Ion Chromatographic Determination of Oxyhalides and Bromide at Trace Level Concentrations in Drinking Water Using Direct Injection

**INTRODUCTION**

The U.S. EPA Information Collection Rule (ICR) requires drinking water utilities serving more than 100,000 customers to report the concentration of target microorganisms present, the removal process used, and the concentration of disinfection byproducts (DBP) present in their waters. The monitoring period began in July 1997 and will continue for 18 months. The ICR will affect approximately 300 drinking water utilities in the United States.

The U.S. EPA recommends Method 300.0 (B), which specifies ion chromatography with chemically suppressed conductivity detection, to monitor chlorite, bromate, and chloride in drinking water. Bromide, a precursor to bromate, must also be monitored down to levels as low as 10 ppb, because bromate has been classified as a potential carcinogen, even at low ppb levels, by the U.S. EPA and the World Health Organization. Under the ICR, utilities using hypochlorite solution as a disinfectant are required to monitor chlorate; those using chlorine dioxide are required to monitor chlorite, chlorate, and bromate; and those using ozone are required to monitor bromate. All utilities are required to monitor bromide.

This Application Note describes an isocratic separation using the IonPac® AS9-HC column to determine trace levels of oxyhalides and bromide in the presence of common anions in drinking water, as well as their detection limits and linear concentration ranges. The AS9-HC column method was developed to improve the separation between bromate and chloride, thus allowing lower detection limits of bromate in the presence of high chloride concentrations. Unlike previous IC methods for these ions, no pretreatment cartridges are required to remove high concentrations of common ions such as chloride, bicarbonate, and sulfate. The instrumentation, techniques, and representative applications of this method are discussed in this Note.

**EQUIPMENT**

Dionex DX-500 Ion Chromatography system consisting of:
- GP40 Gradient Pump
- CD20 Conductivity Detector
- AS40 Automated Sampler
- LC20 Chromatography Enclosure equipped with a rear-loading injection valve
- 4-L Plastic bottle assemblies (for external water mode)
- PeakNet Chromatography Workstation

**REAGENTS AND STANDARDS**

Deionized water, Type I reagent grade, 18 MΩ-cm resistance or better
- 0.5 M Carbonate Anion Eluent Concentrate (in deionized water) (Dionex P/N 37162)
- Sodium and Potassium salts, ACS reagent grade, for preparing anion standards (see Table 1) (Fisher Scientific, EM Science)
**CONDITIONS**

Columns: IonPac AS9-HC Analytical, 4 x 250 mm (P/N 51786)
IonPac AG9-HC Guard, 4 x 50 mm (P/N 51791)

Eluent: 9 mM Sodium carbonate

Run Time: 25 min

Flow Rate: 1 mL/min

Sample Vol.: 200 µL

Detection: Suppressed conductivity, ASRS™-II, 4 mm, AutoSuppression™ external water mode

**PREPARATION OF SOLUTIONS AND REAGENTS**

**Standard Solutions**

**Stock Anion Standard Solution (1000 mg/L)**

Dissolve the corresponding mass of the salt for each of the anions of interest (see Table 1) in 1000 mL of deionized water. Standards are stable for at least one month when stored at 4 °C.

<table>
<thead>
<tr>
<th>Anion</th>
<th>Compound</th>
<th>Mass (g)</th>
</tr>
</thead>
<tbody>
<tr>
<td>F⁻</td>
<td>Sodium fluoride (NaF)</td>
<td>2.210</td>
</tr>
<tr>
<td>ClO₂⁻</td>
<td>Sodium chlorite (NaClO₂•2H₂O)</td>
<td>2.409</td>
</tr>
<tr>
<td>BrO₃⁻</td>
<td>Sodium bromate (NaBrO₃)</td>
<td>1.180</td>
</tr>
<tr>
<td>Cl⁻</td>
<td>Sodium chloride (NaCl)</td>
<td>1.648</td>
</tr>
<tr>
<td>NO₂⁻</td>
<td>Sodium nitrite (NaNO₂)</td>
<td>1.500</td>
</tr>
<tr>
<td>Br⁻</td>
<td>Sodium bromide (NaBr)</td>
<td>1.288</td>
</tr>
<tr>
<td>ClO₃⁻</td>
<td>Sodium chlorate (NaClO₃)</td>
<td>1.276</td>
</tr>
<tr>
<td>NO₃⁻</td>
<td>Sodium nitrate (NaNO₃)</td>
<td>1.371</td>
</tr>
<tr>
<td>H₂PO₄</td>
<td>Potassium phosphate, monobasic (KH₂PO₄)</td>
<td>1.433</td>
</tr>
<tr>
<td>SO₄²⁻</td>
<td>Potassium sulfate (K₂SO₄)</td>
<td>1.814</td>
</tr>
<tr>
<td>HCO₃⁻</td>
<td>Sodium bicarbonate (NaHCO₃)</td>
<td>1.377</td>
</tr>
</tbody>
</table>

**Working Standard Solutions**

Dilute each analyte to the required concentration with deionized water using the 1000-mg/L standards prepared above. Working standards containing less than 100-µg/L anions should be prepared daily.

**Eluent Solution**

9 mM Sodium carbonate

Dilute 18 mL of 0.5 M sodium carbonate concentrate to 1 L with deionized water. Transfer to an eluent container and blanket with helium at 0.055 MPa (8 psi).

**Preservation Solution**

45 g/L Ethylenediamine preservation solution

Dilute 10 mL of 99% ethylenediamine (Fluka) to 200 mL with water. Use 1 mL of this solution per liter of sample.

**SAMPLE PREPARATION**

Sparge samples for 5 minutes to remove any reactive gases (e.g., chlorine dioxide or ozone). To prevent oxidation of chlorite to chlorate or formation of bromate from hypobromite, preserve samples by adding 1 mL of ethylenediamine preservation solution per liter of sample.

