five times the estimated instrument detection limit.

Table 1 shows the linear concentration ranges investigated, the resulting coefficients of determination (r^2), and calculated MDLs for the six cations. The high capacity of the CS16 column results in a calibration curve that is linear over three orders of magnitude for most of the cations, except for ammonium. Suppressed conductivity detection typically is linear over a wide range of analyte concentrations, but deviation from the linear dependence of peak area/height on amount is observed for analytes that form weak acids or weak bases in the suppressor. Ammonium cation forms a weak base in the suppressor, where changes in dissociation lead to the nonlinear calibration curve [6,7]. A quadratic curve fitting function extends the calibration curve for ammonium to a concentration of 40 mg/l.

The EG40 conveniently generates a high-purity MSA eluent with a very reproducible composition. The EG40 increases the level of automation for this method while providing results comparable to, or better than, a manually prepared eluent [8]. In Table 2, this is reflected in the typical retention time (t_R) and peak area precision (expressed as RSD) de-

Table 2
Precision for inorganic cations and ammonium

Cation	QCS standard (mg/l)	t_R precision (RSD, %)	Area precision (RSD, %)
Li^+	1	0.08	0.93
Na^+	4	0.09	0.97
NH_4^+	5	0.10	0.83
K^+	10	0.15	0.99
Mg^{2+}	5	0.19	0.93
Ca^{2+}	5	0.22	1.15

termined from seven replicate injections of a low mg/l level quality control sample (QCS). Summarizing the results shown in Tables 1 and 2, the method provides acceptable linearity, MDLs are in the low-μg/l range, and good retention time and peak area precision are obtained.

Environmental water samples present a significant analytical challenge because trace amounts of certain analytes must often be resolved from high concentrations of other analytes in a wide range of matrices varying in ionic strength, acidity or alkalinity, and the presence of interferences. Fig. 2 provides an illustration of the diverse samples that might be encountered in environmental water analysis. Methods are favored that are robust with respect to sample matrix and that provide a wide dynamic range. The performance of ion chromatographic methods for environmental analysis has steadily improved with the development of higher-capacity ion-exchange columns. The IonPac CS16, with a capacity of 8400 μequiv./column, provides a significant advance in method performance for cation analysis.

For example, the higher cation-exchange capacity of the CS16 improves its performance in determination of low concentrations of ammonium in environmental waters by providing better resolution of ammonium from sodium. Fig. 3 shows the determination of trace level ammonium in the presence of a 6000-fold excess of sodium. In this tap water sample, ammonium at 0.03 mg/l elutes on the tail of a large sodium peak (200 mg/l), but is still clearly resolved and easily measured.

The IonPac CS16 packing is also compatible with acidic eluents and samples. This is important because sample treatment in environmental analysis often requires acidification of samples to preserve target analytes, or addition of acid to mobilize analytes or

Table 1
Linear range and MDLs for inorganic cations and ammonium

Cation	Range (mg/l)	Linearity (r^2)	MDL standard (μg/l)	Calculated MDL[a] (μg/l)
Li^+	0.05–80	0.9999	1	0.19
Na^+	0.1–1000	0.9999	4	1.81
NH_4^+	0.05–40	0.9993[b]	5	1.23
K^+	0.05–80	0.9999	10	2.64
Mg^{2+}	0.05–80	0.9999	5	1.00
Ca^{2+}	0.05–80	0.9998	5	1.09

