

Determination of Inorganic Cations and Ammonium in Environmental Waters by Ion Chromatography Using the Dionex IonPac CS16 Column

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Introduction

The common alkali and alkaline earth cations are not considered primary drinking water contaminants in the U.S.; however they are monitored and reported by many public water suppliers here and are regulated in the EU and Japan. Calcium and magnesium are also routinely measured to determine water hardness, an important parameter for corrosion control.

Ammonia is a colorless, pungent gas. It is highly soluble in water, where it exists in equilibrium between a molecular form associated with water and the ionized form (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. Ammonium cation is routinely measured in the U.S. for wastewater discharge compliance monitoring and in the EU and Japan in both wastewater and drinking water.¹

Alkali and alkaline earth cations are commonly determined by using spectroscopic techniques such as AAS or ICP, but 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.² Furthermore, the latter two methods may also require a separate distillation step before ammonia can be determined in wastewater. Ion chromatography (IC) in a single run can determine ammonium plus all the important inorganic cations, including lithium, sodium, potassium, magnesium, and calcium.

The Thermo Scientific™ Dionex™ IonPac™ CS16 Column is a high-capacity cation exchange column with 100% solvent compatibility and medium hydrophobicity. The high capacity of 8400 $\mu\text{eq}/\text{column}$ 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 resolving higher concentration ratios of sodium and ammonium.

This Application Note describes the use of ion chromatography with a Dionex IonPac CS16 cation-exchange column, an electrolytically generated methanesulfonic acid (MSA) eluent, and suppressed conductivity detection to determine dissolved alkali and alkaline earth cations and ammonium in drinking water, wastewater, and aqueous soil extracts. This Note discusses the linear range, method detection limits, and analyte recoveries obtained with the Dionex IonPac CS16 column and evaluates the effect of potential interferences on method performance during the analysis of typical environmental samples.

Equipment

Dionex DX-600 chromatography system* consisting of:

- GP50 Gradient Pump with vacuum degas option
- EG40 Eluent Generator
- EluGen EGC-MSA cartridge
- ED50A Electrochemical Detector with conductivity cell and DS3 Detector Stabilizer
- AS50 Automated Sampler with thermal compartment
- Thermo Scientific Dionex PeakNet 6.1 Chromatography Workstation
- Syringe filters

*Equivalent or improved results can be achieved using the Thermo Scientific Dionex ICS-5000⁺, the Thermo Scientific Dionex ICS-4000, or the Thermo Scientific Dionex ICS-2100.

Reagents and Standards

- Deionized water, Type I reagent grade, 17.8 MΩ-cm resistivity or better
- Lithium standard, 1000 mg/L
- Sodium standard, 1000 mg/L
- Ammonium standard, 1000 mg/L
- Potassium standard, 1000 mg/L
- Magnesium standard, 1000 mg/L
- Calcium standard, 1000 mg/L
- Lithium chloride (LiCl)
- Sodium chloride (NaCl)
- Ammonium chloride (NH₄Cl)
- Potassium chloride, (KCl)
- Magnesium chloride hexahydrate (MgCl₂•6H₂O)
- Calcium chloride dihydrate (CaCl₂•2H₂O)
- Thermo Scientific Dionex Combined Six Cation Standard-II

Conditions

Columns:	Dionex IonPac CS16 Analytical, 5 × 250 mm Dionex IonPac CG16 Guard, 5 × 50 mm
Eluent:	26 mM MSA
Eluent Source:	Thermo Scientific Dionex EG40 Eluent Generator
Flow Rate:	1.5 mL/min
Temperature:	30 °C
Injection:	10 µL
Detection:	Suppressed conductivity, Thermo Scientific™ Dionex™ CSRS™ ULTRA Cation Self Regenerating Suppressor (4 mm), Autosuppression Recycle mode, current setting 100 mA
Background:	< 1 µS
Noise:	~0.2 nS peak-to-peak
Backpressure:	~2300 psi
Run Time:	30 min

Preparation of Solutions and Reagents

Reagent Water

Type I reagent grade distilled or deionized water with a specific resistance of 17.8 MΩ-cm or greater, filtered through a 0.2 µm filter immediately before use.

Eluent Solution

Generate 26 mM MSA eluent on-line by pumping reagent water through the Dionex EG40/EGC-MSA. Dionex PeakNet software tracks the amount of MSA used and calculates the remaining lifetime.

