Determination of Inorganic Anions Using the Dionex IonSwift MAX-200 Monolith Column with Capillary Ion Chromatography

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Overview

Purpose: To demonstrate the fast determination of bromate in a municipal drinking water using the monolith-based Thermo Scientific Dionex IonSwift™ MAX-200 capillary column.

Methods: Bromate is separated from other inorganic anions using an hydroxide gradient and detected by suppressed conductivity detection.

Results: A minimum of 1 µg/L bromate can be detected. Good linearity and recovery of bromate are observed.

Introduction

Ion chromatography (IC) with suppressed conductivity detection is a well-established technique for the determination of inorganic and organic ions in the water analysis industry. The recent introduction of high-pressure capillary IC brings additional advantages to the analysis of inorganic ions such as speed and high resolution. Due to low consumption of eluent, capillary IC systems can be operated continuously and are always ready for analysis, thus redefining the workflow for IC and improving method performance. The operation of capillary IC at higher pressures and/or higher flow rates improves separation efficiency and/or speed. This work shows the determination of inorganic anions and oxyhalides using the Dionex IonSwift MAX-200 capillary column.

Methods

Sample Preparation

Bromate at 10 µg/L was spiked into a municipal drinking water sample.

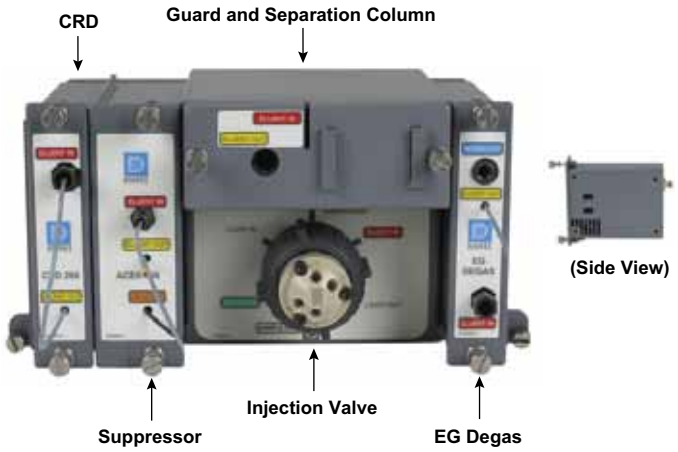
Ion Chromatography Equipment and Data Analysis

Thermo Scientific Dionex ICS-5000 RFIC™ Capillary Ion Chromatography System consisting of:

- DP Dual Isocratic Capillary Pump
- DC Detector/Chromatography Module
- Thermo Scientific Dionex IC Cube™ Capillary Module (Figure 1)
- ICS-5000 CD Capillary Conductivity Detector for anions and cations
- EG Eluent Generator Module
- Thermo Scientific Dionex AS-AP Autosampler with diverter valve
- Thermo Scientific Dionex Chromeleon™ Chromatography Data System software

The Dionex ICS-5000 IC Cube contains the consumables with easy-to-install cartridges: the EG Degas module, column tray, four-port injection valve with 0.4 µL internal loop, suppressor module, and Carbonate Removal Device (CRD) module.

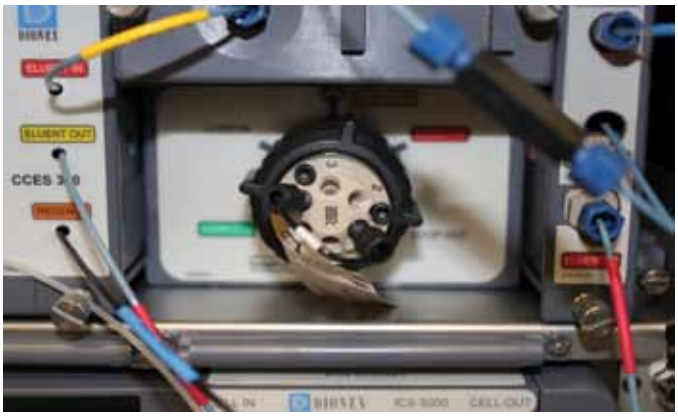
FIGURE 1. Dionex ICS-5000 IC Cube Module.



Conditions

All the experimental conditions are listed Figures 4–8. A six-port injection valve with a 3 µL sample loop (Figure 2) was used for all separations replacing the standard four-port injection valve and 0.4 µL sample loop.

FIGURE 2. A six-port injection valve with 3 µL sample.



