Fast Determinations of Inorganic Cations in Influent and Effluent Wastewater Samples Using High-Pressure IC

Terri Christison and Linda Lopez
Sunnyvale, CA, USA

Technical Note 117

Introduction

Determination of anions and cations in wastewater samples are important to municipal agencies to ensure water cleanliness and public health safety. Incoming wastewater (influent) is monitored to assess the conditions of the feed water. Similarly, outgoing (effluent) wastewater is monitored prior to discharging into the water system to prevent any adverse environmental effects and comply with discharge permits. High-pressure Reagent-Free™ ion chromatography (RFIC™) systems, the latest advancement in IC instrumentation, can operate continuously at 5000 psi for both analytical and capillary scale, allowing faster separations while maintaining nearly baseline resolved peaks. Flow rates can be increased well above the standard flow rates, resulting in increased sample throughput while saving time and money.

In this study, inorganic cations in influent and effluent municipal wastewater samples are separated in 3.5 min by cation-exchange chromatography using a Thermo Scientific™ Dionex™ IonPac™ CS12A-5µm column, using an electrolytically generated eluent flowing at 0.75 mL/min and suppressed conductivity detection. This fast separation was enabled on a high-pressure Reagent-Free Thermo Scientific™ Dionex™ ICS-5000$^+$ HPIC™ system.

Equipment

Dionex ICS-5000$^+$ HPIC system

- SP/DP Pump module
- EG Eluent Generator module with high pressure degas module
- DC Detector/Chromatography module
- Thermo Scientific Dionex AS-AP Autosampler
- Thermo Scientific™ Dionex™ Chromeleon™ Chromatography Data System (CDS) software, ver. 6.8 or 7.1

Reagents and Standards

18.2 MΩ-cm degassed deionized water

Thermo Scientific Dionex Combined Six Cation II Standard (Dionex P/N 046070)

Conditions

Columns:	Dionex IonPac CG12A-5µm, 3 × 30 mm
	Dionex IonPac CS12A-5µm, 3 × 150 mm
Eluent Source:	Thermo Scientific Dionex EGC 500 MSA cartridge with high-pressure Thermo Scientific Dionex CR-CTC 500 trap column
Eluent:	30 mM MSA
Flow Rate:	A: 0.25, 0.50, 0.75 mL/min for flow rate experiments B: 0.75 mL/min for samples
Column Temp.:	30 °C
Inj. Volume:	25 µL
Detection:	Suppressed conductivity, Thermo Scientific™ Dionex™ CSRS™ 300 suppressor, recycle mode, 44 mA
Background Conductance:	0.6–0.8 µS
Noise:	2–3 nS
System backpressure:	2000*–3100 psi

* Backpressure tubing was added prior to the injection valve for those conditions running below < 2000 psi to bring the total system pressure above 2000 psi needed for the Dionex EGC 500 cartridge.

Thermo SCIENTIFIC

Table 1. Consumables.

Product name	Type	Dionex Part Number
Dionex EGC 500 MSA	Cation Eluent Generator cartridge	075779*
Dionex CR-CTC 500	Cation electrolytic trap column	075551*
Dionex IonPac CG12A-5µm	Cation guard column, 3 × 30 mm	057184
Dionex IonPac CS12A-5µm	Cation separation column, 3 ×150 mm	057185
Dionex CSRS 300	Cation suppressor	064557*
Dionex HP Degas Module	High pressure analytical Degas module	075522*
Dionex HP fittings (blue)	Bolts / Ferrules	074449 / 074373*

* High pressure device.

Standard and Sample Preparation

The Dionex Six Cation II Standard was diluted 500-fold with deionized water for the flow rate experiments and diluted appropriately for calibration. The municipal wastewater samples were diluted 1:5 with deionized water to minimize any unknown matrix effects, and filtered with a 0.45 µm IC syringe filter to remove particulates prior to analysis.

Instrument Setup and Installation

Tip: To achieve the best chromatography with high-pressure IC, it is important to use high-pressure connectors and ferrules (see Table 1) for all connections prior to the suppressor. The high-pressure Reagent-Free Dionex ICS-5000⁺ HPIC system is designed to operate from 2000 to 5000 psi. To set up this application, plumb the consumables and modules of the Dionex ICS-5000⁺ HPIC system, according to Figure 1.