Alternatively, prepare 26 mM MSA by diluting 65 mL of 0.4 N Methanesulfonic Acid Eluent Concentrate to 1.0 L with reagent water. Degas the eluent by sonicating under vacuum for 10 minutes or by sparging with helium. Store the eluent in plastic labware.

Or, prepare a 1.0 N MSA stock solution. Carefully add 96.10 g of methanesulfonic acid (MSA, > 99%) to a 1 L volumetric flask containing about 500 mL of deionized water. Dilute to the mark and mix thoroughly. Prepare 26 mM MSA by diluting 26 mL of the 1.0 N MSA stock solution to 1.0 L with reagent water. Degas the eluent. Store the eluent in plastic labware.

Stock Standard Solutions

Purchase certified solutions or prepare 1000 mg/L stock standard solutions of each of the cations of interest. Dry reagent-grade salts to a constant weight and accurately weigh the amounts given in Table 1. Dissolve in reagent water in a 100 mL plastic volumetric flask. Dilute to volume with reagent water. Store in plastic containers at 4 °C. Stock standards are stable for at least three months.

Working Standard Solutions

Prepare composite working standards at lower concentrations by diluting appropriate volumes of the 1000 mg/L stock standards with reagent water. Prepare working standards daily if they contain less than 100 mg/L of the cations.

Table 1. Mass of compound required to prepare 100 mL of 1 g/L solution of cation.

Cation	Compound	Mass (g)
Li ⁺	LiCl	0.6108
Na ⁺	NaCl	0.2542
NH ₄ ⁺	NH ₄ Cl	0.2965
K ⁺	KCl	0.1907
Mg ⁺²	MgCl ₂ •6H ₂ O	0.8365
Ca ⁺²	CaCl ₂ •2H ₂ O	0.3668

Sample Preparation

Filter all water samples through a 0.45 μm IC syringe filter. Discard the first 300 μL of filtrate and filter the remainder directly into a clean plastic autosampler vial.

Prepare aqueous soil extracts by adding 30 mL of either deionized water or 26 mM MSA to 3.0 g of soil. Extract in an ultrasonic bath for 30 minutes and filter through a 0.45 μm IC syringe filter as above.

System Preparation and Set-Up

Prepare the Dionex CSRS ULTRA suppressor for use by hydrating the eluent chamber. Use a disposable plastic syringe to slowly push approximately 3 mL of 200 mM NaOH through the Eluent Out port and 5 mL of 200 mM NaOH through the Regen In port. Allow the suppressor to sit for approximately 20 minutes to fully hydrate the suppressor screens and membranes. (For more information on Dionex CSRS suppressor operation, see the Installation and Troubleshooting Instructions for the Dionex CSRS-ULTRA Suppressor).

Install the Dionex EG40 generator, connect it to the system, and configure it with the PeakNet chromatography data system. Condition the Thermo Scientific Dionex EluGen MSA cartridge as directed in the Dionex EG40 generator manual by running a gradient from 1 to 60 mM MSA in 20 minutes, then 60 mM for 40 minutes at 1 mL/min. (For instructions on Dionex EG40 generator installation and use, see the Operator's Manual for the Dionex EG40 Eluent Generator System).

Remove the backpressure tubing temporarily installed during conditioning of the Dionex EluGen cartridge. Install a 5 $\times$ 50 mm Dionex IonPac CG16 column and a 5 $\times$ 250 mm Dionex IonPac CS16 column. Make sure that the system pressure displayed by the pump is at least 2000 psi when 26 mM MSA is delivered at 1.5 mL/min, because the Dionex EG40 generator high pressure degas tubing assembly requires at least 2000 psi (14 MPa) of backpressure to efficiently remove hydrolysis gas from the eluent. If necessary, install backpressure coils supplied with the Dionex EG40 generator ship kit to bring the system pressure to between 2000 and 2800 psi. Because the system pressure can rise over time, occasional trimming of the backpressure coil may be necessary to maintain system pressure under 3000 psi. Do not exceed 3000 psi.

The Dionex IonPac CS16 column storage solution is 30 mM MSA; before use, equilibrate the column with 26 mM MSA eluent for 60 minutes. Prior to sample analysis, analyze a system blank of reagent water. An equilibrated system has a background signal of less than 1 μS , and peak-to-peak noise should be about 0.2 nS. There should be no peaks eluting at the same retention time as the cations of interest.

