Determination of Inorganic Anions in Acid Rain Using a High-Pressure Modular Capillary Ion Chromatography System

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Technical Note 123

Key Words
Environmental water analysis, Fast IC, High resolution, Small particle column, HPIC, Cap IC

Goal

Demonstrate fast separations of inorganic anions in acid rain by increasing flow rates using high-pressure capillary IC.

Introduction

Acid rain is a global problem due to its adverse impact on plants, aquatic animals, infrastructures, and human health. It is primarily produced by the reaction of water in the atmosphere with SO_2 and NO_x released from natural occurrences including volcanic eruptions and lightning strikes. Some human activities, such as burning coal in power plants and exhaust from motor vehicles can also contribute to the contamination of SO_2 and NO_x in the air. Because of widespread deterioration of the environment caused by acid rain, many countries have regulations to enforce the reduction of SO_2 and NO_x released to the air. In the U.S., Congress passed a series of amendments to the Clean Air Act in 1989, establishing the Acid Rain Program to control emissions of SO_2 and NO_x.[1] The monitoring of air and rain has become an important task worldwide for investigating the effects of pollutants on global ecology and assessing the progress of pollution control measures.[2]

Ion chromatography (IC) is a well-established technique for the analysis of inorganic anions in acid rain.[3,4,5] This Technical Note describes the determination of inorganic anions in rainwater samples using a Thermo Scientific™ Dionex™ ICS-5000⁺ capillary HPIC™ (High-Pressure Ion Chromatography) system, which can be operated continuously at up to 5000 psi. This high-pressure capability, combined with a 4 µm particle ion-exchange column, such as the Thermo Scientific™ Dionex™ IonPac™ AS18-4µm anion-exchange column, achieves both high sample throughput (when many samples need to be analyzed) and excellent resolution simply by increasing the flow rate. Scaling down from standard bore to capillary scale brings many benefits to IC users.

One of the most important values is that the system can always be on and ready for analysis because of its low consumption of eluent (15 mL/day of water at 0.010 mL/min). The amount of waste generated is significantly decreased and the Eluent Generation Cartridge (EGC) lasts up to 18 months under normal continuous operation, which translates into reduced overall cost of ownership.

Equipment

- Dionex ICS-5000⁺ HPIC high-pressure capillary IC system
- Dionex ICS-5000⁺ DC Detector/Chromatography module with high pressure degas cartridge
- Thermo Scientific™ Dionex™ IC Cube™
- Dionex ICS-5000⁺ DP Dual Pump module with high-pressure capillary pumps
- Dionex ICS-5000⁺ EG Eluent Generator module
- Thermo Scientific Dionex AS-AP Autosampler
- Thermo Scientific™ Dionex™ Chromeleon™ Chromatography Data System (CDS) software, version 7.1 or higher

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Reagents and Standards

18 M -cm resistivity degassed deionized water and Ultra Scientific 1000 mg/L Certified IC Standard stock solutions

Samples

Rain samples were collected at Sunnyvale, CA and Campbell, CA

Conditions	
Columns:	Dionex IonPac AG18-4µm, 0.4 × 50 mm Dionex IonPac AS18-4µm, 0.4 × 150 mm
Eluent Source:	Thermo Scientific Dionex EGC-KOH Cartridge (Capillary)
Eluent:	23 mM KOH
Flow Rate:	A: 0.010, 0.020, and 0.025 mL/min for standard solutions B: 0.025 mL/min for samples
Column Temp.:	30 °C*
Inj. Volume:	0.4 µL
Detection:	Suppressed conductivity, Thermo Scientific™ Dionex™ ACES™ 300 Anion Capillary Electrolytic Suppressor, recycle mode, 9 mA (0.015 mL/min); 10 mA (0.02 mL/min) 13 mA (0.025 mL/min)
Background Conductance:	1–2 µS
Noise:	2–3 nS
System backpressure:	1600 psi (0.010 mL/min) 3100 psi (0.020 mL/min) 3800 psi (0.025 mL/min)

*The temperature of the capillary column is specified by setting the temperature of the Dionex IC Cube because the capillary column is installed in the Dionex IC Cube, not in the bottom column compartment, which used for analytical scale columns.

Part numbers of the consumables used in this document are listed in Table 1.

Standard and Sample Preparation

Mixed standard was prepared by diluting 1000 mg/L stock solutions with 18 M -cm resistivity degassed deionized water. The rain samples were filtered with a 0.20 µm IC syringe filter to remove particulates prior to injection.

It is important to use 18 M -cm resistivity, deionized water for standard, eluent, and autosampler flush solutions to avoid system contamination, decreased sensitivity, and poor calibration. Degassing the deionized water by vacuum filtration prior to use is a good practice.

