# Determination of Inorganic Anions in Municipal Water Using High-Pressure Modular Capillary Ion Chromatography

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Technical Note 132

**Key words**
Environmental water analysis, HPIC, Wastewater, ICS-5000+, 4 µm particle column, IonPac AS18-4µm

## Goal

Demonstrate fast separation of inorganic anions in municipal water samples by increasing flow rates using a high-pressure capillary IC system and 4 µm resin particle column.

## Introduction

Ion chromatography (IC) has been widely adopted to determine inorganic anions in environmental waters, including surface, ground, drinking and wastewaters. In the U.S., the contamination level of wastewater is regulated by the Clean Water Act to minimize discharge of pollutants into the environment. The integrity and safety of drinking water is ensured through the Safe Drinking Water Act. Many other countries (e.g., Germany, France, Italy, China and Japan) have similar health and environmental standards and a considerable number of regulatory IC methods have been published. In addition, many standards organizations (including the International Organization for Standardization (ISO), American Society for Testing and Materials (ASTM), and American Water Works Association (AWWA) have validated IC methods for the analysis of inorganic anions in drinking water.[1, 2] For some anions, their concentration in drinking water is regulated due to their toxic effects. For example, high levels of fluoride cause skeletal and dental fluorosis[3], while nitrite and nitrate can cause methemoglobulinemia[4], which can be fatal to infants. Other inorganic anions, such as chloride and sulfate, are considered secondary contaminants and can affect odor, color, and other aesthetic characteristics.

This Technical Note describes the determination of inorganic anions in municipal drinking water samples using the Thermo Scientific™ Dionex™ ICS-5000+ HPIC™ capillary system in combination with the Thermo Scientific™ Dionex™ IonPac™ AS18-4µm column, which is the column of choice for compliance monitoring of water samples in accordance with U.S. EPA Methods 300.0 (A)[5] and 300.1.[6] By increasing the flow rate, multiple samples can be quickly analyzed, resulting in high throughput. Scaling down from standard bore (4 mm i.d.) to capillary format (0.4 mm i.d.) brings many benefits to IC users. The system can be always on and ready for analysis because of its low eluent consumption (15 mL of water a day at 0.01 mL/min flow rate). Additionally, the amount of waste generated is significantly reduced and the eluent generation cartridge (EGC) can last 18 months under standard continuous operation, which translates into reduced overall cost of ownership.

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## Equipment

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

## Reagents and Standards

- 18.2 MΩ-cm degassed deionized water
- Anion Standard solution made from 1000 mg/L stocks

## Samples

- Municipal drinking and wastewater diluted as indicated with deionized water

| Conditions | |
|---|---|
| Column: | Dionex IonPac AS18-4µm, 0.4 × 150 mm |
| Eluent Source: | Thermo Scientific Dionex EGC-KOH Cartridge (Capillary) with Thermo Scientific Dionex CR-ATC Continuously Regenerated Anion Trap Column |
| Eluent: | 23 mM KOH |
| Flow Rate: | 0.025 mL/min |
| Column Temp.: | 30 °C |
| Inj. Volume: | 0.4 µL |
| Detection: | Suppressed conductivity, Thermo Scientific™ Dionex™ ACES™ 300 Anion Capillary Electrolytic Suppressor, recycle mode |
| Background Conductance: | 0.3–0.5 µS |
| Noise: | Less than 3 nS |
| System Backpressure: | ~3500 psi |

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

Table 1. Consumables list.

| Product Name | Description | Dionex Part Number |
|---|---|---|
| Dionex EGC-KOH (Capillary) | Eluent generator cartridge | 072076 |
| Dionex CR-ATC (Capillary) | Electrolytic trap column | 072078 |
| Dionex IonPac AS18-4µm | Separation column | 082314 |
| Dionex IonPac AG18-4µm | Guard column | 076033 |
| Thermo Scientific Dionex CRD Bypass cartridge | Bypass (needed for flow path) | 072056 |
| Dionex ACES 300 | Suppressor | 072052 |
| Dionex HP fittings (blue) | Bolts / Ferrules | 074449/ 074373 |
| Thermo Scientific™ Dionex™ CRD 180 Carbonate Removal Cartridge | For 4 µm particle capillary columns | 079960 |
| EG Degas cartridge (Capillary) | High-pressure degas cartridge, up to 5000 psi | AAA-074459 |
| Dionex AS-AP Autosampler vials | Package of 100, 10 mL, polystyrene vials, caps, blue septa | 074228 |

## Standard and Sample Preparation

The anion standards were prepared by diluting ~1000 mg/L stock solutions with18 MΩ-cm degassed deionized water. The municipal wastewater samples were diluted 1000-fold and drinking water 5-fold with 18 M Ω-cm degassed deionized water and filtered with a 0.2 µm syringe filter prior to injection.