Prepare a 500X dilution of the Dionex Six Cation Standard-II and make a 10 μL full loop injection. The column is equilibrated when two consecutive injections of standard produce the same retention times. Confirm that the resulting chromatogram resembles the chromatogram in Figure 1A.

Peak area precision and accuracy depend on autosampler performance. Replace the water in the flush reservoir daily with freshly filtered and degassed reagent water. Inspect the Dionex AS50 autosampler daily for bubbles in the sample syringe or its tubing. Purge to remove any bubbles by following the instructions in the Dionex AS50 autosampler manual.

The precision and accuracy of the Dionex AS50 autosampler will vary depending on the mode of injection. The most accurate and precise injections can be made with a calibrated sample loop in the full loop injection mode. To conserve sample, use one of the partial loop injection modes. Refer to the Dionex AS50 autosampler reference manual for a complete discussion of the different injection modes.

Make sure that the correct sample loop size and sample syringe volume are entered in the Dionex AS50 autosampler plumbing configuration screen.

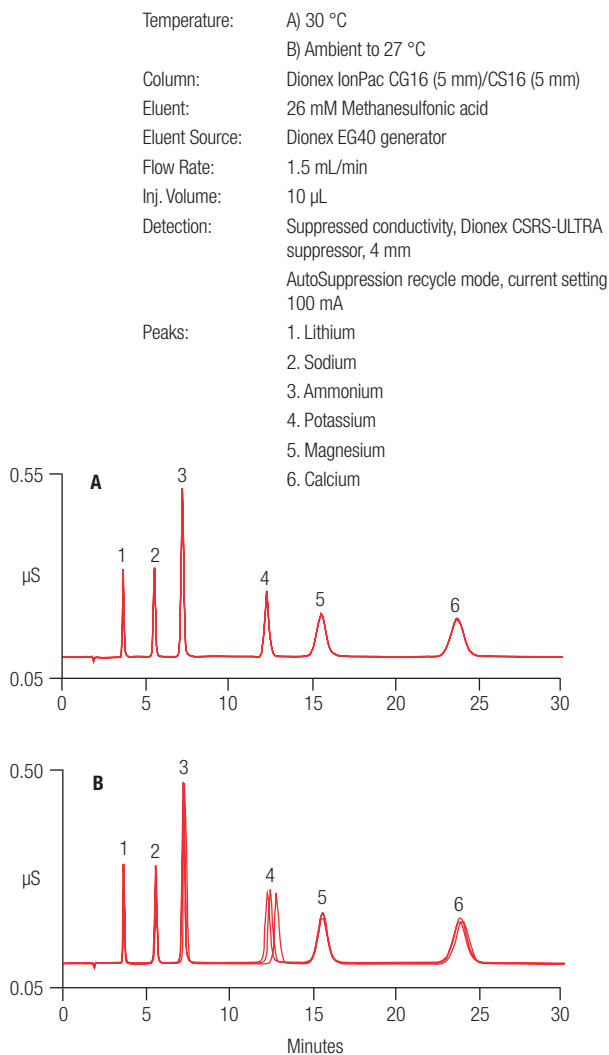


Figure 1. Temperature control improves RT reproducibility.

Results and Discussion

Three chromatograms of a cation standard performed at a constant 30 °C are overlaid in Figure 1A, demonstrating the good retention time reproducibility that results from temperature control. On the Dionex IonPac CS16 column, the retention time of cations will vary somewhat with temperature. This variability can be exploited to optimize selectivity among analytes, but maintaining a constant temperature ensures the best possible retention time reproducibility. If run at ambient temperature, this method will provide good selectivity between the cations, as shown in Figure 1B. In Figure 1B, a cation standard was run once at ambient temperature and then two more times as the temperature was increased to 27 °C. Note that the retention time of potassium is especially variable. Retention time variability could lead to misidentified peaks if the sample contains amines or other unknown compounds that elute near the standard cations. Use a thermal compartment for the best retention time reproducibility. Under these conditions lithium, sodium, ammonium, potassium, magnesium, and calcium are baseline resolved within 25 minutes.

Table 2 summarizes the calibration data and method detection limits (MDLs) obtained for the six cations. The high capacity of the Dionex IonPac CS16 column results in a calibration curve that is linear over three orders of magnitude for most of the cations, except for ammonium. The nonlinear dependence of peak height (or area) on amount is common for analytes that form weak acids or weak bases in the suppressor.^{3,4} A quadratic curve fitting function extends the calibration curve for ammonium to a concentration of 40 mg/L.

