

Low-cost determination of inorganic cations and ammonium in environmental waters

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Introduction

In the United States (U.S.), water quality is regulated through the Safe Drinking Water Act (SDWA) and the Clean Water Act (CWA) and enforced through the United States Environmental Protection Agency (U.S. EPA).¹ As a well-accepted technique, ion chromatography (IC) has been used for compliance monitoring inorganic anions in water, including surface, ground, drinking, and waste waters following U.S. EPA Methods 300 and 300.1.² Although the common alkali and alkaline earth cations, and ammonium are not considered primary drinking water contaminants in the U.S., they are routinely monitored and reported here and are regulated in Europe and Japan. Ammonium is measured in the U.S. for waste water discharge compliance according to the criteria for the protection of aquatic life from the toxic effects of ammonia in freshwater published by U.S. EPA in 2013.³

This work demonstrates the determination of cations and ammonium in environmental waters by IC using a Thermo



Scientific™ Dionex™ IonPac™ CS16 column set on a Thermo Scientific™ Dionex™ Easion™ Chromatography system in Displacement Chemical Regeneration (DCR) mode. Figure 1 shows a diagram of the system setup. The Dionex Easion IC system is an integrated, single-channel low-cost system designed for isocratic applications with suppressed conductivity detection. Coupled to the Thermo Scientific™ Dionex™ AS-DV Autosampler, it provides a low-cost choice for routine water analysis.

Equipment and consumables

- Dionex Easion IC system
- Dionex AS-DV Autosampler
- Thermo Scientific™ Dionex™ Chromeleon™ 7.2.10 MuA Chromatography Workstation

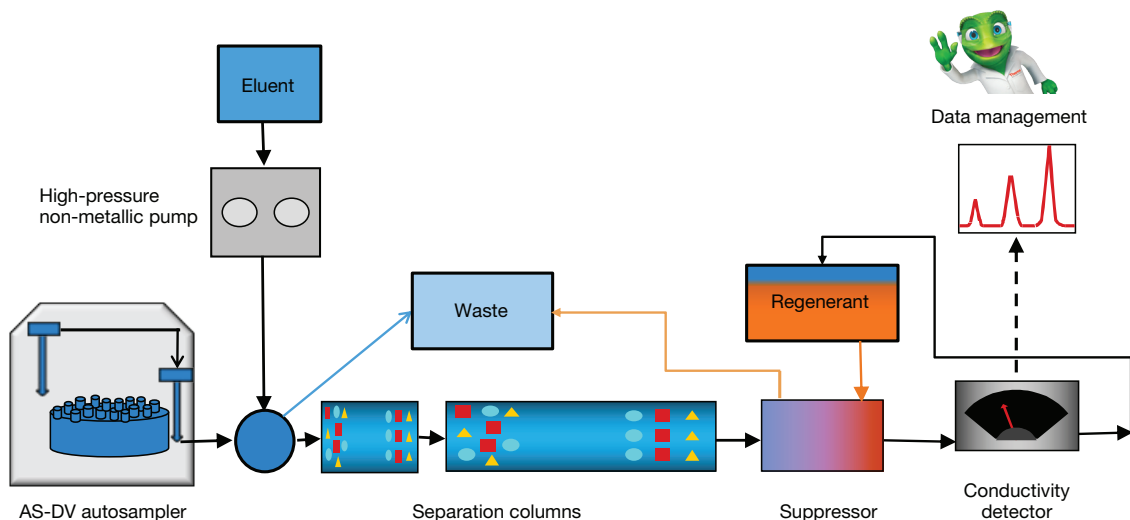


Figure 1. Illustration of an IC system in DCR mode.

Table 1. Consumables

Product name	P/N
Thermo Scientific™ Dionex™ DCR Installation Kit for 2 mm column	056882
Thermo Scientific™ Dionex™ CCRS 500 Chemically Regenerated Suppressor (2 mm)	085093
Thermo Scientific™ Dionex™ IonPac™ CS16 Guard Column (3 x 50 mm)	079931
Thermo Scientific™ Dionex™ IonPac™ CS16 Analytical Column (3 x 250 mm)	059596
Thermo Scientific™ Dionex™ Displacement Chemical Regeneration (DCR) Reagent, Cation regenerant concentrate (2.06 M tetrabutylammonium hydroxide)	057556
Thermo Scientific™ Dionex™ Cation Eluent Concentrate	057558
Thermo Scientific™ Dionex™ AS-DV Autosampler PolyVial (5 mL) with filter cap (20 µm), 250 pack	038141
Thermo Scientific™ Dionex™ Combined Six Cation Standard-II	046070

Experimental

All reagents (eluent, regeneration solution, and standard) were prepared with degassed deionized (DI) water with 18 MΩ-cm resistance or better.