It is important to use 18 MΩ-cm resistivity, deionized water for standard, eluent, and autosampler flush solutions to avoid system contamination resulting in decreased sensitivity and poor calibration. Degassing the deionized water by vacuum filtration prior to use is a good practice. It prevents the formation of gas bubbles and increases the reproducibility of results.

## 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".[7]

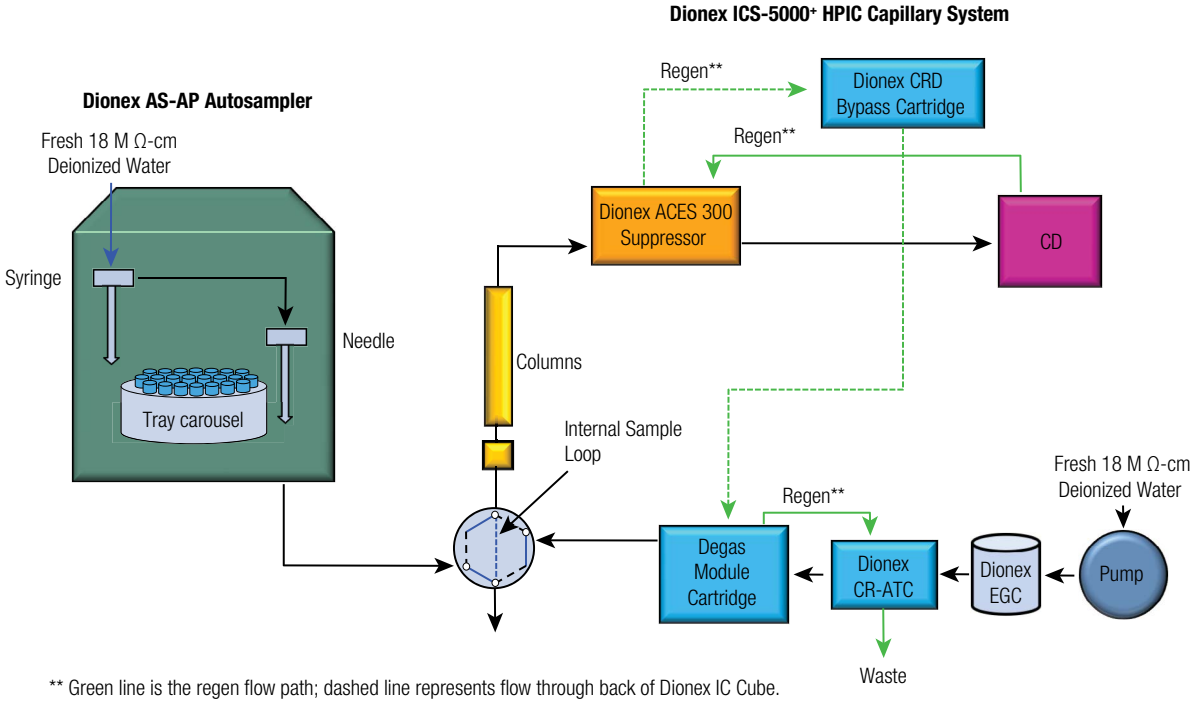


Figure 1. Flow diagram for the Dionex ICS-5000⁺ HPIC capillary system.

To set up this application, plumb the consumables and modules of the Dionex ICS-5000⁺ HPIC capillary system according to Figure 1. Install and hydrate the Dionex EGC-KOH cartridge, Dionex CR-ATC column, and suppressor following the instructions in the product manuals. The Dionex CRD Bypass Cartridge was installed for all experiments in this technical note. To achieve optimal column efficiencies and greatest removal of carbonate introduced by samples, install a Dionex CRD 180 Carbonate Removal Device. This device is optimized for 4 µm particle separation columns. 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 131, the product manuals, and the instrument installation and operator's manuals.[8–12]

## Results and Discussion

As illustrated in Figure 2, the time to separate nine inorganic anions was reduced from seven to less than three minutes by increasing the flow rate from 0.010 to 0.025 mL/min. This shortened run time enables increased throughput when analyzing large numbers of samples. At this higher flow rate, the backpressure of the system was about 3800 psi, which is above the 3000 psi limit of many IC systems, but well below the limit of the Dionex ICS-5000⁺ HPIC system (5000 psi). The use of higher flow rates, while maintaining resolution, is made possible by the 4 µm particle size of the Dionex IonPac AS18-4µm resin, which is about half the diameter of the previously available resin (7.5 µm). These 4 µm columns possess both higher capacity and efficiency. Despite the use of a faster flow rate, there is still only a modest amount of water consumed and waste generated (36 mL/day) keeping labor and waste disposal costs to a minimum.