Results

Inorganic Anions Separation on Dionex IonSwift MAX-200 Capillary Column

Dionex IonSwift MAX-200 capillary column is designed to provide high-speed, high-resolution inorganic anions separations using a hydroxide gradient delivered by an eluent generator. Speed and resolution are two competing performance factors in conventional chromatography separations using porous media. A solution for this problem is a new generation of separation media: monolithic structures. Monoliths contain a network of large separation pores where the mass transfer is achieved primarily by convective flow instead of diffusion during separation. The highly improved mass transfer at high-flow velocity in monoliths removes the peak broadening problem in conventional porous separation media. High-speed separations can be achieved with minimal loss of resolution. Therefore, monoliths offer high-resolution and high-speed separations similar to well constructed nonporous media. Figure 3 shows the structure of the Dionex IonSwift MAX-200 capillary column. Determination of inorganic anions at different flow rates is shown in Figure 4. Figures 5 and 6 demonstrate that inorganic anions can be determined within 10 min at 25 µL/min flow rate taking advantage of the high-pressure capabilities of capillary IC and the relatively low back pressure provided by a monolith column.

FIGURE 3. Structure of Dionex IonSwift MAX-200 column.

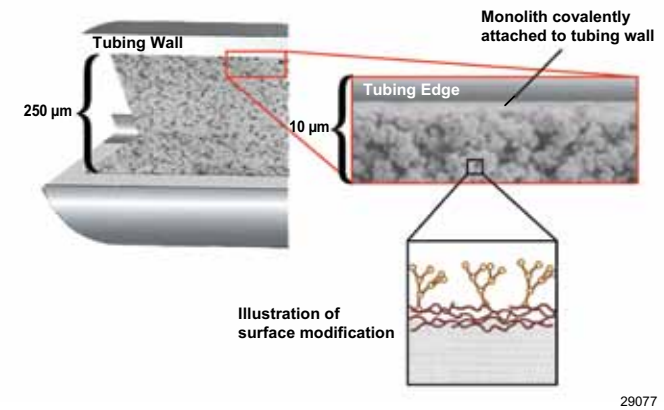


FIGURE 4. Fast determination of inorganic anions using the Dionex IonSwift MAX-200 capillary column.

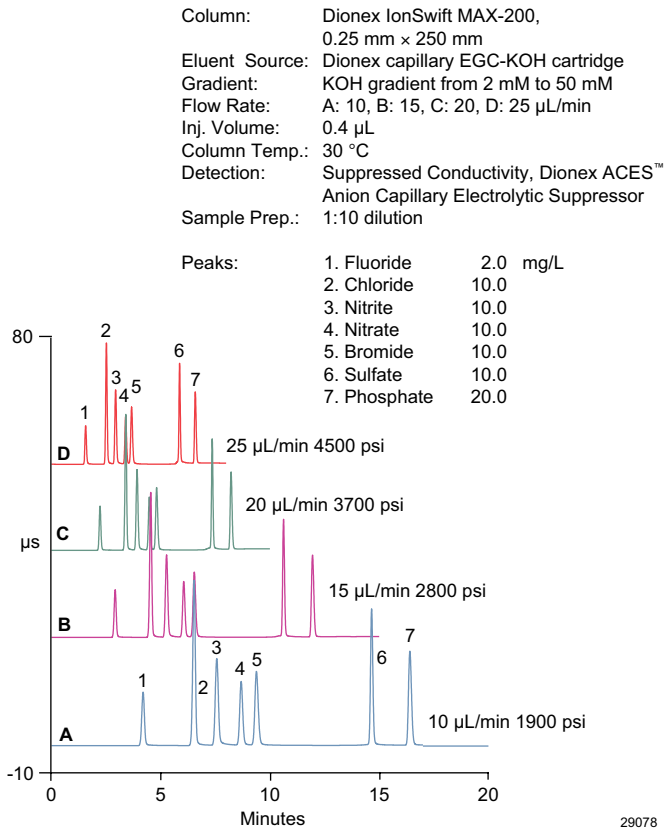


FIGURE 5. Fast determination of inorganic anions in a municipal wastewater sample.

Column:	Dionex IonSwift MAX-200, 0.25 mm × 250 mm
Eluent Source:	Dionex capillary EGC-KOH cartridge
Gradient:	KOH gradient from 2 mM to 50 mM
Flow Rate:	A: 10, B: 20, C: 25 µL/min
Inj. Volume:	0.4 µL
Column Temp.:	30 °C
Detection:	Suppressed Conductivity, Dionex ACES™ Anion Capillary Electrolytic Suppressor,
Sample Prep.:	1:10 dilution
Peaks:	1. Chloride 25.5 mg/L 2. Nitrate 73.3 3. Sulfate 10.0

