

Determination of Trace Concentrations of Oxyhalides and Bromide in Municipal and Bottled Waters Using a Hydroxide-Selective Column with a Reagent-Free™ Ion Chromatography System

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Introduction

All drinking water municipalities share the same goal of providing their communities with a reliable source of safe drinking water. To achieve this goal, most water systems must treat their water. The type of treatment used varies depending on the size, source, and water quality.¹ Disinfection protects public water systems (PWSs) from potentially dangerous microbes. The most common chemical disinfectants are chlorine, chlorine dioxide, chloramine, and ozone.^{1,2} These chemical disinfectants can react with natural organic and inorganic matter in the source water to produce disinfection byproducts (DBPs) that are potentially harmful to humans. For example, chlorination of drinking water can produce trihalomethanes, haloacetic acids, and chlorate. While chlorine dioxide treatment generates the inorganic oxyhalide DBPs chlorite and chlorate, and the presence of chloramine has also been known to generate chlorate.² Ozone reacts with naturally occurring bromide to produce bromate. The International Agency for Research on Cancer has identified bromate as an animal carcinogen and potential human carcinogen.³ The World Health Organization (WHO) has estimated⁴ an excess lifetime cancer risk of 10^{-5} for drinking water containing bromate at 3 µg/L.*

* Probable increase in deaths due to a cancer, $10^{-5} = 1$ in 100,000 people

From July 1997 to December 1998, the U.S. Environmental Protection Agency (EPA) documented the occurrence of bromate and other DBPs through a comprehensive collection of sampling data mandated by the Information Collection Rule (ICR).⁵ The ICR required that PWSs serving 100,000 or more connections report the concentration of target microorganisms present, the removal process used, and the concentration of DBPs present in their drinking water. In 1998, the EPA set the maximum contaminant level (MCL) for bromate at

10 µg/L and chlorite at 1000 µg/L under the Disinfectants/Disinfection Byproducts (D/DBP) Stage 1 Rule.⁶ This rule resulted in the promulgation of EPA Method 300.1 as an update to Method 300.0. Method 300.1 reduced the detection limit for bromate from 20 to 1.4 µg/L to allow the PWSs' laboratories to meet the MCL requirement set by the EPA.⁷ The European Union (EU Directive 98/83/EC) also proposed the same regulatory value of 10 µg/L bromate (previously at 50 µg/L) in drinking water.⁸

The U.S. EPA reconvened in 2003 to establish the Stage 2 Rule of the D/DBP. Based on a thorough evaluation, the EPA could not estimate the additional benefits of reducing the MCL for bromate. Therefore, this rule resulted in no changes to the current MCL for either chlorite or bromate. However, additional methods for determining low µg/L bromate were promulgated under the Stage 2 Rule and included ion chromatography (IC) with postcolumn reaction (EPA Methods 317.0 and 326.0) and IC/ICP-MS (EPA Method 321.8). The addition of these methods resulted in improved sensitivity and selectivity for bromate.⁹ Recently, the WHO reduced their bromate guideline value from 25 µg/L to a provisional value of 10 µg/L bromate.⁴ This change resulted from the availability of improved analytical methods capable of determining low µg/L concentrations of bromate in environmental waters.

Unlike tap water, bottled water is treated as a food product in the U.S. and therefore regulated by the U.S. Food and Drug Administration (FDA). Bottled water is an increasingly popular product in the U.S. From 1997 to 2002, bottled water sales increased from roughly 6% to 13% per year of total beverage sales, according to the Beverage Marketing Corporation.¹⁰ Because some bottled water companies use ozone or other disinfection treatments, the FDA adopted the EPA's MCLs for chlorite and bromate and the analytical methods used to monitor these contaminants in public drinking water.¹¹ The FDA also requires that bottled water manufacturers monitor their finished product for these contaminants at least once each year under current good manufacturing practice as stated in part 129 of the Code of Federal Regulations (21 CFR part 129).

