# Determination of Trace-Level Bromate and Perchlorate in Environmental Samples Using Two-Dimensional Capillary Ion Chromatography with Suppressed Conductivity and Mass Spectrometry Detection

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## INTRODUCTION

Interest in the development of capillary ion chromatography (IC) systems and methods for determination of ionic analytes has increased significantly in recent years. The practice of IC using capillary columns has a number of advantages; capillary IC systems offer improved capability for continuous operation with minimal intervention, and thus minimize problems associated with system startup and shutdown. Using capillary columns can improve separation efficiency and/or speed. Separation processes in the capillary format require only a fraction of the sample volume and thus capillary IC systems offer improved compatibility with applications where sample amount is limited. The operation of capillary IC at low flow rates improves the system compatibility with mass spectrometer.

The determination of analyte ions at very low concentrations (µg/L or lower) in environmental samples is a challenging analytical task because matrix ions present at much higher concentrations (e.g., mg/L or higher) often interfere with the separation of analyte ions. The use of automated two-dimensional IC methods has gained increasing popularity in the determination of analyte ions in environmental samples because those methods provide convenient on-line matrix elimination or diversion and eliminate the need for off-line sample pretreatment steps.

Here we report our ongoing efforts in the development of capillary Reagent-Free™ IC (RFIC™) systems with suppressed conductivity and mass spectrometry detection for determination of target ionic analytes. We discuss the performance characteristics of two-dimensional (2-D) capillary IC methods and demonstrate the advantages of using these methods for determination of parts-per-trillion levels of perchlorate and bromate in water samples.

## EXPERIMENTAL

Figure 1 illustrates a prototype capillary RFIC system constructed in this study. The typical prototype capillary RFIC system is similar to the conventional RFIC system in terms of basic system components. The capillary pump is used to deliver a stream of deionized water into the capillary KOH eluent generator which consists of a high-pressure generation chamber containing a Pt cathode and a low-pressure electrolyte reservoir containing Pt anode. Under the applied electrical field, the potassium ions migrate across the ion exchange connector to combine with hydroxide ions to form KOH eluent. The downstream system components, including the miniaturized degas unit, sample injector, separation column, electrolytic suppressor, and conductivity detector are optimized for operations under capillary flow conditions. Thermo Scientific™ Dionex™ Chromeleon™ Chromatography Data System software was used for instrument control, data collection, and processing. Table 1 summarizes the typical conventional and capillary RFIC system operating parameters.
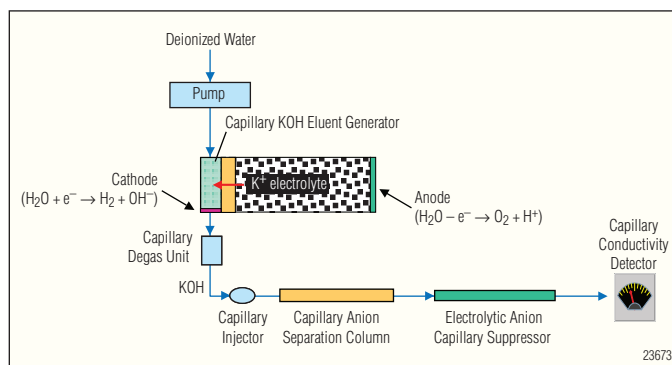


*Figure 1. Prototype capillary RFIC system with suppressed conductivity detection.*

| Table 1. Typical Conventional and Capillary RFIC System Operating Parameters | | |
|---|---|---|
| | **Conventional IC** | **Capillary IC** |
| Column i.d. | 4 mm | 400 µm |
| Flow Rate | 1.0 mL/min | 10 µL/min |
| Injection Loop | 25 µL | 0.25 µL |
| Suppressor Dead Volume | 60 µL | 0.6 µL |
| EG Current (50 mM KOH) | 80.4 mA | 0.804 mA |
| EG Current (200 mM KOH) | 321.6 mA | 3.216 mA |
| $K^+$ Consumption/Year | 26.3 moles (50 mM KOH) | 0.263 moles (50 mM KOH) |
| $H_2O$ Consumption/Year | 525.6 L | 5.256 L |

