

Fast Determinations of Inorganic Cations in Municipal Wastewater Using High-Pressure Capillary IC

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Key words

Environmental, Dionex IonPac CS16, cations, wastewater, HPIC, Dionex ICS-5000⁺, Capillary IC

Goal

Demonstrating the rapid separation and quantification of inorganic cations in municipal wastewater using high pressure capillary ion chromatography.

Introduction

Analysis of cations and anions are important to municipal drinking water and wastewater treatment plants for compliance monitoring. Cationic determinations are necessary as part of the water monitoring program's secondary water specification of acceptable taste. In municipal wastewater, cation determinations ensure that no environmental effects occur as a result of discharging high-salt concentrations into the water system.

High Pressure Capillary ion chromatography is the latest advancement in ion chromatography instrumentation. Typically with a Reagent Free™ ion chromatography (RFIC™) system, the system pressure is limited to < 3000 psi because of the limitations of materials in the RFIC accessories. Now with high pressure capabilities, the Thermo Scientific™ Dionex™ ICS-5000⁺ HPIC™ IC capillary system can operate continuously at 5000 psi system pressures. This advance in technology allows increased flow rates with all the same advantages as standard pressure capillary IC, faster analysis, and both lower consumption of water (30 to 40 mL/d of water) and low waste generation. In capillary IC, the system can remain on without any loss in resources, i.e., capillary IC is always on and ready for analysis. These advantages result in:

- Faster analysis, less calibration and equilibration
- Greater ease-of-use
- Longer eluent generator cartridge life
- Lower cost of ownership.



Additionally, with the increase in mass sensitivity, comparable results are achieved as with standard bore system using a sample injection of only 0.4 μL . In a previous study published in Application Brief 133, inorganic anions and cations were determined on a drinking water sample using standard pressure capillary IC.¹ In this study, inorganic cations in a municipal wastewater sample are separated by cation-exchange chromatography on a Thermo Scientific™ Dionex™ IonPac™ CS16 capillary IC column. This column, which was designed for separations of disparate concentrations of ammonium and sodium, was selected for these high pressure applications because of the column's high capacity and peak efficiency. In these experiments, the separations of inorganic cations using electrolytically-generated 30 mM methanesulfonic acid were compared at 10 and 30 $\mu\text{L}/\text{min}$. At 30 $\mu\text{L}/\text{min}$ flow rate conditions, the system backpressure approached 3700 psi which is well within the new high pressure tolerances while reducing the run time from 20 to 7 min. The analytes are detected by suppressed conductivity detection, using the Thermo Scientific™ Dionex™ CCES™ Cation Capillary Electrolytic Suppressor, specifically optimized for capillary IC.

Equipment

- Dionex High Pressure ICS-5000+ HPIC Reagent-Free capillary system
 - ICS-5000+ SP Single Pump module with high pressure capillary pumps
 - ICS-5000+ EG Eluent Generator module
 - ICS-5000+ DC Detector/Chromatography module with Thermo Scientific™ Dionex™ IC Cube™ and high pressure degas cartridge
 - Thermo Scientific Dionex AS-AP Autosampler
- Thermo Scientific™ Dionex™ Chromeleon™ Chromatography Data system (CDS)

* The Dionex ICS-5000 capillary IC system can also be used if it has been configured to operate at 5000 psi. Capillary systems shipped prior to February 2011 may need to be upgraded to operate at 5000 psi.

Reagents and Standards

- 18 M Ω -cm degassed deionized water
- Thermo Scientific Dionex Combined Six Cation II Standard (Dionex P/N 046070)

Samples

Municipal wastewater samples, influent and effluent

Conditions

Columns:	Dionex IonPac CS16, 0.5 × 250 mm
Eluent Source:	Thermo Scientific Dionex EGC-MSA capillary cartridge with Thermo Scientific Dionex CR-CTC Continuously Regenerated Cation Trap Column
Eluent:	30 mM MSA
Flow Rate:	A: 10 μ L/min B: 30 μ L/min
IC Cube Temp.:*	40 °C
Compartment Temp.:	15 °C
Inj. Volume:	0.4 μ L
Detection:	Suppressed conductivity, Thermo Scientific Dionex CCES 300, recycle mode; A: 8 mA; B: 13 mA
Background Conductance:	0.3–0.8 μ S conductance
Noise:	< 0.3 nS
System Backpressure:	A: 1250 psi; B: 3720 psi

* The Dionex IC Cube heater controls the separation temperature by controlling the column cartridge temperature. The original term of “column temperature” refers to the temperature in the bottom DC compartment which is not used for capillary IC.

The part numbers of the consumables for this method are shown in Table 1.

Table 1. Consumables list.