Previous methods developed for determining low $\mu\text{g/L}$ concentrations of bromate by direct injection have focused primarily on using columns specifically designed for carbonate eluents.^{12,13} Columns designed for use with hydroxide eluents have not been widely used for the determination of trace bromate in environmental waters due to their lack of appropriate column selectivity and the difficulty in preparing contaminant-free hydroxide eluents. The introduction of electrolytic eluent generation has not only eliminated the difficulty in preparing hydroxide eluents, but has simplified the development of optimized methods. In this application note, we use the Thermo Scientific™ Dionex™ IonPac™ AS19 column, a column specifically designed for use with hydroxide eluents and developed with an optimized selectivity for the determination of trace DBPs and bromide in environmental waters. We describe the linearity, method detection limits, and the recovery and precision of spiked municipal and bottled waters.

Equipment

- Thermo Scientific Dionex ICS-2000 Reagent-Free Ion Chromatography (RFIC™)* System was used in this work. The Dionex ICS-2000 is an integrated ion chromatograph and consists of:
 - Eluent Generator
 - Column Heater
 - Pump with Degasser
 - Thermo Scientific Dionex EluGen™ EGC II KOH Cartridge (P/N 058900)
 - Thermo Scientific Dionex CR-ATC Continuously Regenerated Anion Trap Column (P/N 060477)
- Thermo Scientific Dionex AS50 Autosampler
- Thermo Scientific Dionex Chromeleon™ Chromatography Workstation

*This application note is also applicable to other RFIC systems.

Reagents and Standards

- Deionized water, Type I reagent grade, 18 M Ω -cm resistivity or better
- Sodium and Potassium salts, A.C.S. reagent grade or better, for preparing anion standards (VWR or other)
- Fluoride standard 1000 mg/L, 100 mL (P/N 037158)
- Chloride standard 1000 mg/L, 100 mL (P/N 037159)
- Sulfate standard 1000 mg/L, 100 mL (P/N 037160)

- Bromide standard 1000 mg/L, 100 mL (Ultra Scientific, VWR P/N ICC-001)
- Sodium Chlorite, 80% (Fluka Chemical Co.)
- Sodium Bromate (EM Science, VWR P/N EM SX0385-1)
- Ethylenediamine, 99% (Sigma-Aldrich)

Conditions

| | |
|-------------------------|---|
| Columns: | Dionex IonPac AS19 Analytical, 4 × 250 mm (P/N 062885) Dionex IonPac AG19 Guard, 4 × 50 mm (P/N 062887) |
| Eluent: | 10 mM KOH from 0 to 10 min, 10–45 mM from 10 to 25 min* |
| Eluent Source: | Dionex ICS-2000 EG with Dionex CR-ATC |
| Flow Rate: | 1.0 mL/min |
| Temperature: | 30 °C |
| Injection: | 250 μL |
| Detection: | Suppressed conductivity, Thermo Scientific Dionex ASRS™ ULTRA II Suppressor, 4 mm (P/N 061561) auto-suppression, recycle mode, 130 mA current |
| Background Conductance: | <1 μS |
| System Backpressure: | ~2200 psi |
| Run Time: | 30 min |

*Method returns to 10 mM KOH for 3 min prior to injection

Preparation of Solutions and Reagents

Stock Standard Solutions

For several of the anions of interest, 1000 mg/L standard solutions can be purchased from us or other commercial sources. When commercial standards are not available, 1000 mg/L standards can be prepared by dissolving the appropriate amounts of the required analytes in 100 mL of deionized water according to Table 1. Stock standards for most anions are stable for at least 6 months when stored at 4 °C. The chlorite standard is only stable for two weeks when stored protected from light at 4 °C. The nitrite and phosphate standards are only stable for one month when stored at 4 °C.