Figure 2 illustrates the prototype 2-D IC system developed in this study. In this system, analyte ions are partially resolved from matrix ions on a conventional IC column (e.g., 4 mm i.d.) in the first dimension, collected onto a capillary concentrator column, then resolved from residual matrix ions on a capillary IC column (e.g., 400 μm i.d.) in the second dimension. It is important to determine the optimum cut time from the first dimension to ensure that the target analyte is efficiently retained on the concentrator column before determining it in the second dimension. For determination of perchlorate, 4 mm Thermo Scientific Dionex IonPac™ AG16/AS16 columns were used in the first dimension, a prototype AS20 column was used in the second dimension, and the cut time window of 19 to 24 min was used to load 5000 μL of the first-dimension effluent onto the capillary concentrator column. For determination of bromate, 4 mm Dionex IonPac AG19/AS19 columns were used in the first dimension, a prototype AS20 column was used in the second dimension, and the cut time window of 7.5 to 10 min was used to load 2500 μL of the first-dimension effluent onto the capillary concentrator column.
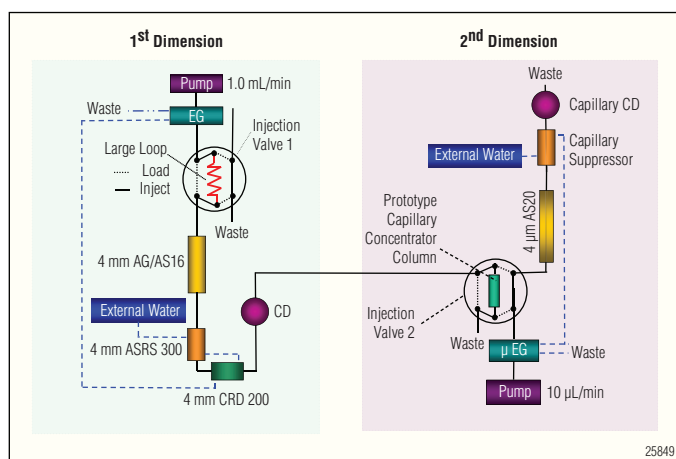


Figure 2. Prototype 2-D RFIC system using a capillary column in the second separation dimension.

## RESULTS AND DISCUSSION

The RFIC systems developed in this study use prototype capillary electrolytic eluent generators to generate acid or base eluents on-line using deionized water as the carrier stream. The electrolytic eluent generator in the capillary format provides an ideal eluent generation and delivery platform for both isocratic and gradient capillary separations for several reasons: First, the electrolytic eluent generators can be prepared with small dead volumes. Second, electrolytic eluent generators are capable of providing high-fidelity gradient profiles at low-μL/min flow rates through precise current and flow rate controls. Third, it is much more practical to generate higher concentrrations of eluents at low-μg/min flow rates.

The electrolytic suppressor is another key component of a capillary RFIC system. The desired characteristics of capillary IC suppressors include low dead volume, high suppression capacity, and low baseline noise. The capillary IC suppressors should be capable of continuous operation, easy to operate without requiring external acid or base regenerant solution, and it must be rugged and reliable. It is desirable that the capillary IC suppressors are compatible with mass spectrometry detection. The prototype capillary-scale suppressors developed in this study offer these characteristics.

The prototype capillary RFIC systems with suppressed conductivity detector are capable of providing performance comparable to or better than those used in the conventional RFIC systems. Figure 3 shows the gradient separation of a complex mixture of 22 anions on a prototype capillary Dionex IonPac AS19 column at a flow rate of 10 μL/min. The results demonstrate that the capillary IC system provided highly reproducible separation of target analytes under the gradient elution conditions with retention time % RSDs ranging from 0.09 for arsenate to 0.18 for fluoride. Capillary RFIC systems are capable of providing improved determination of target analytes at trace levels using small volumes of sample. Figure 4 shows determination of trace-level bromate in drinking water using a prototype capillary Dionex IonPac AS19 column. The results demonstrate that the system was able to determine bromate at low-μg/L levels using only 10 μL of sample.
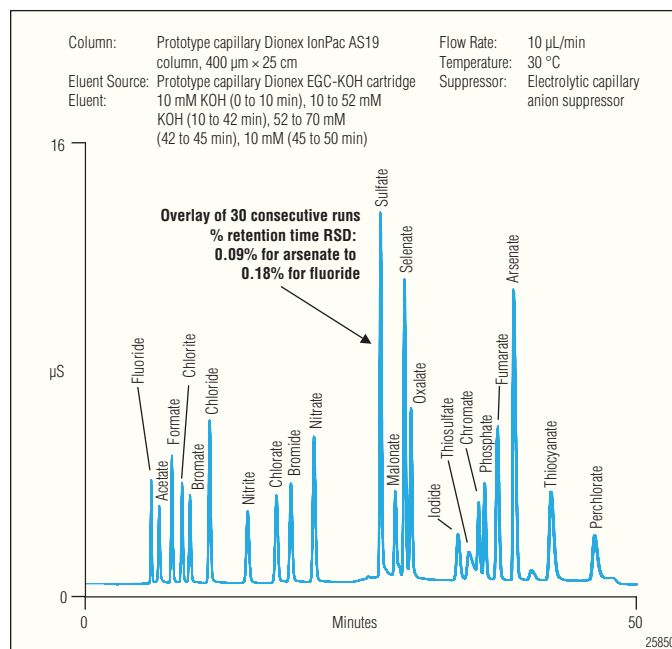