[a] The MDLs were calculated as MDL=$(t)\cdot(S)$ 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.
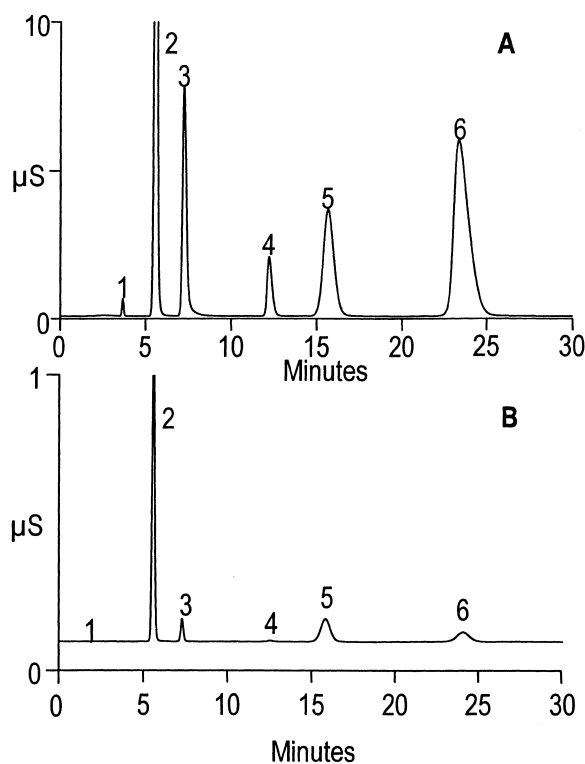
[b] Quadratic fit; see text for details.

Fig. 2. Examples of diverse sample matrices encountered in environmental water analysis. Conditions: as for Fig. 1, except; injection volume, 10 μl; (a) sample, wastewater from a septic tank; solutes: 1=lithium (0.40 mg/l), 2=sodium (48 mg/l), 3=ammonium (120 mg/l), 4=potassium (17 mg/l); 5= magnesium (24 mg/l); 6=calcium (89 mg/l). (b) Sample, spring surface water; solutes: 1=lithium (<0.2 mg/l), 2=sodium (3.6 mg/l), 3=ammonium (0.24 mg/l), 4=potassium (<0.2 mg/l); 5=magnesium (0.46 mg/l); 6=calcium (0.40 mg/l).

decompose the sample matrix. Acid digests, acid-preserved samples or acidic soil extracts that contain up to 100 m*M* hydronium ion can be injected onto the IonPac CS16 without pH adjustment. Fig. 4 shows a comparison between a water extract of a soil sample (Fig. 4A) and the same sample extracted with 26 m*M* MSA (Fig. 4B). In this example, the acid extracted significantly more of the cations than did a simple water extraction. The asymmetry of the magnesium and calcium peaks is typical for such a large amount of the cations. Further dilution would have been necessary for quantification because the amounts of magnesium and calcium exceeded the calibration limits.

A typical way to validate the performance of methods used for environmental analysis is through
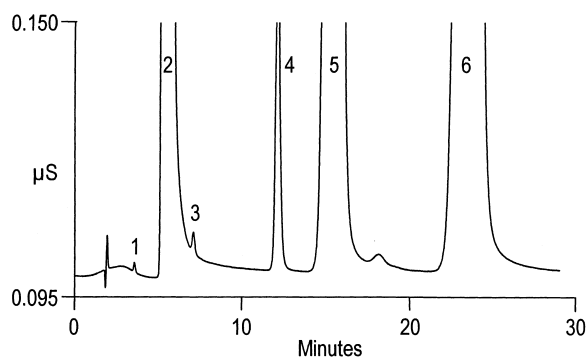