| | | Peaks: | |
|---|---|---|---|
| Column: | Dionex IonPac AG18, Dionex IonPac AS18-4µm (0.4 × 150 mm) | 1. Fluoride | 0.1 mg/L |
| | | 2. Chlorite | 1.0 |
| Eluent Source: | Dionex EGC-KOH Cartridge (Capillary) | 3. Chloride | 0.6 |
| | | 4. Nitrite | 1.0 |
| Eluent: | 23 mM KOH | 5. Carbonate | – |
| Inj. Volume: | 0.4 µL | 6. Bromide | 2.0 |
| Col. Temp.: | 30 °C | 7. Sulfate | 2.0 |
| Flow Rate: | A. 0.010 mL/min | 8. Nitrate | 2.0 |
| | B. 0.015 mL/min | 9. Chlorate | 2.0 |
| | C. 0.025 mL/min | | |
| Detection: | Suppressed conductivity, Dionex ACES 300, recycle mode | | |

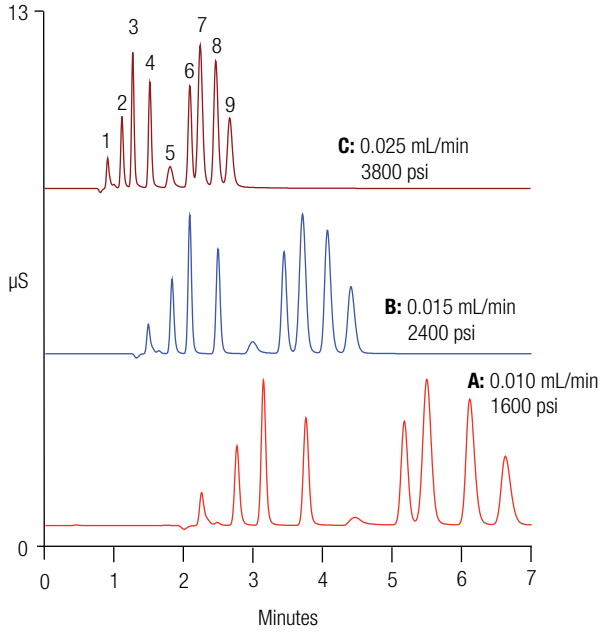


Figure 2. Rapid determination of inorganic anions using high-pressure capillary IC.

Figure 3 shows that inorganic anions in municipal drinking water samples were separated in less than three minutes when a flow rate of 0.025 mL/min was used. The concentration of fluoride that was measured ranged from 0.05 to over 1 mg/L, a 20-fold difference. Nitrate had the largest variance among the samples analyzed ranging from 0.16 for the lowest concentration detected to 17 mg/L for the highest, a difference of > 100-fold.

| | |
|---|---|
| Column: | Dionex IonPac AG18-4µm,<br>Dionex IonPac AS18-4µm,<br>(0.4 × 150 mm) |
| Eluent Source: | Dionex EGC-KOH Cartridge (Capillary) |
| Eluent: | 23 mM KOH |
| Flow Rate: | 0.025 mL/min |
| Inj. Volume: | 0.4 µL |
| Column Temp.: | 30 °C |
| IC Cube Temp.: | 15 °C |
| Detection: | Suppressed conductivity, Dionex ACES 300,<br>Anion Capillary Electrolytic Suppressor<br>recycle mode |
| Sample Prep: | A, C: Diluted 5-fold<br>B, D: Undiluted |
| Samples: | A: City 1<br>B: City 2<br>C: City 3<br>D: City 4 |

| Peaks: | A | B | C | D | |
|---|---|---|---|---|---|
| 1. Fluoride | 0.61 | 0.95 | 0.05 | 1.14 | mg/L |
| 2. Chloride | 8.36 | 5.76 | 38.80 | 13.90 | |
| 3. Carbonate | – | – | – | – | |
| 4. Sulfate | 50.10 | 18.00 | 66.90 | 20.30 | |
| 5. Nitrate | 7.09 | 0.16 | 17.00 | – | |