Figure 3. Gradient separation of 22 anions on prototype capillary Dionex IonPac AS19 column.

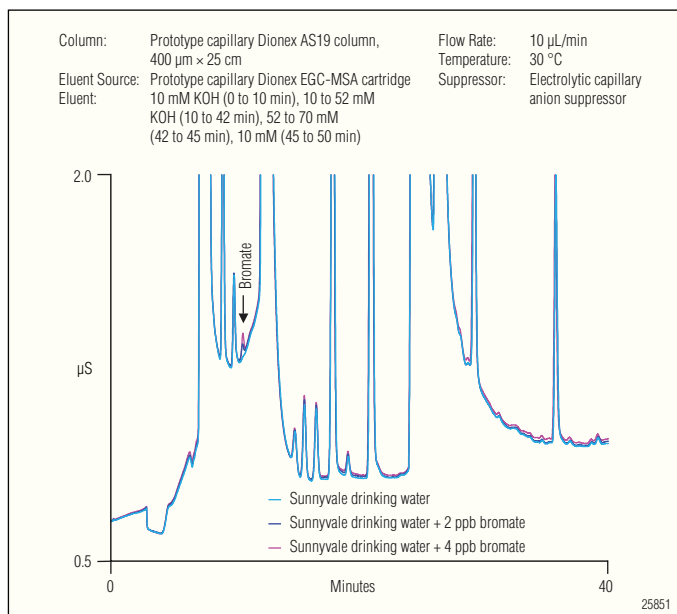| Column: | Prototype capillary Dionex AS19 column, 400 µm × 25 cm | Flow Rate: | 10 µL/min |
| Eluent Source: | Prototype capillary Dionex EGC-MSA cartridge | Temperature: | 30 °C |
| Eluent: | 10 mM KOH (0 to 10 min), 10 to 52 mM KOH (10 to 42 min), 52 to 70 mM (42 to 45 min), 10 mM (45 to 50 min) | Suppressor: | Electrolytic capillary anion suppressor |

*Figure 4. Determination of trace-level bromate in drinking water samples using a prototype capillary Dionex AS19 column and large loop (10 µL) injection.*

In the prototype 2-D IC system RFIC system with a second-dimension capillary column, a predefined volume of suppressed effluent from the first separation dimension is concentrated on the capillary concentrator. Because the suppressed effluent from the hydroxide eluent in the first dimension is water, it provides the ideal environment for ion-exchange retention and concentration before the target analyte is transferred to the second dimension. Because the second-dimension column has only $\frac{1}{10}$ the cross-sectional area of the first-dimension column, detection sensitivity is theoretically enhanced by a factor of 100. In addition, the 2-D IC method makes it possible to combine two different column chemistries for enhanced separation selectivity. Figure 5 shows determination of trace-level perchlorate using a prototype 2-D RFIC system with a second-dimension capillary column. For a 4000 µL injection of a 1 µg/L perchlorate standard, the first-dimension separation yielded a response of 0.0115 µS/min for perchlorate, and the second-dimension separation produced a response of 1.75 µS/min, or signal enhancement factor of about 152.
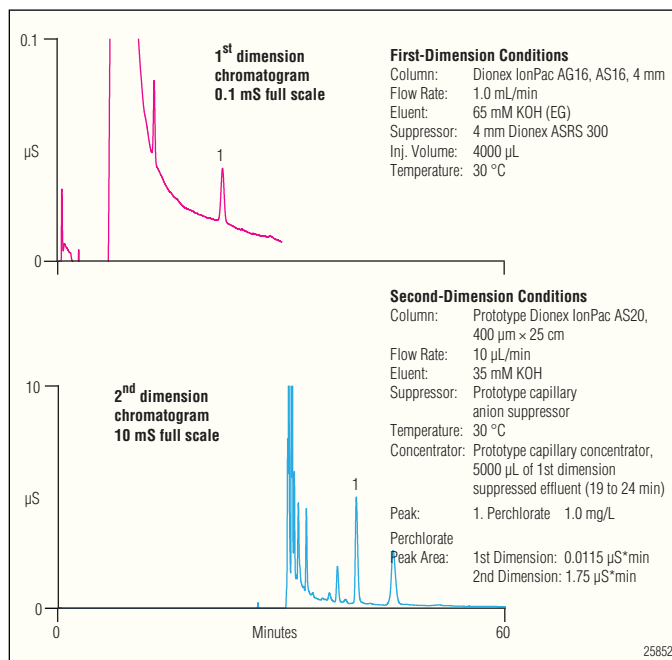


