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

Terri Christison and Linda Lopez
Thermo Fisher Scientific, Sunnyvale, CA, USA

Technical Note 124

Key Words
Environmental water analysis, Fast IC, Dionex IonPac AS18-4µm, ICS-4000, HPIC, Acid rain, Capillary IC

Goal
Demonstrate fast separations of inorganic anions in an acid rain sample using high pressure capillary IC on a Dedicated Capillary IC system.

Introduction
Acid rain is closely monitored by many countries due to its negative effects on plants, aquatic animals, human health and infrastructures. The cause of acid rain is related to the reaction of water in the atmosphere with sulfur dioxide (SO_2) and nitrous oxides (NO_x) released from natural phenomena, such as volcanic eruption and lightning strikes. Some human activities, for example, coal power plants and motor vehicles, contribute to the level of SO_2 and NO_x in the air as well. With the growth of population and industry, the problem of acid rain has drawn greater attention in many regions of the United States, Europe, Canada, Japan, and China. In the U.S., Congress passed Clean Air Amendments in 1990, establishing the Acid Rain Program to limit the power plant emissions of SO_2 and NO_x.[1] Air and rain monitoring has become an important task worldwide for investigating the effects of pollutants on the global ecology and assessing the effectiveness of pollution control.[2]

Ion chromatography is a well-established technique for determining inorganic anions in acid rain.[3–5] This Technical Note describes the determination of inorganic anions in rain samples by employing high-pressure ion chromatography on the Thermo Scientific™ Dionex™ ICS-4000 HPIC™ system, which is an integrated and dedicated capillary system designed to meet the demands of routine and fast IC analysis. By using high pressure components, such as the pump, eluent generation cartridge, and eluent generation degasser, the Dionex ICS-4000 system allows continuous operation at up to 5000 psi backpressures. This capability enables high sample throughput by combining high flow rates and the use of 4 µm particle size columns.

Scaling down from standard bore to capillary format generates a number of beneficial improvements for IC users. A significant and key advantage is that the system can be always on and ready for analysis because of its low consumption of eluent (15 mL of source deionized water per day at a 0.010 mL/min flow rate). The volume of waste generated is significantly decreased and the eluent generation cartridge lasts up to 18 months under normal continuous operation mode, which translates into reduced overall cost of ownership.

Equipment
- Dionex ICS-4000 HPIC system*
- Thermo Scientific Dionex AS-AP Autosampler
- Thermo Scientific™ Chromeleon™ Chromatography Data System (CDS) software, version 7.1 with SR2 MUa build or later

* A Thermo Scientific™ Dionex™ ICS-6000 HPIC™ system can be used for equivalent results.

Thermo SCIENTIFIC

The consumables for this application are shown in Table 1.

Table 1. Consumables list.

Product Name	Type: High-Pressure, Capillary	Dionex Part Number
Thermo Scientific™ Dionex™ EGC-KOH Cartridge	Anion eluent generator cartridge	072076
Thermo Scientific™ Dionex™ CR-ATC Continuously Regenerated Anion Trap Column	Anion electrolytic trap column	072078
Thermo Scientific™ Dionex™ EG Degas Cartridge	EG Degas cartridge	AAA-074459
Thermo Scientific™ Dionex™ IonPac™ AS18-4µm Column	Separation column	082314
Dionex IonPac AG18-4µm Column	Guard column	076033
Thermo Scientific™ Dionex™ CRD Carbonate Removal Device Bypass Cartridge	Bypass (needed for flow path)	072055
Thermo Scientific™ Dionex™ CRD 180 Carbonate Removal Device	Carbonate removal device cartridge for 4 µm particle capillary columns	079960
Thermo Scientific™ Dionex™ ACES™ Anion Capillary Electrolytic Suppressor	Anion suppressor cartridge	072052
Black PEEK (Vitrex PLC) Tubing	Tubing from pump to Dionex IonPac ATC-500 anion trap column	078497
Dionex IonPac ATC-500 Anion Trap Column	2 mm trap column between pump and EGC cartridge	079018
Dionex AS-AP Autosampler vial kits, Package of 100	10 mL: polystyrene vials vials, caps, blue septa	074228
	1.5 mL: polypropylene vials	079812

Reagents and Standards

The reagents and standards used in this technical note are listed in Table 2.

Table 2. Reagent/standards list.