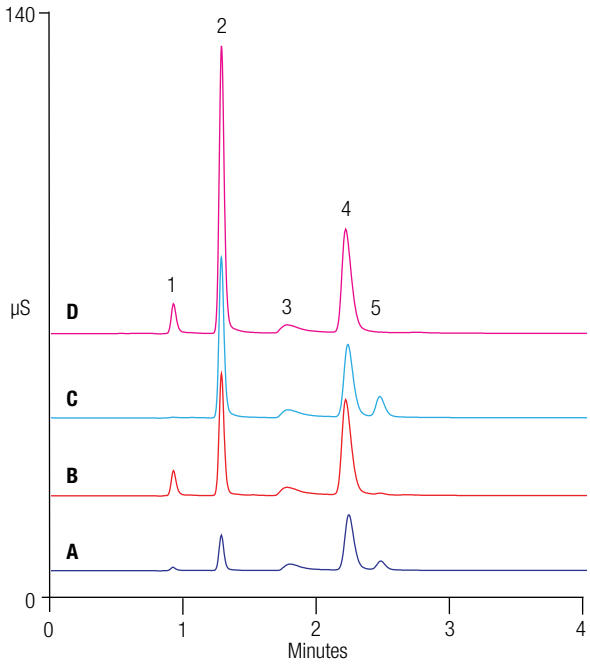


Figure 3. Determination of inorganic anions in municipal drinking water samples using high-pressure capillary IC.

In Figure 4, concentration of the inorganic anions in municipal wastewater were determined. Due to the high concentrations of ions present, these samples were diluted 1000-fold so that the quantities injected were well within the column capacity. Both nitrite and nitrate had a large range of concentrations in samples from different stages of the wastewater treatment process (25- and 18-fold, respectively).

| | |
|---|---|
| Column: | Dionex IonPac AG18-4µm,<br>Dionex IonPac AS18-4µm,<br>(0.4 × 150 mm) |
| Eluent Source: | Dionex EGC-KOH Cartridge (Capillary) |
| Eluent: | 23 mM KOH |
| Flow Rate: | 0.025 mL/min |
| Inj. Volume: | 0.4 µL |
| Column Temp.: | 30 °C |
| IC Cube Temp.: | 15 °C |
| Detection: | Suppressed conductivity, Dionex ACES 300,<br>Anion Capillary Electrolytic Suppressor<br>recycle mode |
| Sample Prep: | Diluted 1000-fold, filtered, 0.2 µm |
| Samples: | A: Influent<br>B: Primary effluent<br>C: Trickling effluent<br>D: Final effluent |

| Peaks: | A | B | C | D | |
|---|---|---|---|---|---|
| 1. Chloride | 76.5 | 146.0 | 154.0 | 130.0 | mg/L |
| 2. Nitirite | 1.5 | 2.1 | 37.4 | 1.6 | |
| 3. Carbonate | – | – | – | – | |
| 4. Sulfate | 41.6 | 88.9 | 84.8 | 91.8 | |
| 5. Nitrate | 28.8 | 7.2 | 31.7 | 128.0 | |

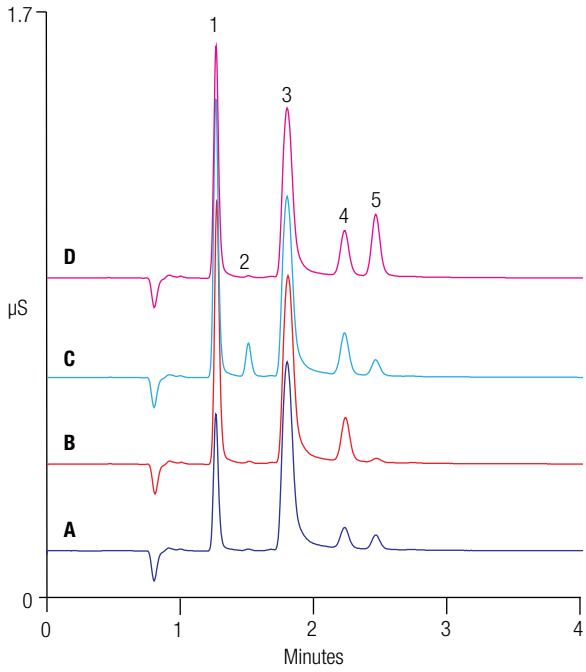


Figure 4. Determination of inorganic anions in municipal wastewater using high-pressure capillary IC.

## Conclusion

This Technical Note demonstrates that the Dionex ICS-5000+ capillary HPIC system, when combined with the Dionex IonPac AS18-4µm column, provides an ideal solution for the analysis of inorganic anions in municipal water samples. The high-pressure capability of this system permits the use of higher flow rates resulting in short run times, while the 4 µm resin particle column ensures good peak resolution.

For information on inorganic ion determinations in water using standard and microbore flow rates, see Application Notes 130 and 154.[13, 14]

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