Table 1. Consumables list.

Product Name	Description, Capillary	Dionex Part Number
Thermo Scientific Dionex EGC-KOH Cartridge (Capillary)	Eluent generator cartridge	072076
Thermo Scientific Dionex CR-ATC Continuously Regenerated Anion Trap Column (Capillary)	Electrolytic capillary trap column	072078
Dionex IonPac AS18-4µm	Separation column	082314
Dionex IonPac AG18-4µm	Guard column	076033
Thermo Scientific Dionex CRD Bypass	Used in place of the Dionex CRD 180 or Dionex CRD 200 Carbonate Removal Device. Necessary for the flow path.	072054
Dionex CRD 180 Carbonate Removal Device	Carbonate removal cartridge for 4 µm capillary columns.	079960
Dionex ACES 300	Suppressor cartridge	072052
Dionex HP Fittings (Blue)	Bolts/Ferrules	074449/074373
Capillary EG Degas	High-pressure degas cartridge, up to 5000 psi	AAA-074459
Dionex IonPac ATC-500 Trap Column	2 mm trap column between pump and EGC cartridge with black PEEK™ tubing	085359
Dionex AS-AP AutoSampler Vials	Package of 100, polystyrene vials, caps, blue septa	074228

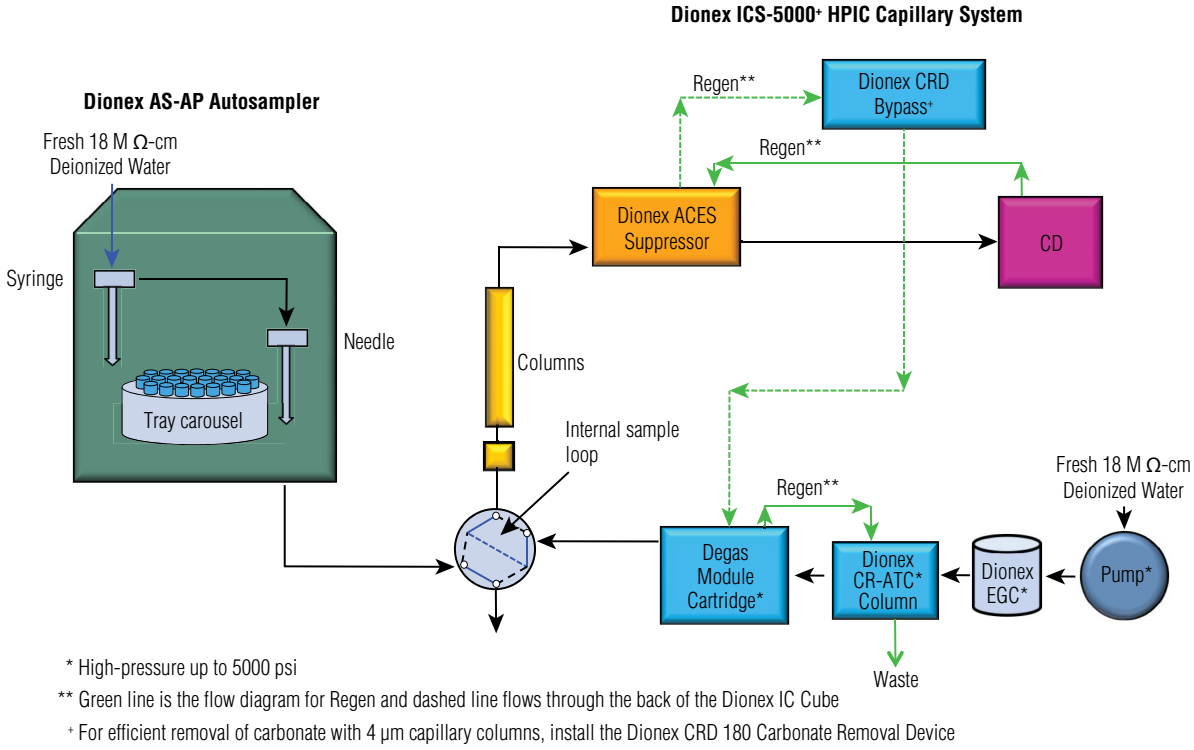

Figure 1. Flow diagram.