Reagent or Standard	Supplier	P/N
18 MΩ-cm degassed deionized water	—	—
Fluoride standard 1000 mg/L	Thermo Scientific Dionex	037158
Chloride standard 1000 mg/L	Thermo Scientific Dionex	037159
Sulfate standard 1000 mg/L	Thermo Scientific Dionex	037160
Nitrate standard 1000 mg/L	Thermo Scientific Dionex	056497
Bromide standard 1000 mg/L	Ultra Scientific	ICC-001
Nitrite standard 1000 mg/L	Ultra Scientific	ICC-007
Phosphate standard 1000 mg/L	Ultra Scientific	ICC-005

Samples

Rain water sample

Conditions	
Columns:	Dionex IonPac AG18-4µm, 0.4 × 50 mm
	Dionex IonPac AS18-4µm, 0.4 × 150 mm
Eluent Source:	Dionex EGC-KOH Cartridge (Capillary)
Eluent:	23 mM KOH
Flow Rate:	A: 0.025 mL/min for sample B: 0.010, 0.020, and 0.025 mL/min for standards
Column Temp.:	30 °C
Compartment Temp.:	15 °C
Inj. Volume:	0.4 µL (full loop injection mode)
Detection:	Suppressed conductivity, Dionex ACES 300 suppressor, recycle mode, 8 mA at 0.010 mL/min; 13 mA at 0.025 mL/min
Background Conductance:	< 1 µS
Noise:	< 1 nS
System backpressure:	~1600 psi (0.010 mL/min); ~2900 psi (0.020 mL/min); ~3500 psi (0.025 mL/min)

Standard and Sample Preparation

The mixed standard solution was prepared by diluting each of the stock standard solutions in deionized water. The rain water sample was filtered prior to injection with a 0.20 µm IC syringe filter to remove particulates. It is important to use 18 MΩ-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.

Instrument Setup and Installation

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

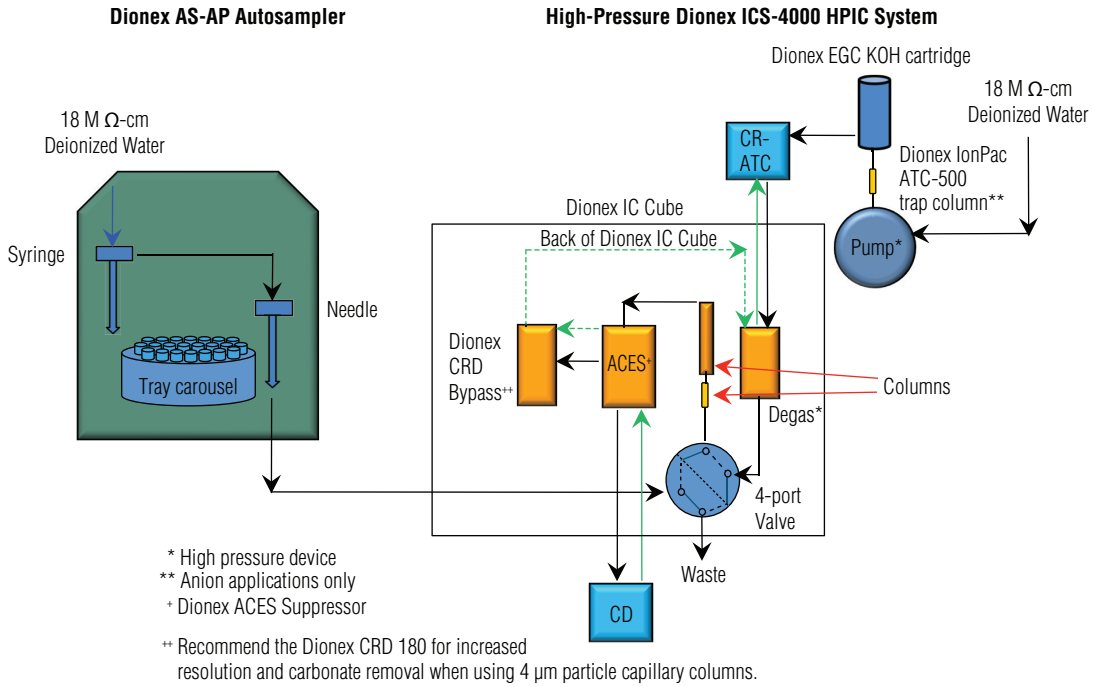

Figure 1. Flow diagram of Dionex ICS-4000 HPIC system.