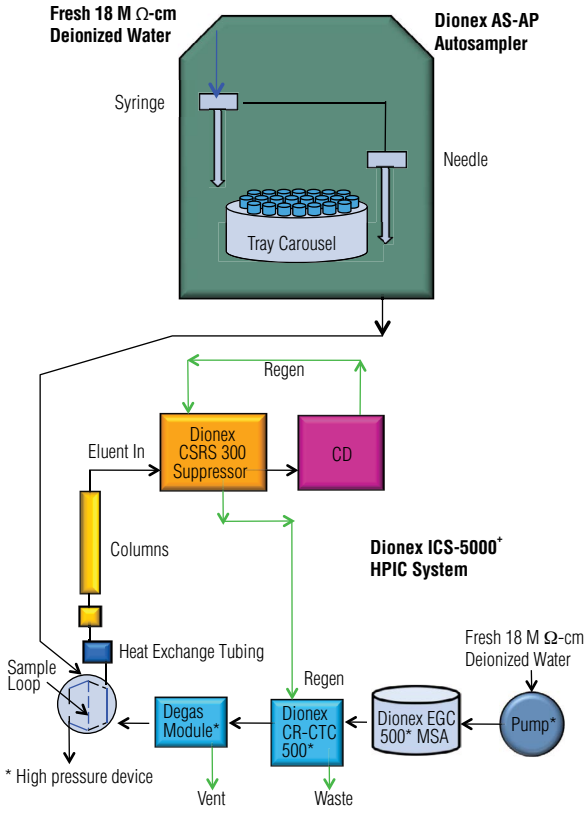

Figure 1. Flow diagram for the high-pressure, Reagent-Free Dionex ICS-5000⁺ HPIC system. (Similar to Figure 1 in TN 129)

Install and hydrate the Dionex EGC 500 MSA cartridge, Dionex CR-CTC 500, electrolytic trap column, and Dionex CSRS 300 suppressor according to the product manual instructions. Complete the installation according to flow diagram. Use high-pressure connectors and ferrules (blue) for all of the fittings from the pump to prior to the suppressor. Standard pressure fittings can be used for the suppressor and detector connections. Detailed instructions are described in Technical Note 129, the product manuals, and the instrument installation and operator's manuals.[1–4]

Results and Discussion

In Figure 2 the separations of a diluted six cation standard are compared at three flow rates, 0.25, 5.0, and 0.75 mL/min. These chromatograms demonstrate the short run times possible while obtaining nearly baseline resolution of all peaks. Run time was reduced from 9 min at the standard flow rate of 0.25 mL/min to 3.5 min at 0.75 mL/min, causing system backpressures to increase from 1100 psi to 3100 psi.

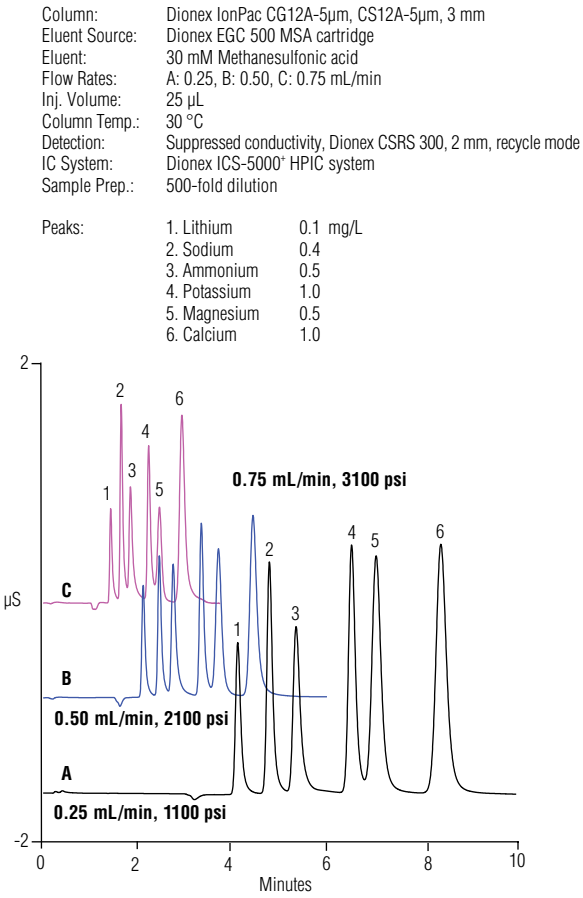

Figure 2. Fast Separations of a Six Cation Standard Using High Pressure IC.

(The total backpressure was always maintained above 2000 psi by installing backpressure tubing as needed.) While this system backpressure is marginally above the previously operating limitations of 3000 psi for an RFIC system, these conditions and short run times are only possible with high pressure capabilities of the Dionex ICS-5000⁺ HPIC system. Using this fast separation, sample throughput is three times the previous sample throughput.

The linearity of peak area response with concentrations was determined by duplicate injections of the 10-, 20-, 50-, 100-, and 500-fold diluted Dionex Combined Six Cation II Standard. Using a linear regression curve resulted in linear coefficients of $r^2 > 0.9999$. Ammonium peak response exhibited the typical quadratic relationship with concentration.