Table 2. Linear range and MDLs for cations and ammonium.

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

^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 Quadratic fit

The method detection limit (MDL) is 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. To establish the single operator, within-day MDL for each analyte, make seven replicate injections of reagent water fortified with each analyte at a concentration of three to five times the estimated instrument detection limit. Perform all the calculations defined in the method and report the concentration values in the appropriate units.⁵

Suppressed conductivity detection allows detection down to the low µg/L level if 10 µL of sample is injected. Depending on the ionic strength and nature of the sample matrix, you may be able to achieve lower detection limits by injecting more sample.

The Dionex EG40 generator conveniently generates a high purity MSA eluent with a very stable composition. The Dionex EG40 generator increases the level of automation for this application while providing results comparable to a manually prepared eluent. This is reflected in the retention time (t_R) and peak area reproducibility summarized in Table 3 for seven injections of a QCS standard.

A typical way to validate the performance of methods used for environmental analysis is through precision and bias studies on spiked samples.⁶ 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.

Table 3. Precision for cations and ammonium.

Cation	QCS Standard (mg/L)	t _R Precision (%RSD) ^a	Area Precision (%RSD) ^a
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

^a Relative standard deviation, n = 7

Then we spiked the samples with the analytes at a level that was 50–100% of the amount in the native sample. Table 4 summarizes the spike recovery of inorganic cations from various environmental water matrices. This method using the Dionex IonPac CS16 column provides acceptable recovery (i.e., 80–120%) of the inorganic cations from all matrices. Because the Dionex IonPac CS16 column is a high capacity column, environmental samples with a wide range of ionic strength can be analyzed without interference from the matrix, as illustrated in Figure 2.

The Dionex IonPac CS16 column is a high capacity cation-exchange column that replaces the Dionex IonPac CS15 column for disparate concentration ratios of ammonium and sodium in diverse sample matrices. The Dionex IonPac CS16 column is ideal for the determination

of low concentrations of ammonium in environmental waters. It provides improved resolution of sodium from ammonium and alkanolamines, even for samples high in ionic strength. Figure 3 illustrates the determination of trace level ammonium in the presence of high sodium.

Table 4. Inorganic cation recoveries using the Dionex IonPac CS16 column.

Reagent Water		
Cation	Amount Added (mg/L)	Recovery (%)
Lithium	2	100
Sodium	2	97
Ammonium	2	107
Potassium	2	82
Magnesium	2	86
Calcium	2	82
Domestic Wastewater		
Lithium	2	109
Sodium	50	97
Ammonium	50	107
Potassium	20	94
Magnesium	20	105
Calcium	2	101
Drinking Water		
Lithium	1	103
Sodium	20	101
Ammonium	1	105
Potassium	1	84
Magnesium	30	100
Calcium	20	105
ASTM Wastewater		
Lithium	2	99
Sodium	100	95
Ammonium	2	109
Potassium	20	95
Magnesium	3	95
Calcium	2	86

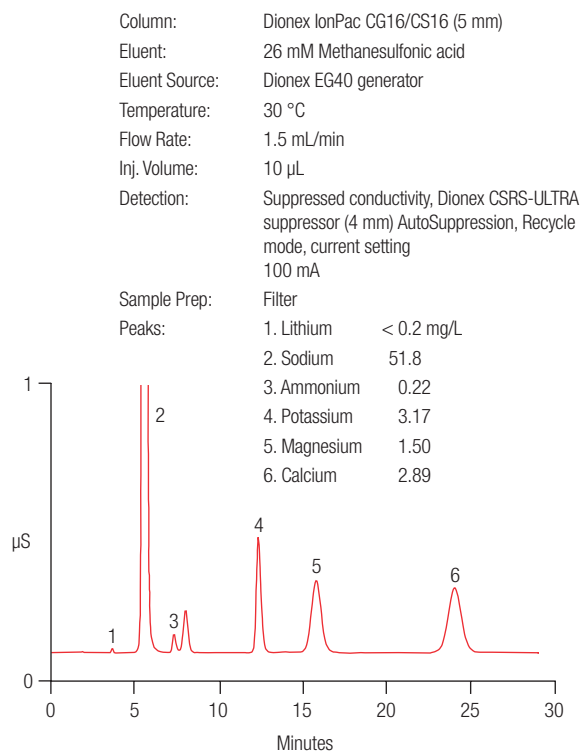


Figure 2. Determination of inorganic cations and ammonium in industrial wastewater with the Dionex IonPac CS16 column.