Figure 1 shows the flow diagram of this application. Install the Dionex IonPac ATC-500 anion trap column from the pump with black PEEK tubing (P/N 078497) and the Dionex EGC KOH cartridge but temporarily leave the tubing to the Dionex EGC KOH cartridge disconnected to flush the trap column. 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 or CRD 180 Carbonate Removal Device, and suppressor capillary cartridges are installed in the Thermo Scientific™ Dionex™ IC Cube™ as shown in Figure 2. All above the devices, in addition to the Dionex EGC KOH cartridge and the Dionex CR-ATC column should be hydrated prior to use following the instructions in product and installation manuals.[7–9] The CRD Bypass cartridge was installed for all experiments in this technical note. To achieve the optimal column efficiencies and highest efficient carbonate removal introduced by the samples, install a Dionex CRD 180 Carbonate Removal Device cartridge. This device is optimized for Dionex 4 µm particle separation columns. Detailed instructions are described in Technical Note TN 134.[10] Create new Instrument Methods using Chromeleon Wizard by entering information from the Conditions section in this document and the instructions described in Technical Note TN 134.[10]

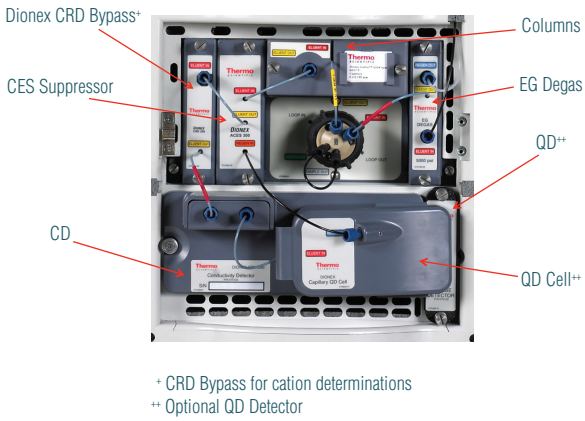

Figure 2. Dionex ICS-4000 IC Cube.

Results and Discussion

Figure 3 demonstrates the fast separations possible of a nine anion standard solution on the Dionex IonPac AS18-4µm column using the Dionex ICS-4000 HPIC system. In the first chromatogram in Figure 3, the flow rate is at the optimum level for peak resolution of 0.010 mL/min. The same standard is then analyzed at faster flow rates, at 0.020 mL/min for the middle chromatogram and at 0.025 mL/min for the top chromatogram. As the flow rate increases, the system backpressure increases from 1900 psi to 3500 psi. These flow rates are only possible with the high-pressure capable system, such as the Dionex ICS-4000 HPIC system.

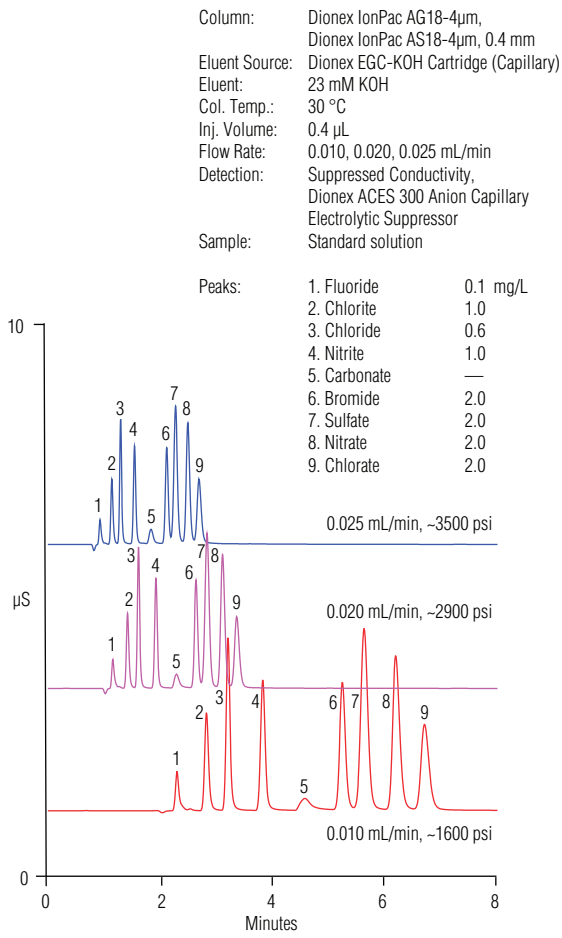

Figure 3. Fast determination of inorganic anions with different flow rates.

Figure 4 shows the separation of inorganic anions in a rain water sample within 4 min on the same column and system at 0.025 mL/min. Sulfate and chloride are the predominant analytes in the rain water sample. Low quantities of nitrite and nitrate are detected indicating low levels of NO_x in the atmosphere when this precipitation occurred.