Product name	Type, Capillary	Dionex Part Number
Dionex EGC-MSA	Eluent Generator cartridge	072077
Dionex CR-CTC	Electrolytic trap column	072079
Dionex IonPac CS16	Separation column	075401
Dionex CRD Bypass cartridge	Bypass (needed for flow path)	072055
Dionex CCES	Suppressor	072053
Dionex HP fittings (blue)	Bolts / Ferrules	074449 / 074373
EG Degas HP cartridge	High pressure degas cartridge, up to 5000 psi	074459
Dionex AS-AP autosampler vials	Package of 100, 10 mL, polystyrene vials, caps, blue septa	074228

Standard and Sample Preparation

The Dionex Six Cation II Standard was diluted appropriately for calibration. The municipal wastewater samples were diluted 1:50 with deionized water to minimize any unknown matrix effects, and filtered with a 0.45 μ m, IC syringe filter to remove particulates prior to analysis.

Tip: It is important to use 18 M Ω -cm resistivity, deionized water for standards, eluent, and autosampler flush solution. It is recommended to degas the deionized water intended for eluent. (An appropriate degassing method is vacuum filtration.) Using deionized water with resistivity less than 18 M Ω -cm can reduce sensitivity, introduce contamination, and affect calibration, thereby resulting in inaccurate quantification. Results can vary and contamination introduced from samples can affect the chromatography.

Instrument Setup and Installation

Tip: To achieve the best chromatography with capillary IC, it is important to minimize void volumes between connections by using precision cut tubing, high pressure connectors and fittings (colored blue), and by seating the ferrule >2 mm above the end of the tubing. These tips are thoroughly discussed in “Technical Note 113: Practical Guidance for Using Capillary Anion Chromatography”.² Extra care should be used to prevent introducing air into any of the consumables or tubing by observing a steady liquid flow before installing the next device in line. The high pressure Dionex ICS-5000+ HPIC capillary IC system is designed to operate continuously up to 5000 psi which results in very low noise and increased pump stability. To setup this application, plumb the consumables and modules of the Dionex ICS-5000+ HPIC system, according to Figure 1.

Dionex ICS-5000* HPIC Capillary System

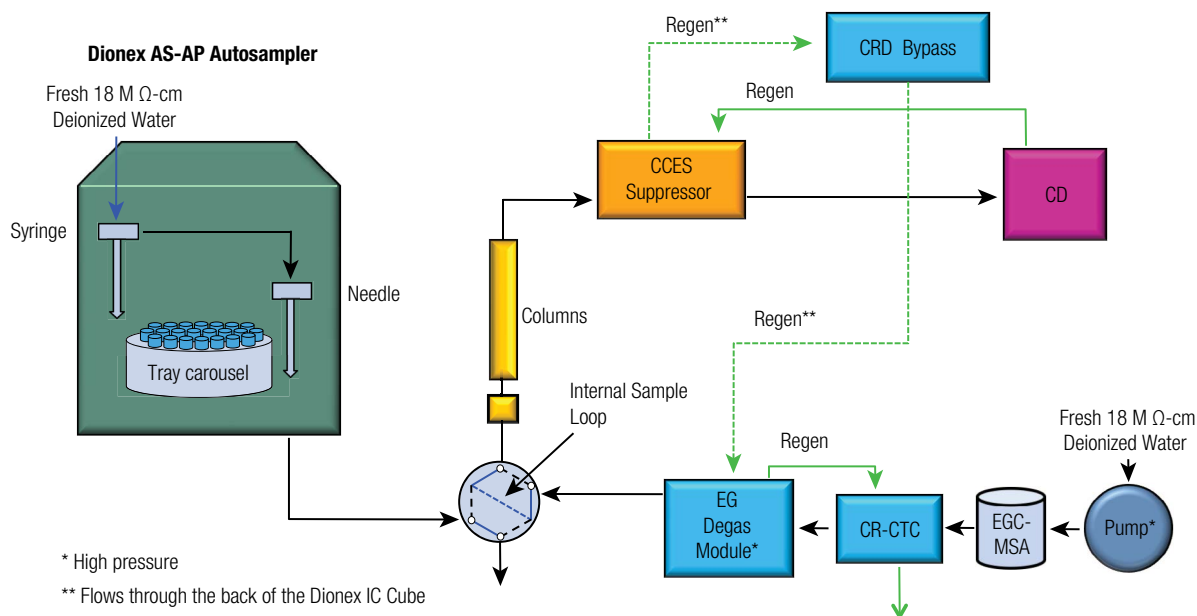


Figure 1. Flow diagram.