*Figure 5. Determination of trace-level perchlorate using a prototype 2-D RFIC system with a second-dimension capillary column.*

Figure 6 shows the overlay of three second-dimension chromatograms obtained for samples including deionized water, 30 ng/L perchlorate in deionized water, and 30 ng/L perchlorate in 1000 mg/L chloride, sulfate and bicarbonate. The results indicate clearly that the prototype system is capable of determining perchlorate at ultratrace levels (e.g., 30 ng/L perchlorate) even in high-ionic-strength matrices.
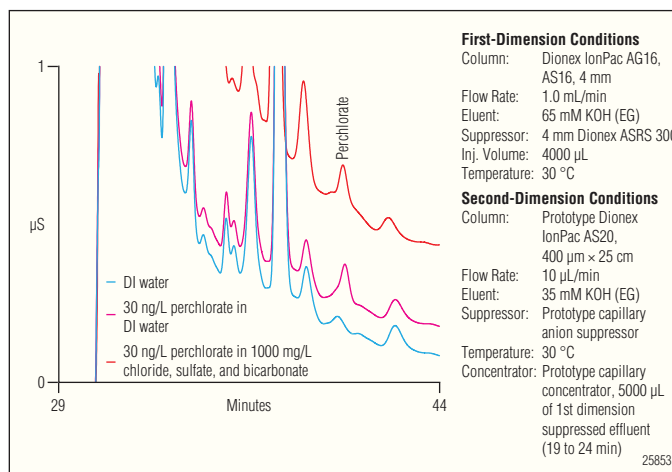


*Figure 6. Determination of trace-level perchlorate using a prototype 2-D RFIC system with a second-dimension capillary column.*

Table 2 summarizes the 2-D RFIC system calibration and method detection limit data for perchlorate. When compared to the two-dimensional RFIC system using the 2 mm ID column in the second dimension, the prototype 2-D RFIC System, using the 400 μm ID capillary column in the second dimension, provided improved performance in terms of method linearity range and detection limits for perchlorate.

| Table 2. 2-D RFIC System Calibration and Method Detection Limit Data for Perchlorate | | | | | |
|---|---|---|---|---|---|
| 2-D RFIC System | Range (μg/L) | Linearity (r²) | MDL Standard (μg/L) | SD (μg/L) | Calculated MDL (μg/L) |
| Thermo Scientific Dionex ICS-3000 (4 mm/2 mm columns) | 0.05–10 | 0.9999 | 0.05 | ± 0.006 | 0.018 |
| Prototype Capillary IC System (4 mm/400 μm columns) | 0.01–10 | 0.9999 | 0.03 | ± 0.001 | 0.003 |

In this study, the 2-D IC RFIC system with a second-dimension capillary column was applied to determine perchlorate and bromate levels in samples of drinking water and ground water. Figure 7 shows the overlay of second-dimension chromatograms obtained for bottled water samples. Both Brand A and Brand B bottled waters were naturally carbonated. The results indicate they contained 263 ng/L perchlorate and 38.5 ng/L perchlorate, respectively.
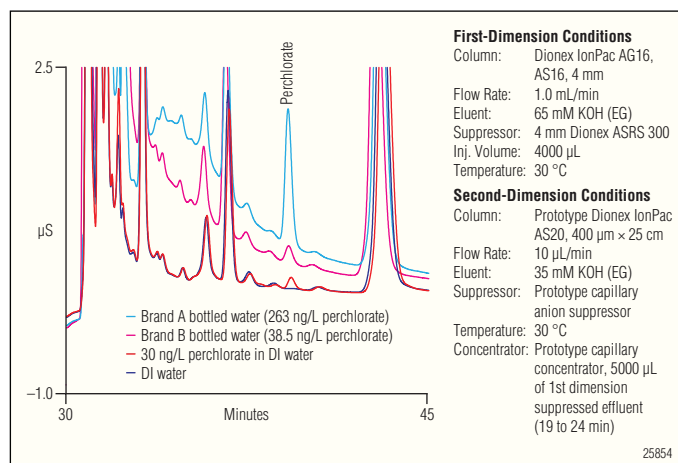