Instrument Setup and Installation

To achieve the best chromatography with capillary IC, it is important to minimize void volumes in each connection by using precision cut tubing, high-pressure connectors and fittings (blue color), and seating the ferrule > 2 mm above the end of the tubing. Extra care should be used to prevent air in all consumables or tubing by observing steady liquid flow before installing the next device in line. A thorough discussion can be found in "Technical Note 113 Practical Guidance for Capillary IC".[6]

Figure 1 shows the flow diagram of this application. The Dionex IonPac ATC-500 trap column is installed between the pump and the Dionex EGC KOH cartridge. Install the trap column to the pump using the black PEEK tubing (P/N 078497). Temporarily route the free end of the tubing to waste during the following flush step. To flush the trap column, first initiate the priming function on the pump (1 mL/min), point the Dionex IonPac ATC-500 column upward, and flush for 30 min to allow air to escape. After 30 min, turn off the the pump prime, and connect the tubing to the Dionex EGC KOH cartridge. The Dionex EG Degas, Dionex CRD Bypass, and Dionex ACES suppressor cartridges and both columns are all installed in the Dionex IC Cube (Figure 2). Prior to use, the Dionex ACES suppressor and Dionex CR-ATC trap column should be hydrated, and the Dionex EGC cartridge and Dionex IonPac columns should be

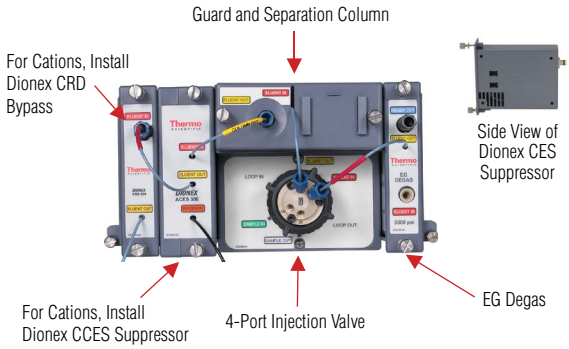

Figure 2. Dionex IC Cube.

conditioned. The Dionex CRD Bypass cartridge does not require hydrating. For efficient carbonate removal when using 4 µm columns, install and hydrate a Dionex CRD 180 Carbonate Removal Device cartridge. When the CRD 180 cartridge is installed, the eluent flow path runs from the suppressor to the Dionex CRD 180, and then the detector. The regenerant flow path runs from the detector to the suppressor, then to the Dionex CRD 180 cartridige and bypass. The instructions can be found in the section 3.18 of the Dionex ICS-5000+ installation manual.[7] Detailed instructions are also described in Technical Note 131, the product manuals, and the instrument installation and operator's manuals.[7–11]

Results and Discussion

As shown in Figure 3, the separation of seven inorganic anions can be shortened to less than 3 minutes when the flow rate is increased from 0.010 to 0.025 mL/min. At this higher flow rate, the backpressure of the system was about 3800 psi, which is well below 5000 psi, the operational limit of Dionex HPIC systems. With Dionex IonPac AS18-4µm column, fast analysis was achieved without compromising peak pair resolution. This new generation column utilizes 4 µm particle columns, resulting in both high capacity and efficiency, which are desired for fast analysis of environmental water samples.

Column:	Dionex IonPac AG18-4µm, Dionex IonPac AS18-4µm, 0.4 × 150 mm
Eluent Source:	Dionex EGC-KOH Cartridge
Eluent:	23 mM KOH
Flow Rate:	A: 0.010, B: 0.015, C: 0.020, D: 0.025 mL/min
Inj. Volume:	0.4 µL
Column Temp.:	30 °C
Detection:	Suppressed conductivity, Dionex ACES 300 Anion Capillary Electrolytic Suppressor, recycle mode
Sample:	Standard solution

Peaks:		
	1. Fluoride	0.1 mg/L
	2. Chlorite	1.0
	3. Chloride	0.6
	4. Nitrite	1.0
	5. Carbonate	—
	6. Bromide	2.0
	7. Sulfate	2.0
	8. Nitrate	2.0
	9. Chlorate	2.0

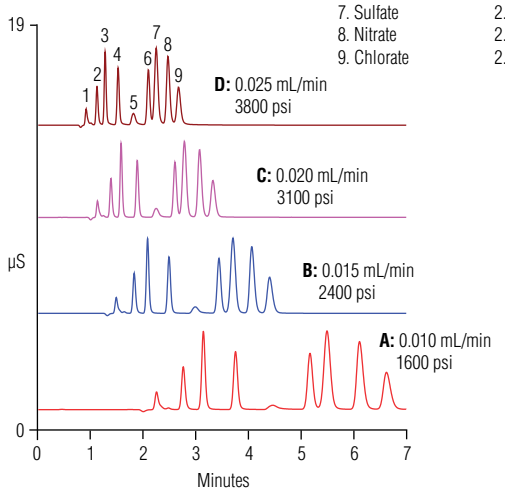

Figure 3. Fast determination of inorganic anions using the Dionex IonPac AS18-4µm column.