Individual cation standard stock solutions (1000 mg/L) were prepared by dissolving its water-soluble salt (chloride, nitrate, or sulfate salt, A.C.S. reagent grade or better) in DI water. Aliquots of these standard were combined and

diluted with DI water to prepare mixed calibration standards (Table 2). The combined six cation standard stock can also be used.

A drinking water sample was collected locally. An environmental water sample was obtained from the local water district lab. No filtration was needed as filter caps were used on the Dionex AS-DV autosampler vials.

The chromatography conditions are listed in Figures 2 and 3.

Table 2. Calibration standards (mg/L)

Level	1	2	3	4	5	6	7	8	9	10
Lithium	0.01	0.05	0.25	0.5	1	6.25	12.5	25	-	-
Sodium	0.04	0.2	1	2	4	25	50	100	250	500
Ammonium	0.05	0.25	1.25	2.5	5	31.25	62.5	125	-	-
Magnesium	0.05	0.25	1.25	2.5	5	31.25	62.5	125	-	-
Potassium	0.1	0.5	2.5	5	10	62.5	125	250	-	-
Calcium	0.1	0.5	2.5	5	10	62.5	125	250	-	-

Results and discussion

Figure 2 shows a separation of common inorganic cations and ammonium within 25 min using the Dionex IonPac CS16 column. This method is the modification of the method in AN 141.⁴ As this figure shows, the six cations are well resolved. The Dionex IonPac CS16 column can be used for monitoring common inorganic cations and ammonium in water.

Figure 3 shows the determination of common inorganic cations and ammonium in a drinking water sample and a waste water sample. The results show that the drinking

water sample contains low level of sodium (20.3 mg/L), magnesium (2.4 mg/L), calcium (10.9 mg/L) with less than 1 mg/L of ammonium (0.8 mg/L), and potassium (0.7 mg/L). The waste water contains higher levels of sodium (146.0 mg/L), magnesium (28.3 mg/L), potassium (13.9 mg/L), and calcium (24.8 mg/L) with less than 1 mg/L of ammonium (0.4 mg/L). Both water samples are safe and meet the freshwater ammonia aquatic life ambient water quality criteria at both CCC (Criterion Continuous Concentration; less than 1.9 mg TAN/L 30-day average), and CMC (Criterion Maximum Concentration, less than 17 mg TAN/L 1-day average). TAN is total ammonia nitrogen.