This fast analysis demonstrates the advantages of combining separations on an 4 µm resin particle column, such as the Dionex IonPac AS18-4 µm column, with the high-pressure capable Dionex ICS-4000 HPIC system. The high efficiency provided by this new generation Dionex IonPac AS18 column resulted in good resolution of adjacent peaks with significantly decreased analysis time. This key benefit is highly desired for high throughput analysis of environmental water samples. These experiments, shown in Figures 3 and 4, have similar results as those previously demonstrated on another capillary HPIC system, Thermo Scientific Dionex ICS-5000+ HPIC modular IC system (TN 123).[11]

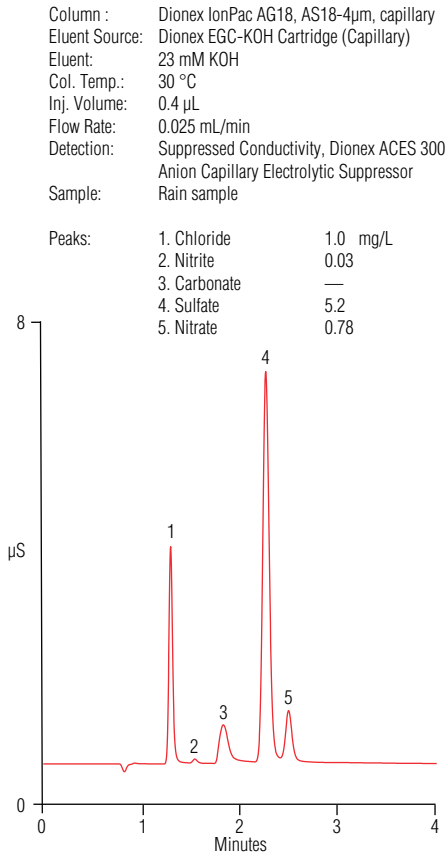

Figure 4. Fast determinations of inorganic anions in a rain water sample.

Conclusion

This Technical Note demonstrates rapid analysis of determining inorganic anions in rainwater with the newly introduced high-pressure Dionex ICS-4000 HPIC dedicated capillary IC and the 4 µm particle size Dionex IonPac AS18-4µm column. The Dionex ICS-4000 HPIC system provides the numerous benefits of capillary IC benefits: ease of use, longer life of consumables, low waste generation, and high pressure operational limit. The small footprint of this system saves bench space for other instruments. The capillary scale makes this system an excellent analysis tool for routine and rapid determination of rain water samples. The capillary HPIC technology is now available on two instruments: the Dionex ICS-4000 Dedicated HPIC system and the Dionex ICS-5000+ Modular HPIC system.

References

1. Acid Rain, U.S. Environmental Protection Agency (EPA), http://www.epa.gov/airmarkets/progsregs/arp/nox.html
2. Thermo Fisher Scientific, *Determination of Nitrate and Sulfate Collected on Air Filters*, Application Note 2, LPN 034635. Sunnyvale, CA, 2003.
3. Thermo Fisher Scientific, *Determination of Inorganic Anions in Wastewater in Environmental Waters Using a Hydroxide-Selective Column*, Application Note 154, LPN 1539. Sunnyvale, CA, 2003.
4. Thermo Fisher Scientific, *Determination of Anions in Acid Rain by Ion Chromatography*, Application Note 31, LPN 032133. Sunnyvale, CA, 1992.
5. Thermo Fisher Scientific, *Determination of Anions in Acid Rain by Ion Chromatography*, Application Update 146, LPN 1541. Sunnyvale, CA, 2003.
6. Thermo Fisher Scientific, Technical Note 113, *Practical Guidance to Capillary IC*, LPN 3043, Sunnyvale, CA, 2012.
7. Thermo Fisher Scientific. Dionex ICS-4000 Installation manual. Doc No. 065468, Sunnyvale, CA, 2013.
8. Thermo Fisher Scientific. Dionex Product Manual for CES 300 Suppressors. Doc No. 065386, Sunnyvale, CA, 2010.
9. Thermo Fisher Scientific. Dionex AS-AP Operator's Manual. Doc No. 065361, Sunnyvale, CA, 2012.
10. Thermo Fisher Scientific. Technical Note 134, *Configuring a High Pressure Integrated Capillary IC System*, P/N TN70476_E, Sunnyvale, CA, 2012.
11. Thermo Fisher Scientific. Technical Note 123, *Determination of Inorganic Anions in Acid Rain Using a High Pressure Modular Capillary Ion Chromatograph*, PN TN70675_E, Sunnyvale, CA, 2013.

ThermoFisher SCIENTIFIC

©2017 Thermo Fisher Scientific Inc. All rights reserved. All trademarks are the property of Thermo Fisher Scientific and its subsidiaries. This information is presented as an example of the capabilities of Thermo Fisher Scientific products. It is not intended to encourage use of these products in any manners that might infringe the intellectual property rights of others. Specifications, terms and pricing are subject to change. Not all products are available in all countries. Please consult your local sales representatives for details.

AN70642-EN 1117S