**DISCUSSION AND RESULTS**

The IonPac AS9-HC provides baseline separation of chlorite, chlorate, bromate, and bromide from common anions and provides good resolution between bromate and chloride to allow a low detection level of 5 µg/L (5 ppb) for bromate in the presence of a high chloride (50 mg/L) concentration. Figure 1 shows a typical chromatogram of a separation of common anions and oxyhalides on the IonPac AS9-HC column.

For the best performance at low levels, it is critical that baseline noise be kept to a minimum. From start up, a system for trace analysis typically requires about 5 hours to reach steady state.
establish a stable background conductivity. For this reason, it is best to keep the system running continuously. Ensure that there is an adequate supply of the eluents, external water, and waste containers to allow the system to run unattended. An equilibrated system will have a background conductivity between 20–24 $\mu$S. To keep a conductivity background at that low level throughout a whole day without significant drift, it is absolutely necessary to use external water mode rather than recycle mode. Peak-to-peak noise is typically 6–10 nS. Figure 2 shows the determination of low levels of oxyhalides and bromide in simulated drinking water. Seven injections of this same concentration standard were made to determine method detection limits of oxyhalides and bromide in simulated drinking water. Table 2 shows the results.

The data demonstrate that this method achieves the required method detection limits and exceeds the standard deviation requirements of the current ICR. It is important to establish a linear concentration range to accurately quantify oxyhalides and bromide in the presence of common anions in drinking water. Table 3 summarizes the results of the linearity analyses. In these analyses, seven different concentrations of each analyte were analyzed using a 200-$\mu$L sample injection. Table 3 shows that bromate is linear between 5–40 $\mu$g/L, and chlorite, chlorate, and bromide are linear between 20–500 $\mu$g/L.

The chosen ranges for oxyhalides and bromide are characteristic for the amounts of those analytes commonly found in drinking water. Concentrations outside these ranges were not tested. However, it is expected that the method is linear to higher concentrations. The linearity data also demonstrate method ruggedness and good column performance, which allow accurate and precise achievement of the ICR requirements. The concentration range experiment was repeated with the addition of ethylenediamine preservation solution to all of the samples to establish whether the presence of ethylenediamine would have any significant effect on chromatography and recovery of oxyhalides. No significant differences were observed.

### Table 2

Method detection limits for oxyhalides and bromide in simulated drinking water based on a 200-$\mu$L injection volume using the IonPac AS9-HC column

<table>
<thead>
<tr>
<th>Conc. Std. Dev. RSD MDL*</th>
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</tr>
</thead>
<tbody>
<tr>
<td>(µg/L)</td>
<td>(µg/L)</td>
<td>(µg/L)</td>
</tr>
<tr>
<td>Chlorite</td>
<td>10</td>
<td>0.76</td>
</tr>
<tr>
<td>Bromate</td>
<td>5</td>
<td>0.55</td>
</tr>
<tr>
<td>Bromide</td>
<td>10</td>
<td>0.57</td>
</tr>
<tr>
<td>Chlorate</td>
<td>10</td>
<td>0.34</td>
</tr>
</tbody>
</table>

*MDL = SD x t<sub>0.05</sub> where t<sub>0.05</sub> = 3.14 for n = 7

Sample also contained: Chloride 50 mg/L, Bicarbonate 150 mg/L, Sulfate 50 mg/L.

### Table 3

Linear concentration range study of oxyhalides and bromide in simulated drinking water using the IonPac AS9-HC

<table>
<thead>
<tr>
<th>Conc. Std. Dev. RSD MDL*</th>
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</tr>
</thead>
<tbody>
<tr>
<td>(µg/L)</td>
<td>(µg/L)</td>
<td>(µg/L)</td>
</tr>
<tr>
<td>Bromate</td>
<td>5–40</td>
<td>2.09</td>
</tr>
<tr>
<td>Chlorite</td>
<td>20–500</td>
<td>20.07</td>
</tr>
<tr>
<td>Bromide</td>
<td>20–500</td>
<td>10.32</td>
</tr>
<tr>
<td>Chlorate</td>
<td>20–500</td>
<td>4.05</td>
</tr>
</tbody>
</table>

* Standard deviation was calculated as a function of the response factor. Response factor equals the ratio of area count to concentration.
Figure 3  Large loop injection for µg/L-level oxyhalide analysis.

The effect of injection volume on simulated drinking water analysis was investigated. Figure 3 illustrates that a 500-µL injection is the largest amount of the simulated drinking water sample that can be injected onto the column without considerable loss of resolution between bromate and chloride. With a 750-µL injection, column ion-exchange sites are overloaded, which causes coelution of bromate and chloride. The IonPac AS9-HC column allows large sample loop injections (e.g., 200 µL) to achieve low detection limits even in the presence of high concentrations of chloride, sulfate, and bicarbonate.

**SUMMARY**

An improved column and method for the determination of oxyhalides and bromide in drinking water have been developed. Using this method, these anions can be detected in a concentration range that exceeds the ICR requirements. Linear concentration ranges have been established to accurately quantitate the oxyhalides and bromide in drinking water samples.

**REFERENCES**


**LIST OF SUPPLIERS**

Fisher Scientific, 711 Forbes Avenue, Pittsburgh, Pennsylvania, 15219-4785, USA.
Tel: 1-800-766-7000.

EM Science, 480 Democrat Road, Gibbstown, New Jersey 08027, USA. Tel: 1-609-354-9200.

Fluka Chemika-BioChemika, Fluka Chemie AG, Industriestrasse 25, CH-9471 Buchs, Switzerland.
Tel: 081 755 25 11.