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

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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$_x$. 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.

Ion chromatography (IC) is a well-established technique for the analysis of inorganic anions in acid rain. This Technical Note describes the determination of inorganic anions in rainwater samples using a Thermo Scientific™ Dionex™ ICS-5000+ high-pressure 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.
**Reagents and Standards**

18 M $\Omega$-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**

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

*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 $\Omega$-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 $\Omega$-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.

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

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

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
10. Phosphate 2.0

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.

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

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

Sample:
A: Rainwater of Campbell, CA
B: Rainwater of Sunnyvale, CA

Peaks:
1. Chloride A 0.84 1.37 mg/L
2. Nitrite A 0.035 0.01
3. Carbonate — —
4. Sulfate A 5.4 B 1.56
5. Nitrate A 0.67 B 0.11
6. Phosphate — —
7. Chlorate — —
8. Bromide — —
9. Phosphate — —

µS

Minute
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/progrsregs/arp/ nox.html