Fig. 3. Resolution of trace ammonium from high sodium with the IonPac CS16 column. Conditions: as for Fig. 2, except: sample, Sunnyvale, CA, USA, tap water fortified to 200 mg/l with sodium. Solutes: 1=lithium (<0.2 mg/l), 2=sodium (200 mg/l), 3=ammonium (0.03 mg/l), 4=potassium (0.50 mg/l); 5= magnesium (8.0 mg/l); 6=calcium (20 mg/l).
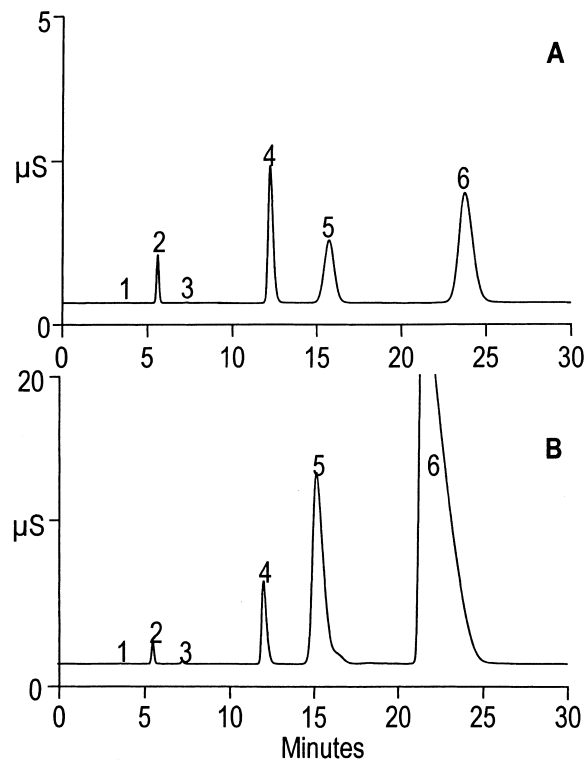

Fig. 4. Determination of inorganic cations and ammonium in aqueous and acidic soil extracts by using the IonPac CS16 column. Conditions: as for Fig. 2, except: sample (A), aqueous soil extract; solutes: 1=lithium (<0.2 mg/l), 2=sodium (2.5 mg/l), 3=ammonium (0.05 mg/l), 4=potassium (20 mg/l); 5= magnesium (7.0 mg/l); 6=calcium (27 mg/l); and sample (B), acidic soil extract; solutes: 1=lithium (<0.2 mg/l), 2=sodium (4.5 mg/l), 3=ammonium (0.60 mg/l), 4=potassium (50 mg/l); 5=magnesium (93 mg/l); 6=calcium (650 mg/l).

Table 3
Single-operator recovery results obtained for environmental water matrices fortified with inorganic cations and ammonium analyzed by using the IonPac CS16 column

	Reagent water		Drinking water		Domestic wastewater		ASTM wastewater[a]	
	Amount added (mg/l)	Recovery (%)	Amount added (mg/l)	Recovery (%)	Amount added (mg/l)	Recovery (%)	Amount added (mg/l)	Recovery (%)
Lithium	2	100	1	103	2	109	2	99
Sodium	2	97	20	101	50	97	100	95
Ammonium	2	107	1	105	50	107	2	109
Potassium	2	82	1	84	20	94	20	95
Magnesium	2	86	30	100	20	105	3	95
Calcium	2	82	20	105	2	101	2	86

[a] The sample was prepared according to Ref. [10].

precision and bias studies on spiked samples representing diverse matrices [9]. We evaluated the performance of this method in a similar way. First we determined the levels of the inorganic cations and ammonium in various environmental water samples. Then we spiked the samples with the analytes at a level that was 50–100% of the amount in the native sample. Table 3 summarizes the spike recovery of inorganic cations from various environmental water matrices. This method using the IonPac CS16 column provides acceptable recovery (i.e., 80–120%) of the inorganic cations from all matrices. Because the CS16 is a high-capacity column, environmental samples with a wide range of ionic strength can be analyzed without interference from the matrix.

4. Conclusions

This method uses the IonPac CS16 column with a 26 m*M* MSA eluent and suppressed conductivity detection to determine inorganic cations and ammonium at concentrations ranging from 0.1 to 80 mg/l. The high capacity of the IonPac CS16 column enables the method to perform well in a wide range of environmental waters, and to resolve trace ammonium in the presence of a 10 000-fold higher concentration of sodium. With eluent preparation automated by using the EG40 eluent generator, the retention time precision is 0.2% RSD or less, and the peak area precision is 1% RSD or less, for standards in the low-mg/l range.

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