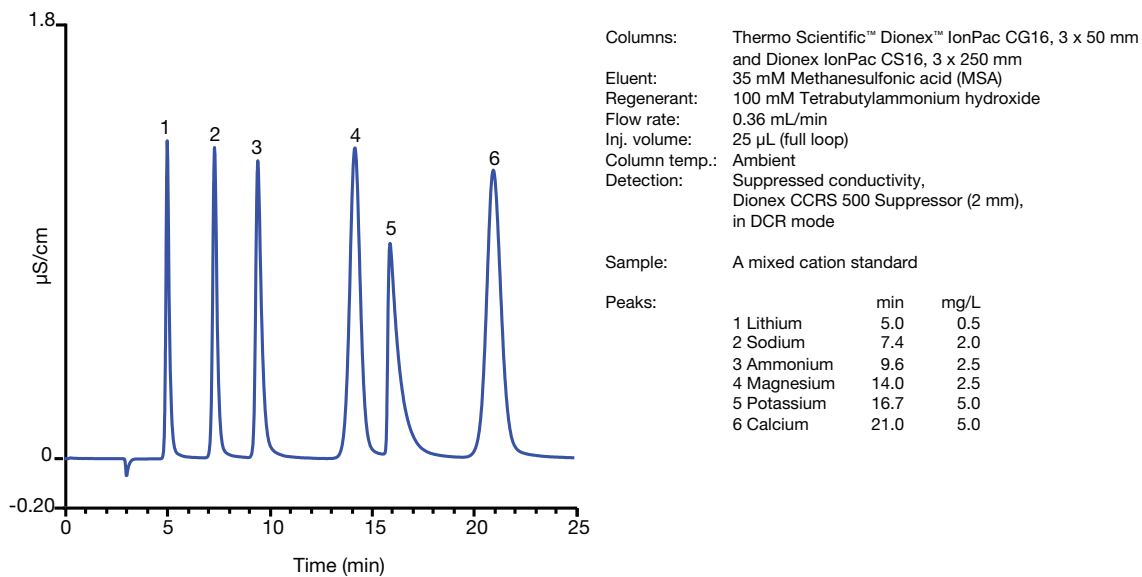


Figure 2. Separation of common inorganic cations and ammonium using a Dionex IonPac CS16 column set.

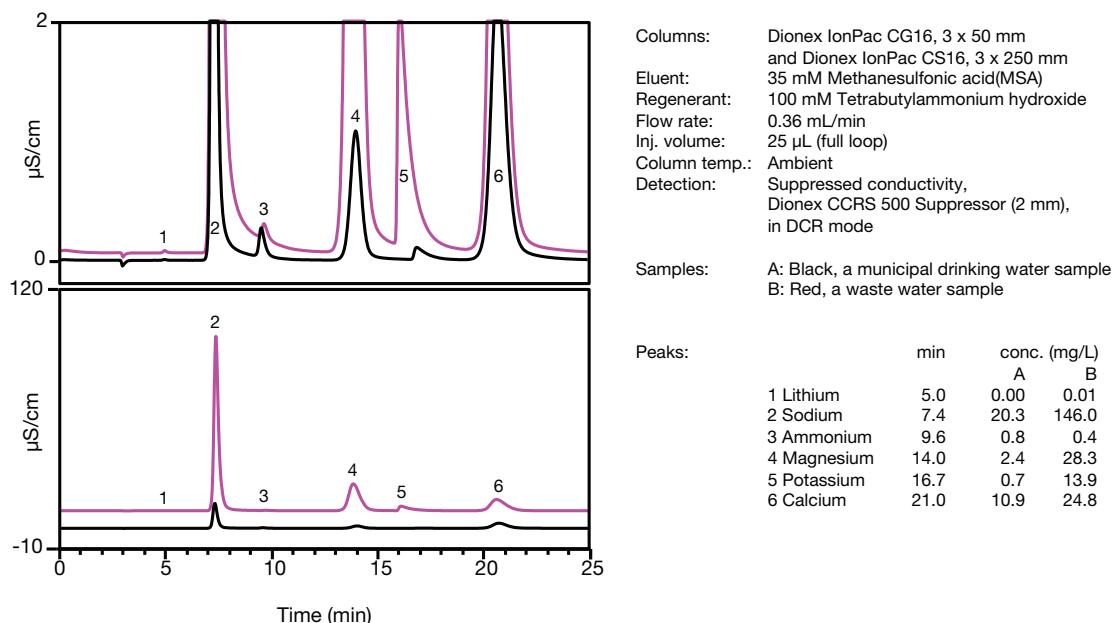


Figure 3. Analysis of a municipal drinking water and a waste water using the Dionex IonPac CS16 columns.

Linearity

Table 3. Linearity obtained using a Dionex IonPac CS16 column with a 25.0 µL injection

Analyte	Range (mg/L)	Coefficient of determination *(r ²)
Lithium	0.01-25	0.999
Sodium	0.04-500	0.999
Ammonium	0.05-125	0.997**
Magnesium	0.05-125	1.000
Potassium	0.1-250	1.000
Calcium	0.1-250	1.000

* Calibration type is linear and forced through the origin.

** Calibration type is quadratic and forced through the origin.

Table 3 shows the calibrations are linear for the common inorganic cations (lithium, sodium, magnesium, potassium and calcium) with r² from 0.999 to 1. The calibration of ammonium is not linear for the range of 0.05 to 125 mg/L, and thus it is better to use a quadratic calibration.

Conclusion

This work shows the determination of inorganic cations and ammonium in a drinking water and a waste water sample using the Dionex Easion IC system in DCR mode. The integrated Dionex Easion IC system coupled with the Dionex AS-DV autosampler provides a simple and low-cost instrument setup for routine determination of inorganic cations and ammonium in water samples.

References

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