Column:	Dionex IonPac CG12A-5µm, CS12A-5µm, 3 mm		
Eluent Source:	Dionex EGC 500 MSA cartridge		
Eluent:	30 mM Methanesulfonic acid		
Flow Rates:	0.75 mL/min		
Inj. Volume:	25 µL		
Column Temp.:	30 °C		
Detection:	Suppressed conductivity Dionex CSRS 300, 2 mm, recycle mode		
IC System:	Dionex ICS-5000⁺ HPIC system		
Sample Prep.:	5-fold dilution, filtered, 0.45 µm		
Samples:	Municipal wastewater A: Influent (Incoming) B: Effluent (Outgoing)		
		A	B
Peaks:	1. Sodium	36.1	25.7 mg/L
	2. Ammonium	8.6	--
	3. Potassium	2.5	1.2
	4. Magnesium	14.7	9.1
	5. Calcium	22.4	11.5

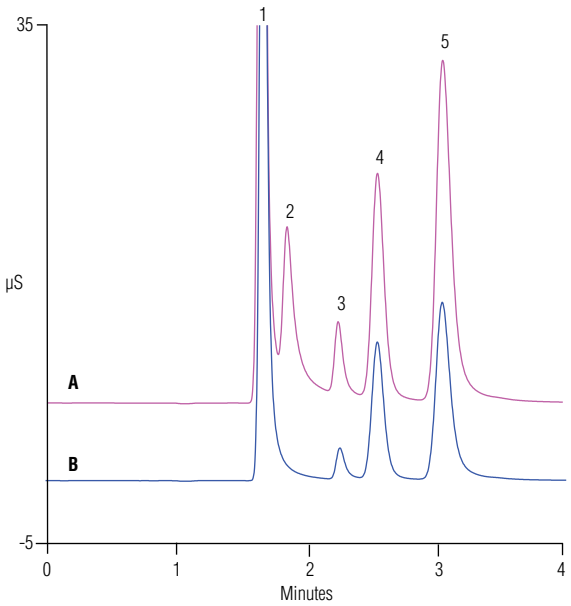

Figure 3. Fast Separations of A) Influent and B) Effluent Wastewater Samples Using High Pressure IC.

Figure 3 shows the 3.5 min separations of five cations in 5-fold diluted, filtered influent and effluent wastewater samples. As expected, the influent sample had higher concentrations of analytes than the effluent sample. Additionally, ammonium was only present in the influent sample, indicating that the treatment process removed the environmentally damaging ammonium prior to discharging the effluent.

Conclusion

This application demonstrates the advantages of high-pressure RFIC systems using a microbore format column to provide high sample throughput by simply increasing the flow rate on a high-pressure Dionex ICS-5000⁺ HPIC system, thereby saving time and money.

Additional information on inorganic cations determinations in environmental water samples using standard bore and microbore IC is reviewed in application note AN 141.[5] High pressure separations by capillary IC are discussed in application brief AB 141 and Environmental Capillary IC Applications at the Dionex Capillary IC Library website.[6,7]

References

1. Christison, T.; Bahten, K.; Briggs, J.; Lopez, L. Technical Note 129: *Configuring High-Pressure IC Systems for Analytical Flow Rates*, TN70317_E, Sunnyvale, CA, 2012.
2. Thermo Fisher Scientific. *Dionex Anion Self-Regenerating Suppressor 300 and Cation Self-Regenerating Suppressor 300 Product Manual*. Dionex Doc No. 031956-06, Sunnyvale, CA, 2009.
3. Thermo Fisher Scientific. Dionex ICS-5000⁺ *Ion Chromatography System Installation Instructions*. Dionex Doc No. 065447-01, Sunnyvale, CA, 2012.
4. Thermo Fisher Scientific. *Dionex AS-AP Autosampler Operator's Manual*. Dionex Doc No. 065361-07, Sunnyvale, CA, 2012.
5. Thermo Fisher Scientific. Dionex AN141: *Determination of Inorganic Cations and Ammonium in Environmental Waters By Ion Chromatography Using the IonPac CS16 Column*, Dionex LPN 1404, Sunnyvale, CA, 2001.
6. Pang, F.; Christison, T.; Jack, R.; Lopez, L. Application Brief 141: *Fast Determination of Inorganic Anions in Municipal Drinking Water Using Capillary Ion Chromatography*, Dionex LPN 3059, Thermo Fisher Scientific, Sunnyvale, CA, 2012.
7. Thermo Fisher Scientific. Environmental Capillary IC Applications in the Capillary IC Library, Dionex website, 2012.

Australia +61 3 9757 4486
Austria +43 1 333 50 34 0
Belgium +32 53 73 42 41
Brazil +55 11 3731 5140
China +852 2428 3282
Denmark +45 70 23 62 60
France +33 1 60 92 48 00
Germany +49 6126 991 0
India +91 22 2764 2735
Italy +39 02 51 62 1267
Japan +81 6 6885 1213
Korea +82 2 3420 8600
Netherlands +31 76 579 55 55
Singapore +65 6289 1190
Sweden +46 8 473 3380
Switzerland +41 62 205 9966
Taiwan +886 2 8751 6655
UK/Ireland +44 1442 233555
USA and Canada +847 295 7500

Thermo SCIENTIFIC
Part of Thermo Fisher Scientific

TN70141_E 01/13S