**First-Dimension Conditions**
Column: Dionex IonPac AG16, AS16, 4 mm
Flow Rate: 1.0 mL/min
Eluent: 65 mM KOH (EG)
Suppressor: 4 mm Dionex ASRS 300
Inj. Volume: 4000 μL
Temperature: 30 °C

**Second-Dimension Conditions**
Column: Prototype Dionex IonPac AS20, 400 μm × 25 cm
Flow Rate: 10 μL/min
Eluent: 35 mM KOH (EG)
Suppressor: Prototype capillary anion suppressor
Temperature: 30 °C
Concentrator: Prototype capillary concentrator, 5000 μL of 1st dimension suppressed effluent (19 to 24 min)

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*Figure 7. Determination of perchlorate in bottled water samples using a proto-type 2-D RFIC system with a second-dimension capillary column.*

Figure 8 shows determination of perchlorate in well water samples using the prototype 2-D RFIC system with a second-dimension capillary column. The samples were collected from a private well in Morgan Hill, CA (near a known perchlorate contamination site), and diluted 1:100 before analysis. The results indicate that the well water contained a relatively high concentration of perchlorate (3410 ng/L) when untreated. The concentration of perchlorate in reversed-osmosis (RO)-treated well water was 3 ng/L. The results suggest that RO process is effective in removing perchlorate from well water samples.
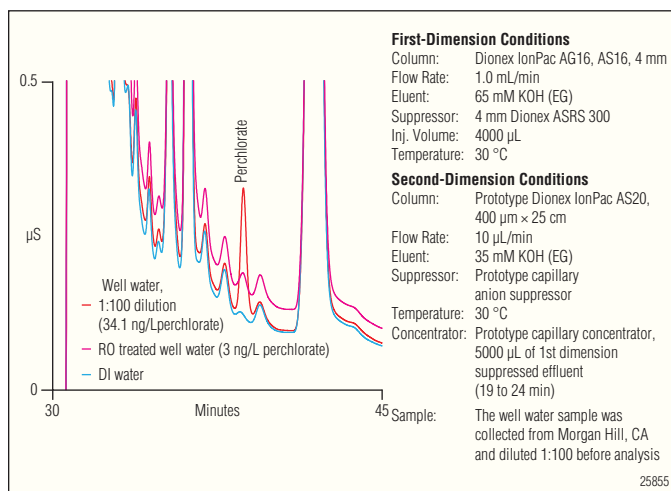


**First-Dimension Conditions**
Column: Dionex IonPac AG16, AS16, 4 mm
Flow Rate: 1.0 mL/min
Eluent: 65 mM KOH (EG)
Suppressor: 4 mm Dionex ASRS 300
Inj. Volume: 4000 μL
Temperature: 30 °C

**Second-Dimension Conditions**
Column: Prototype Dionex IonPac AS20, 400 μm × 25 cm
Flow Rate: 10 μL/min
Eluent: 35 mM KOH (EG)
Suppressor: Prototype capillary anion suppressor
Temperature: 30 °C
Concentrator: Prototype capillary concentrator, 5000 μL of 1st dimension suppressed effluent (19 to 24 min)
Sample: The well water sample was collected from Morgan Hill, CA and diluted 1:100 before analysis

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*Figure 8. Determination of perchlorate in well water samples using a prototype 2-D RFIC system with a second-dimension capillary column.*