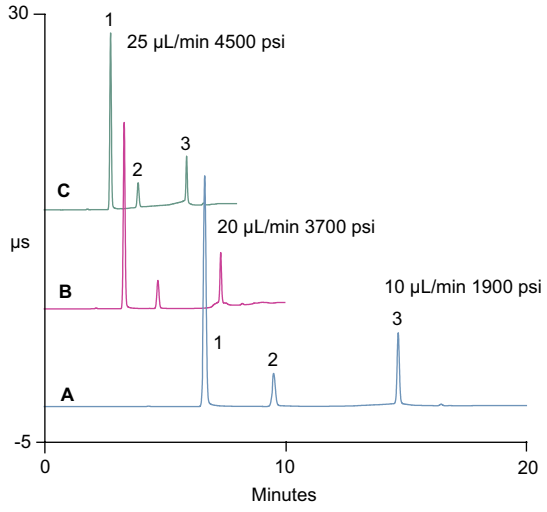


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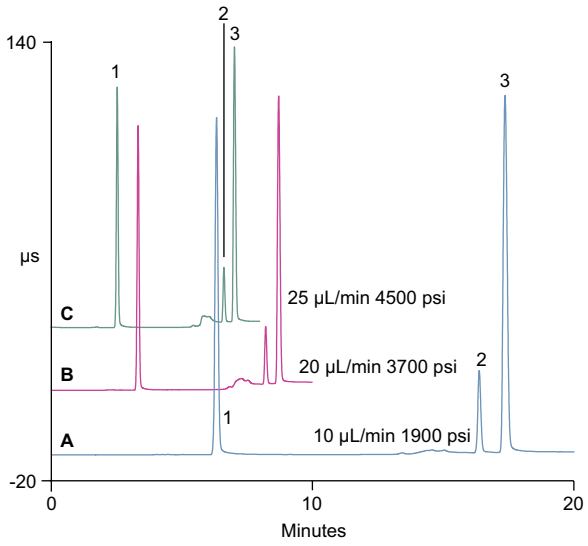
FIGURE 6. Fast separation of anions in a sports beverage by increasing flow rates.

Column:	Dionex IonSwift MAX-200, 0.25 mm × 250 mm
Eluent Source:	Dionex capillary EGC-KOH cartridge
Gradient:	KOH gradient from 2 mM to 50 mM
Flow Rate:	A: 10, B: 20, C: 25 µL/min
Inj. Volume:	0.4 µL
Column Temp.:	30 °C
Detection:	Suppressed Conductivity, Dionex ACES™ Anion Capillary Electrolytic Suppressor
Sample Prep.:	1:10 dilution
Peaks:	1. Chloride 41.3 mg/L 2. Phosphate 34.5 3. Citrate 331



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Oxyhalides Separation on the Dionex IonSwift MAX-200 Capillary Column

The Dionex IonSwift MAX-200 capillary column was selected for this application because the monolith backbone is ideal for fast separations using a hydroxide gradient, and the column chemistry is optimized for oxyhalide separations such as bromate, chlorite, and chlorate. The separation of bromate in municipal drinking water is shown Figure 7. Typically, municipal wastewater samples contain either chlorite and chlorate from chlorination or bromate from ozonation as a result from the disinfection processes. The samples rarely contain both types. However, this wastewater sample selected for bromate-spiking experiments already contained chlorite from the disinfectant treatment. In Figure 8, the chromatogram demonstrates that chlorite and chlorate can be separated from other inorganic anions using the Dionex IonSwift MAX-200 capillary column.

FIGURE 7. Determination of bromate in a municipal drinking water.

Column:	Dionex IonSwift MAX-200, 0.25 × 250 mm
Eluent Source:	Dionex EGC-KOH capillary
Gradient:	2 mM KOH from -10 to 0.1 min, 2–10mM from 0.1 to 10 min, 10–50 mM from 10 to 15 min, 50 mM from 15 to 20 min
Column Temp.:	30 °C
Flow Rate:	10 µL/min
Inj. Volume:	3 µL
Detection:	Suppressed conductivity, Dionex ACES™ Anion Capillary Electrolytic Suppressor, recycle
Sample Prep.:	10 µg/L of bromate was spiked into a municipal drinking water

Peaks:

1. Fluoride	0.84 mg/L
2. Chlorite	—
3. Bromate	0.01
4. Chloride	4.05
5. Nitrate	0.21
6. Sulfate	2.14
7. Phosphate	0.07

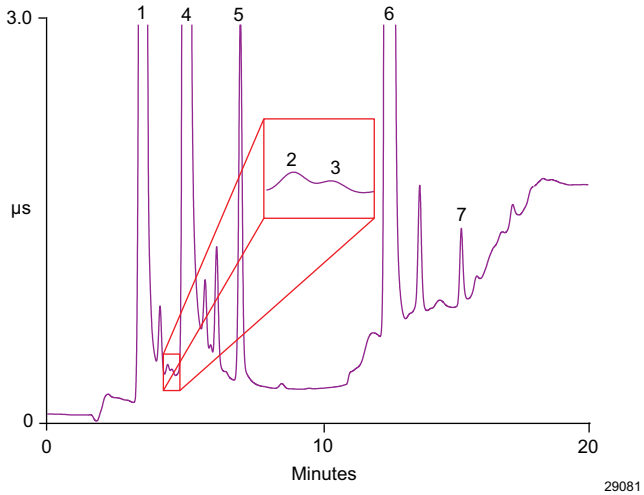
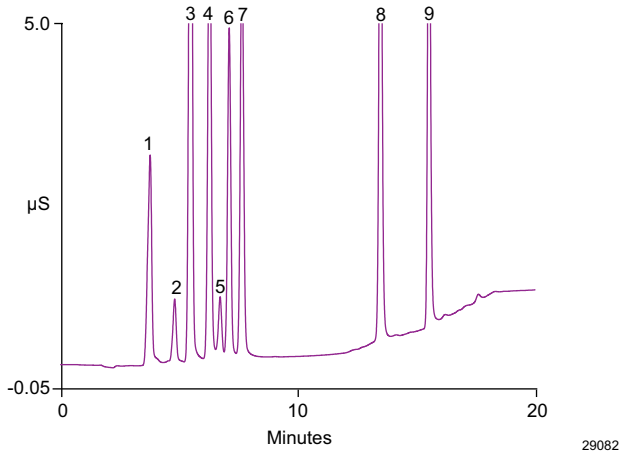


FIGURE 8. Determination of chlorite and chlorate in anion standard solution.

Column:	Dionex IonSwift MAX-200, 0.25 × 250 mm
Eluent Source:	Dionex EGC-KOH capillary
Gradient:	2 mM KOH from -10 to 0.1 min, 2–10 mM from 0.1 to 10 min, 10–50 mM from 10 to 15 min, 50 mM from 15 to 20 min
Column Temp.:	30 °C
Flow Rate:	10 µL/min
Inj. Volume:	3 µL
Detection:	Suppressed conductivity, Dionex ACES™ Anion Capillary Electrolytic Suppressor, recycle
Sample Prep.:	10 µg/L of bromate was spiked into a municipal drinking water

Peaks:

1. Fluoride	0.1 mg/L
2. Chlorite	0.1
3. Chloride	0.5
4. Nitrite	0.5
5. Chlorate	0.1
6. Bromide	0.5
7. Nitrate	0.5
8. Sulfate	0.5
9. Phosphate	1.0



Linearity and Detection Limit Determination

Calibration linearity for bromate was investigated by injecting standard solutions at four different concentrations (Table 1). Good linearity was observed from 3 to 30 µg/L for bromate. The method detection limit (MDL) was estimated to be 1 µg/L by examining the signal-to-noise ratio (3x S/N).

Table 1. Linearity and MDL of Bromate Using the Dionex IonSwift MAX-200 Capillary Column at 10 µL/min Flow Rate Conditions

Concentration of Standards (µg/L)	Correlation Coefficient (r^2)	Calculated MDL (µg/L)
3	> 0.99	1.0
10		
20		
30		

Recovery of Bromate in Municipal Drinking Water

To demonstrate the accuracy of the method, 10 µg/L of bromate was spiked into a municipal drinking water. An average of 87% recovery of bromate with 7% RSD was achieved. Due to co-elution of bromate an chlorite, the integration of bromate was affected resulting in low recovery. However, bromate and chlorite will not be present at the same time in a real municipal drinking water sample because the water is either treated by chlorination, generating chlorite and chlorate, or by ozonization, generating bromate.

Conclusion

The Dionex IonSwift MAX-200 capillary column is a high-speed, high-resolution monolith column designed for the separation of oxyhalides and inorganic anions.[1] This column provides fast separation and high throughput. The high-pressure compatibility of the capillary IC format allows higher system backpressures further benefiting the IC capillary system to run fast, high-resolution ion analysis. Two-dimensional IC with suppressed conductivity or mass spectroscopy detection can be an alternative approach to determine oxyhalides if lower LOD is required.[2,3]

References

1. Thermo Fisher Scientific. *Determination of Trace Concentrations of Chlorite, Bromate, and Chlorate in Bottled Natural Mineral Waters,* Dionex Application Note 184 (LPN 1890), Sunnyvale, CA, 2007.
2. Thermo Fisher Scientific. *Determination of Sub-µg/L Bromate in Municipal and Natural Mineral Waters Using Preconcentration with Two-Dimensional Ion Chromatography and Suppressed Conductivity Detection,* Dionex Application Note 187 (LPN 1943-02), Sunnyvale, CA, 2007.
3. Liu, Y.; Baretto, V.; Slingsby, R.; Pohl, C. *Determination of Trace-Level Bromate and Perchlorate in Environmental Samples Using Two-Dimensional Capillary Ion Chromatography with Suppressed Conductivity and Mass Spectroscopy Detection.* Thermo Fisher Scientific, Dionex Products Poster (LPN 2243), Sunnyvale, CA, 2009.

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