Improved Determination of Trace Concentrations of Perchlorate in Drinking Water with Analytical/Capillary Two-Dimensional Ion Chromatography

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Overview

**Purpose:** An ion chromatography (IC) method for the determination of trace perchlorate in drinking water.

**Methods:** In the two-dimensional (2D) system, perchlorate is partially resolved in the first dimension from the sample matrix, collected onto a concentrator column, and then resolved in the second dimension, followed by suppressed conductivity detection.

**Results:** This method demonstrates a MDL of 0.005 µg/L and recoveries of 101–106% in various sample matrices. The analytical/capillary 2D system allows enhanced automation and minimized reagent consumption.

Introduction

Perchlorate is identified as an environmental contaminant found in drinking, ground, and surface waters. It impairs normal thyroid function by interfering with iodine uptake by the thyroid gland. Some drinking water sources contain high concentrations of anions, which can pose a challenge in determining perchlorate at µg/L concentrations with accuracy and precision. This work presents an improvement to U.S. EPA Method 314.2 by using an analytical/capillary 2D Reagent-Free™ IC (RFIC™) system. Significant enhancement in sensitivity is achieved due to a large increase in the concentration factor using the capillary format in the second dimension. The 2 mm i.d./0.4 mm i.d. 2D configuration is operated with a lower flow rate, thus greatly reducing reagent consumption and system maintenance.

Methods

**Liquid Chromatography**

Thermo Scientific Dionex ICS-5000 system including:

- DP Dual Pump
- EG Eluent Generator
- DC Detector/Chromatography Compartment
- AS-AP Autosampler
**First Dimension**

Columns: Thermo Scientific Dionex IonPac AS20 Analytical, 2 × 250 mm  
Dionex IonPac™ AG20 Guard, 2 × 50 mm

Eluent Source: Thermo Scientific Dionex EGC III KOH  
Eluent Generation Cartridge with Thermo Scientific Dionex CR-ATC Continuously-Regenerated Anion Trap Column

Eluent: 35 mM KOH 0–30 min, step to 60 mM at 30.1 min, 60 mM 30.1–40 min, step to 35 mM at 40.1 min, 35 mM 40.1–45 min

Flow Rate: 0.25 mL/min

Inj. Volume: 500 µL

Temperature: 15 °C (upper compartment)  
30 °C (lower compartment)

Detection: Suppressed conductivity, Thermo Scientific Dionex ASRS 300 Anion Self-Regenerating Suppressor 2 mm, 38 mA, external water mode

**Second Dimension**

Columns: Dionex IonPac AS16 Capillary Analytical, 0.4 × 250 mm  
Dionex IonPac AG16 Capillary Guard, 0.4 × 50 mm

Eluent Source: Dionex EGC-KOH (Capillary) Cartridge with Dionex CR-ATC Continuously Regenerated Anion Trap Column (Capillary)

Eluent: 65 mM KOH

Flow Rate: 0.01 mL/min

Inj. Volume: 1 mL (on the concentrator column from first dimension)

Temperature: 15 °C (upper compartment)  
30 °C (Dionex IC Cube)

Concentrator: Thermo Scientific Dionex IonSwift MAC-200 Monolith Anion Concentrator Column

Detection: Suppressed conductivity, Thermo Scientific Dionex ACES 300 Anion Capillary Electrolytic Suppressor, 12 mA, external water mode
Data Analysis

Thermo Scientific Dionex Chromeleon 7.1 Chromatography Data System (CDS) software was used for chromatographic data collection and processing.

FIGURE 1. Schematic diagram of the analytical/capillary 2D system: perchlorate is resolved from the matrix on a 2 mm Dionex IonPac AS20 column, concentrated on a monolithic capillary concentrator, separated on a 0.4 mm Dionex IonPac AS16 column, and detected by suppressed conductivity detection.