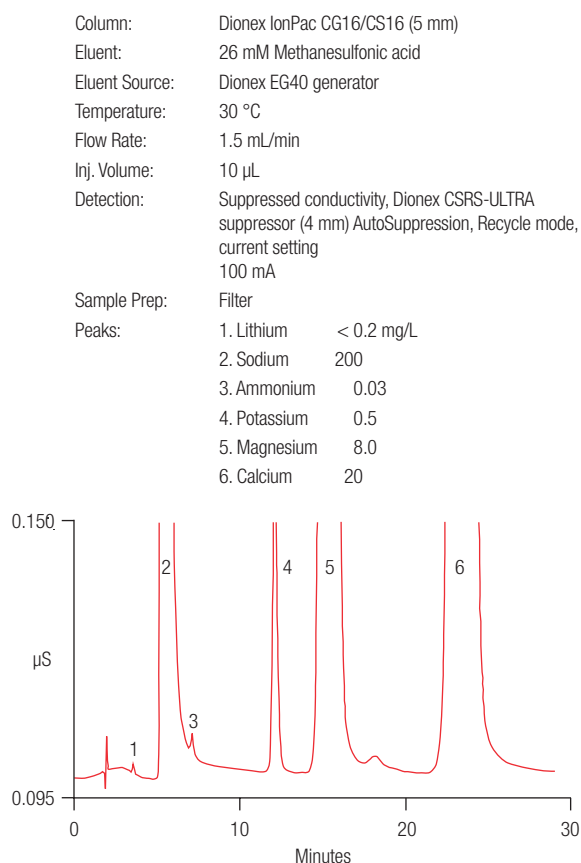


Figure 3. Resolution of trace ammonium from high sodium with the Dionex IonPac CS16 column.

The Dionex IonPac CS16 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 can be injected without pH adjustment. Figure 4 shows this for an acidic soil extract.

Strongly retained compounds from injected environmental water samples can accumulate on the column and degrade its performance. Signs of a fouled column include loss of capacity, loss of resolution, shortened retention times, higher noise and background, spurious peaks, and peak tailing. The Dionex IonPac CS16 column can be flushed with up to 100% acetonitrile to help remove contaminants from the column. (For more information on column troubleshooting and cleanup, see the Installation Instructions and Troubleshooting Guide for the Dionex IonPac CS16 Analytical Column).

Summary

This application uses the Dionex IonPac CS16 column with a 26 mM MSA eluent and suppressed conductivity detection to determine inorganic cations and ammonium at concentrations ranging from 0.1–80 mg/L. The high capacity of the Dionex IonPac CS16 column enables the analysis of a wide range of environmental waters, and also resolves trace ammonium in the presence of a 10,000-fold higher concentration of sodium. 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.

References

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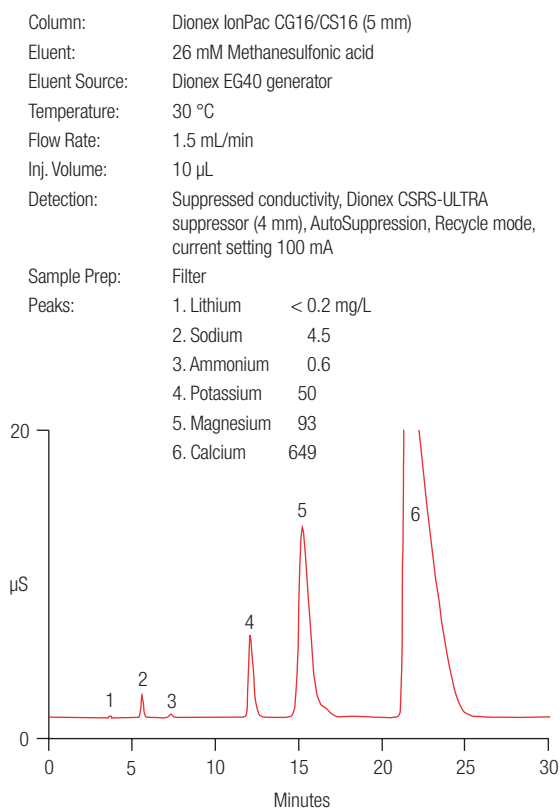


Figure 4. Determination of inorganic cations and ammonium in acidic soil extract with the Dionex IonPac CS16 column.

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