Figure 9 shows determination of bromate in bottled water samples using the prototype 2-D RFIC system with a second-dimension capillary column. The results indicate that the system was capable of determining bromate at parts-per-billion levels in drinking water samples.
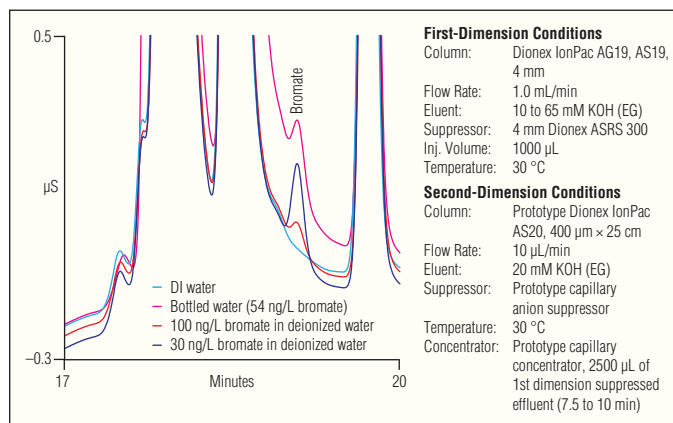


**First-Dimension Conditions**
Column: Dionex IonPac AG19, AS19, 4 mm
Flow Rate: 1.0 mL/min
Eluent: 10 to 65 mM KOH (EG)
Suppressor: 4 mm Dionex ASRS 300
Inj. Volume: 1000 μL
Temperature: 30 °C

**Second-Dimension Conditions**
Column: Prototype Dionex IonPac AS20, 400 μm × 25 cm
Flow Rate: 10 μL/min
Eluent: 20 mM KOH (EG)
Suppressor: Prototype capillary anion suppressor
Temperature: 30 °C
Concentrator: Prototype capillary concentrator, 2500 μL of 1st dimension suppressed effluent (7.5 to 10 min)

*Figure 9. Determination of trace-level bromate in drinking water samples using a prototype 2-D RFIC system with 2-D capillary column.*

In this study, a prototype capillary IC system was interfaced to an MS/MS mass spectrometer system. Table 3 summarizes typical operating conditions of the system.

| Table 3. Operating Conditions of a Prototype Capillary IC System Coupled to MS/MS System | |
|---|---|
| **Capillary IC System** | |
| Column: | Prototype Dionex IonPac AS20, 400 µm x 25 cm |
| Eluent Source: | Prototype capillary Dionex EGC-KOH cartridge |
| Flow Rate: | 10–20 µL/min |
| Temperature: | 30 °C |
| Suppressor: | Prototype electrolytic capillary anion suppressor operated in the external water mode |
| **MS/MS System** | |
| Post-suppressor addition of acetonitrile at 15 µL/min via a grounded 0.15 mm bore mixing tee | |
| Negative ESI with optimized probe position | |
| Optimized multiple reaction monitoring (MRM) channels for target analytes | |

Column: Prototype Dionex IonPac AS20, 400 µm × 25 cm
Eluent Source: Prototype capillary Dionex EGC-KOH cartridge
Eluent: 40 mM KOH
Flow Rate: 20 µL/min
Temperature: 30 °C
Suppressor: Electrolytic capillary anion suppressor
Detection: MS/MS with post suppressor addition of acetonitrile at 15 µL/min; Negative ESI, MRM $m/z$ 99−$m/z$ 83
Inj. Volume: 10 µL
Sample Matrix: 1500 mg/L chloride and sulfate, 800 mg/L carbonate, and 180 mg/L nitrate
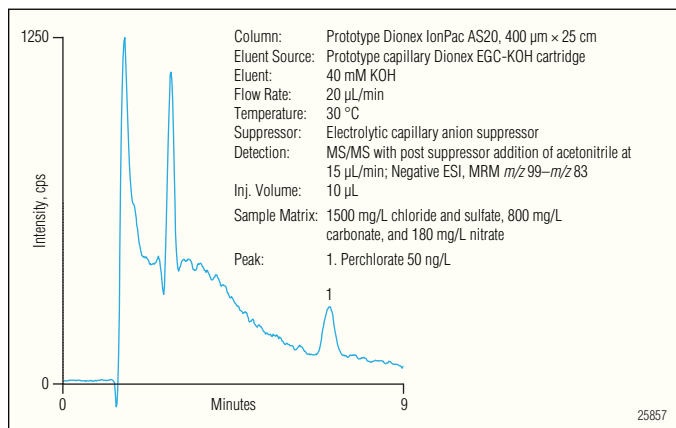Peak: 1. Perchlorate 50 ng/L

*Figure 10. Determination of perchlorate (50 ng/L) in high-ionic-strength matrix without sample preparation using a prototype capillary IC and MS/MS system.*

Figure 11 shows determination of 13 inorganic and organic anions using the prototype capillary IC and MS/MS system. The gradient separation of the thirteen target analytes were performed using KOH eluent on a prototype capillary Dionex IonPac AS20 column. Operating the MS/MS system in the negative ESI mode and optimizing the MRM channels, the capillary IC system was capable of detecting all target analytes at 10 µg/L with excellent signal-to-noise ratios.