Results

For the same amount of analyte injected, the response is inversely proportional to the cross sectional area of the column. The 2 mm i.d./0.4 mm i.d. system in the present work provides a larger increase in concentration factor than the 4 mm i.d./2 mm i.d. 2D system described in EPA Method 314.2, thereby providing improved sensitivity.
FIGURE 2. Chromatogram of 2 µg/L perchlorate standard in reagent water in (A) first dimension and (B) second dimension.

TABLE 1. Calibration data and method detection limits (MDLs) of perchlorate.

<table>
<thead>
<tr>
<th>Analyte</th>
<th>Range (µg/L)</th>
<th>Linearity (r²)</th>
<th>MDL Standard (µg/L)</th>
<th>SD (µg/L)</th>
<th>Calculated MDL (µg/L)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Perchlorate</td>
<td>0.01–10</td>
<td>0.9998</td>
<td>0.02</td>
<td>0.002</td>
<td>0.005</td>
</tr>
</tbody>
</table>

* Quadratic fit, peak area vs. concentration
** MDL = (SD) × (tα), where (tα) is Student's t-value for a 99% confidence level (t = 3.14 for seven replicate injections)
FIGURE 3. Chromatogram of 0.1 µg/L perchlorate standard in reagent water in the second dimension.

FIGURE 4. Chromatograms of synthetic high inorganic water containing 1000 mg/L each of chloride, sulfate, and bicarbonate fortified with 0.2 µg/L perchlorate in (A) first dimension and (B) second dimension.
FIGURE 5. Second dimension chromatograms of drinking water samples fortified with 0.2 µg/L.

TABLE 2. Perchlorate recoveries from laboratory fortified samples.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Amount Found (µg/L)</th>
<th>Amount Added (µg/L)</th>
<th>Replicates</th>
<th>Peak Area Precision (RSD)</th>
<th>Recovery (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Reagent Water</td>
<td>–</td>
<td>0.2</td>
<td>7</td>
<td>2.61</td>
<td>102.4</td>
</tr>
<tr>
<td></td>
<td></td>
<td>2.0</td>
<td>7</td>
<td>0.91</td>
<td>102.6</td>
</tr>
<tr>
<td>HIW*</td>
<td>–</td>
<td>0.2</td>
<td>7</td>
<td>1.70</td>
<td>109.5</td>
</tr>
<tr>
<td></td>
<td></td>
<td>2.0</td>
<td>7</td>
<td>0.34</td>
<td>106.0</td>
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<tr>
<td>Drinking Water A</td>
<td>0.056</td>
<td>0.2</td>
<td>7</td>
<td>1.20</td>
<td>92.8</td>
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<tr>
<td></td>
<td></td>
<td>2.0</td>
<td>7</td>
<td>0.85</td>
<td>102.9</td>
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<tr>
<td>Drinking Water B</td>
<td>0.128</td>
<td>0.2</td>
<td>7</td>
<td>2.93</td>
<td>93.6</td>
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<tr>
<td></td>
<td></td>
<td>2.0</td>
<td>7</td>
<td>0.69</td>
<td>102.5</td>
</tr>
<tr>
<td>Drinking Water C</td>
<td>0.992</td>
<td>0.2</td>
<td>7</td>
<td>0.64</td>
<td>94.4</td>
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<td></td>
<td></td>
<td>2.0</td>
<td>7</td>
<td>0.40</td>
<td>100.8</td>
</tr>
</tbody>
</table>

* HIW = High ionic strength water containing 1000 mg/L each of chloride, sulfate and bicarbonate.
Conclusion

- The 2D configuration using a RFIC system provides enhanced automation and improved precision.
- Significant enhancement in sensitivity is achieved due to a large increase in concentration factor using the capillary format in the second dimension. This method demonstrates an MDL of 0.005 µg/L.
- The 2 mm i.d./0.4 mm i.d. configuration greatly reduces reagent consumption, minimizing instrument maintenance.
- Good selectivity is demonstrated by combining two columns with two different column chemistries in the 2D configuration.

References