Figure 4 demonstrates inorganic anion analysis in two rainwater samples at a flow rate of 0.025 mL/min. Chloride, sulfate, and nitrate were found in both samples from 0.11 to 5.4 mg/L. The rain water sample collected in Sunnyvale, CA had higher concentrations of chloride (1.37 mg/L) while the Campbell, CA rain water sample had higher sulfate (5.4 mg/L). Small amounts of nitrate (0.035 mg/L and 0.01 mg/L) were also detected in both samples.

Column:	Dionex IonPac AG18-4µm, Dionex IonPac AS18-4µm, 0.4 × 150 mm
Eluent Source:	Dionex EGC-KOH
Eluent:	23 mM KOH
Flow Rate:	0.025 mL/min
Inj. Volume:	0.4 µL
Column Temp.:	30 °C
Detection:	Suppressed conductivity, Dionex ACES 300 Anion Capillary Electrolytic Suppressor, recycle mode
Samples:	A: Rainwater of Campbell, CA B: Rainwater of Sunnyvale, CA

Peaks:		A	B	
	1. Chloride	0.84	1.37	mg/L
	2. Nitrite	0.035	0.01	
	3. Carbonate	—	—	
	4. Sulfate	5.4	1.56	
	5. Nitrate	0.67	0.11	

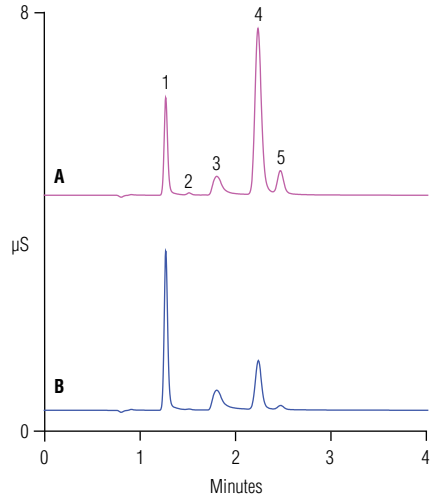

Figure 4. Determination of inorganic anions in rain samples using the Dionex IonPac AS18-4µm column.

Conclusion

This technical note demonstrates that the newly introduced high-pressure Dionex ICS-5000+ HPIC capillary IC system provides a solution to high throughput sample analysis. The high-pressure capability facilitates fast analysis using higher flow rates. Combined with the benefits of Dionex IonPac AS18-4µm column, good resolution is achieved while the analysis time is shortened.

References

1. Acid Rain, U.S. Environmental Protection Agency (EPA), http://www.epa.gov/airmarkets/progsregs/arp/nox.html
2. Thermo Fisher Scientific. Application Note 2, AN 2, *Determination of Nitrate and Sulfate Collected on Air Filters*, LPN 034635. Sunnyvale, CA, 2003.
3. Thermo Fisher Scientific. Application Note 154, AU 154, *Determination of Inorganic Anions in Environmental Waters Using a Hydroxide-Selective Column*, LPN 1539, Sunnyvale, CA, 2003.
4. Thermo Fisher Scientific. Application Note 31, AN 31, *Determination of Anions in Acid Rain by Ion Chromatography*, LPN 032133, Sunnyvale, CA, 1992.
5. Thermo Fisher Scientific. Application Update 146, AU 146, *Determination of Anions in Acid Rain by Ion Chromatography*, LPN 1541, Sunnyvale, CA, 2003.
6. Thermo Fisher Scientific. Technical Note 113, TN 113, *Practical Guidance for Using Capillary Anion Chromatography*, LPN 3043, Sunnyvale, CA, 2012.
7. Thermo Fisher Scientific. Dionex ICS-5000+ Installation Manual, Doc No. 065447, Sunnyvale, CA, 2012.
8. Thermo Fisher Scientific. Technical Note 131, TN 131, *Configuring High-Pressure Capillary IC on the Modular IC System*, Document No. TN70352_E 12/12S, Sunnyvale, CA, 2013.
9. Thermo Fisher Scientific. Product Manual for the Continuously Regenerated Trap Column (CR-TC), Doc No. 031910, Sunnyvale, CA, 2010.
10. Thermo Fisher Scientific. Product Manual for CES 300 Suppressors, Doc No. 065386, Sunnyvale, CA, 2010.
11. Thermo Fisher Scientific. Dionex AS-AP Operator's Manual, Doc No. 065361, Sunnyvale, CA, 2012.

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