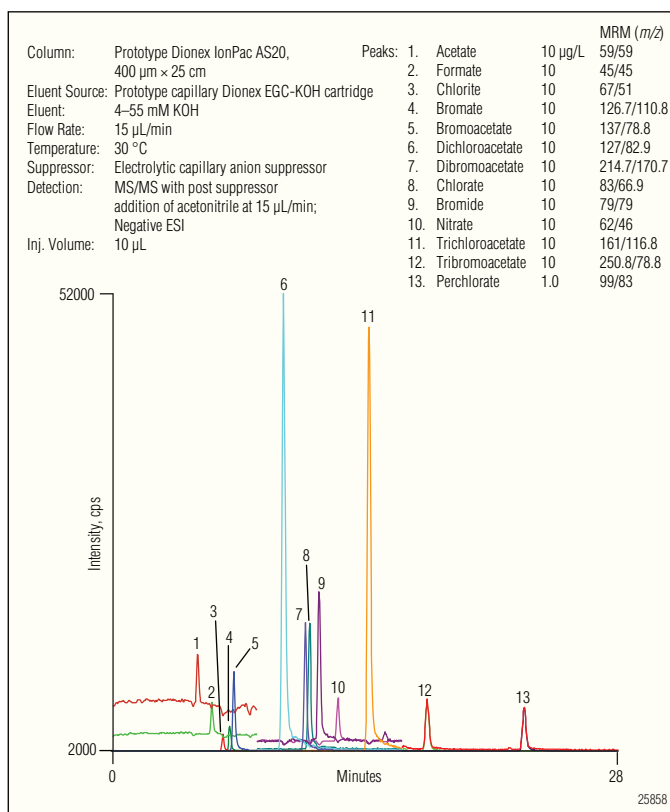| Column: | Prototype Dionex IonPac AS20, 400 µm × 25 cm | | Peaks: | | | | MRM ($m/z$) |
|---|---|---|---|---|---|---|---|
| | | | | 1. | Acetate | 10 µg/L | 59/59 |
| Eluent Source: | Prototype capillary Dionex EGC-KOH cartridge | | | 2. | Formate | 10 | 45/45 |
| Eluent: | 4–55 mM KOH | | | 3. | Chlorite | 10 | 67/51 |
| Flow Rate: | 15 µL/min | | | 4. | Bromate | 10 | 126.7/110.8 |
| Temperature: | 30 °C | | | 5. | Bromoacetate | 10 | 137/78.8 |
| Suppressor: | Electrolytic capillary anion suppressor | | | 6. | Dichloroacetate | 10 | 127/82.9 |
| Detection: | MS/MS with post suppressor addition of acetonitrile at 15 µL/min; Negative ESI | | | 7. | Dibromoacetate | 10 | 214.7/170.7 |
| | | | | 8. | Chlorate | 10 | 83/66.9 |
| | | | | 9. | Bromide | 10 | 79/79 |
| Inj. Volume: | 10 µL | | | 10. | Nitrate | 10 | 62/46 |
| | | | | 11. | Trichloroacetate | 10 | 161/116.8 |
| | | | | 12. | Tribromoacetate | 10 | 250.8/78.8 |
| | | | | 13. | Perchlorate | 1.0 | 99/83 |

*Figure 11. Determination of inorganic and organic anions using a prototype capillary IC and MS/MS system.*

## CONCLUSIONS

Our efforts in the development of capillary Reagent-Free IC systems with on-line electrolytic eluent generation have demonstrated that:

- Prototype capillary RFIC systems with suppressed conductivity detection offer highly reproducible isocratic and gradient separations of target analytes.
- Use of a capillary IC column as the second separation dimension in 2-D RFIC systems can lead to significant sensitivity and selectivity enhancement.
- Capillary RFIC systems with MS detection have the potential to become highly sensitive analytical tools.

Further development of capillary RFIC systems will lead to improved ion chromatographic methods for determination of ionic analytes.

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