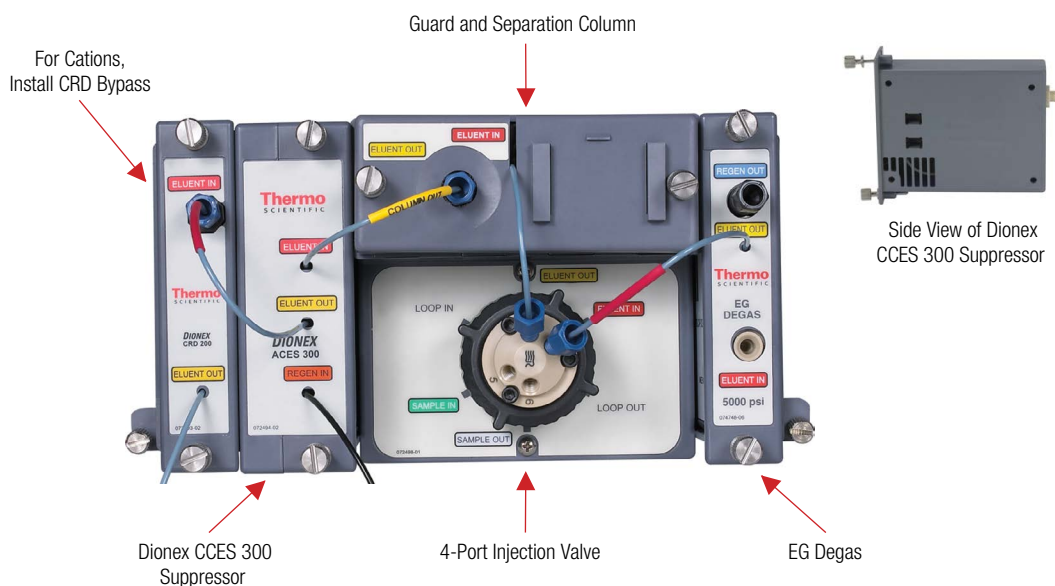


Figure 2. Dionex IC Cube.

Install and hydrate the Dionex EGC-MSA capillary cartridge and Dionex CR-CTC trap. Install the EG Degas cartridge, Dionex CRD Bypass cartridge and the Dionex CCES Cation Capillary Electrolytic Suppressor capillary devices into the Dionex IC Cube (Figure 2). Hydrate the devices according to the product manuals and Section 3.18 of the Dionex ICS-5000 installation manual.²⁻⁶ Install the columns and complete the configuration according to Figure 1. Detailed instructions are described in Technical Note 131, the product manuals, and the instrument installation and operator's manuals.²⁻⁶

Results and Discussion

Due to its toxicity, ammonium is monitored in wastewater effluent as part of the discharge permit requirements.

Additionally as wastewater samples have high concentrations of sodium, it is often important to separate disparate lower concentrations of ammonium in a higher sodium sample matrix. As the high capacity Dionex IonPac CS16 cation exchange column is optimized for disparate concentrations of sodium and ammonium, it was selected for this application. To quantitate the analyte concentrations, we determined the peak area response to concentration by calibrating with duplicate injections of the 50-, 100-, and 200-fold diluted Dionex Combined Six Cation II Standard. A linear regression curve was used for the lithium, sodium, potassium, magnesium, and calcium peaks, resulting in linear coefficients of $r^2 > 0.999$. The ammonium peak response exhibited the typical quadratic relationship with concentration.

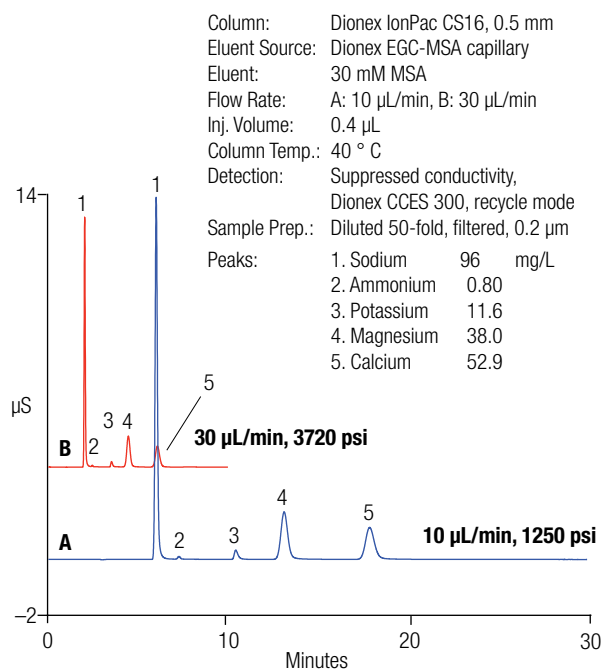


Figure 3. Fast, high-pressure cation separations in a wastewater sample using high-pressure capillary IC.

Figure 3 shows the separations of five cations in a 50-fold diluted, filtered effluent wastewater sample at the standard flow rate of 10 $\mu\text{L}/\text{min}$ and at 3 \times the flow rate (30 $\mu\text{L}/\text{min}$). Chromatogram B shows baseline resolution of all five cations present (sodium, ammonium, potassium, magnesium, and calcium) in less than 7 min. This example demonstrates the high resolving power and high capacity of this column making the small ammonium peak (Peak 2, 0.8 mg/L) easily quantifiable and baseline resolved from the 250 \times larger sodium peak.

Conclusion

This application demonstrates the advantages of high pressure capillary IC using the high capacity Dionex IonPac CS16 capillary cation-exchange column to provide high sample throughput by simply increasing the flow rate on a high pressure capable Dionex ICS-5000⁺ HPIC capillary IC, saving time and money.

For other inorganic cations determinations using capillary IC separations at standard flow rates, review Application Briefs AB 141, AB 133, and Environmental Capillary IC Applications in the Dionex Capillary IC Library website.^{1,7,8} Inorganic cation determinations in environmental water samples using standard bore and microbore size columns IC are thoroughly discussed in AN 141.⁹

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