Table 1. Masses of compounds used to prepare 100 mL of 1000 mg/L ion standards.

| Analyte | Compound | Amount (g) |
|-----------|---|------------|
| Fluoride | Sodium fluoride (NaF) | 0.2210 |
| Chlorite | Sodium chlorite (NaClO ₂), 80% | 0.1676 |
| Bromate | Sodium bromate (NaBrO ₃) | 0.1180 |
| Chloride | Sodium chloride (NaCl) | 0.1649 |
| Nitrite | Sodium nitrite (NaNO ₂) | 0.1500 |
| Chlorate | Sodium chlorate (NaClO ₃) | 0.1275 |
| Bromide | Sodium bromide (NaBr) | 0.1288 |
| Nitrate | Sodium nitrate (NaNO ₃) | 0.1371 |
| Sulfate | Sodium sulfate (Na ₂ SO ₄) | 0.1479 |
| Phosphate | Potassium phosphate, monobasic (KH ₂ PO ₄) | 0.1433 |

Working Standard Solutions

Dilute working standard solutions were prepared using the 1000 mg/L stock standards. Working standards containing less than 100 µg/L anions should be prepared fresh daily. Seven levels of calibration standards were used in this study for chlorite, chlorate, and bromide to cover the expected concentration range found in typical environmental samples. The bromate calibration curve was prepared using eight calibration standards. Additional anions listed in Table 1 were used to prepare a simulated drinking water sample containing 1 ppm fluoride, 50 ppm chloride, 0.1 ppm nitrite, 10 ppm nitrate, 100 ppm carbonate, 50 ppm sulfate, and 0.1 ppm phosphate.

Preservation Solution

Dilute 2.8 mL of 99% ethylenediamine (EDA) to 25 mL with deionized water according to section 7.4 in EPA Method 300.1 to prepare a 100 mg/mL solution of EDA. Use 50 µL of this solution per 100 mL of standard or sample so that the final concentration is 50 mg/L.

Sample Preparation

Filter samples, as necessary, through a 0.45 µm syringe filter, discarding the first 300 µL of the effluent. To prevent degradation of chlorite or the formation of bromate from hypobromous acid/hypobromite, preserve the samples by adding 50 µL of EDA preservation solution per 100 mL of sample.

Results and Discussion

EPA Method 300.1, Part B, currently specifies a Dionex IonPac AS9-HC column using a carbonate eluent and suppressed conductivity detection for the determination of trace DBP anions and bromide in environmental waters, such as drinking water, surface water, and groundwater.⁷ The use of the Dionex IonPac AS9-HC column in EPA Method 300.1 (B) significantly improved the determination for trace bromate compared to the AS9-SC specified in Method 300.0, Part B.¹⁴ The Dionex IonPac AS9-HC column allowed for detection limits to 1.4 µg/L bromate with a 200 µL injection volume, even in the presence of excess chloride. However, the use of a hydroxide eluent for the determination of trace bromate is more appealing than carbonate eluents. Hydroxide eluent has significantly lower suppressed background conductivity, lower noise, and therefore lower detection limits compared to carbonate eluents. Previously, we described the advantages of hydroxide over carbonate eluents for the determination of common anions.¹⁵ Therefore, similar advantages for bromate should be expected using a column with an appropriate selectivity combined with a hydroxide eluent.

The Dionex IonPac AS19 is a high-capacity, hydroxide-selective column specifically designed for the determination of trace bromate and other oxyhalides using a large-volume injection. The novel polymer chemistry of the Dionex IonPac AS19 column yields a higher capacity of 240 µequiv/column compared to the AS9-HC (190 µequiv/column). The Dionex IonPac AS19 column stationary phase is based on a new hyper-branched anion-exchange condensation polymer that is electrostatically attached to the surface of a wide-pore

polymeric substrate. The Dionex IonPac AS19 column selectivity and capacity are optimized to achieve good resolution between bromate and chloride. Unlike previous IonPac columns, the anion-exchange resin of the Dionex IonPac AS19 column contains alternating treatments of epoxy and amines to produce a coating that grows directly off the surface-sulfonated substrate. The number of alternating coating cycles results in a carefully controlled ion-exchange capacity with an extremely hydrophilic polymer. Therefore, the column has excellent selectivity for hydroxide eluents, allowing lower concentrations of hydroxide to be used.¹⁶ Figure 1 shows a separation of common anions and disinfection byproduct anions separated within 30 min using the Dionex IonPac AS19 column with a hydroxide gradient. As this figure shows, the Dionex IonPac AS19 column achieves excellent resolution between bromate and chloride, making it ideal for determining low concentrations of bromate in municipal and bottled water samples.

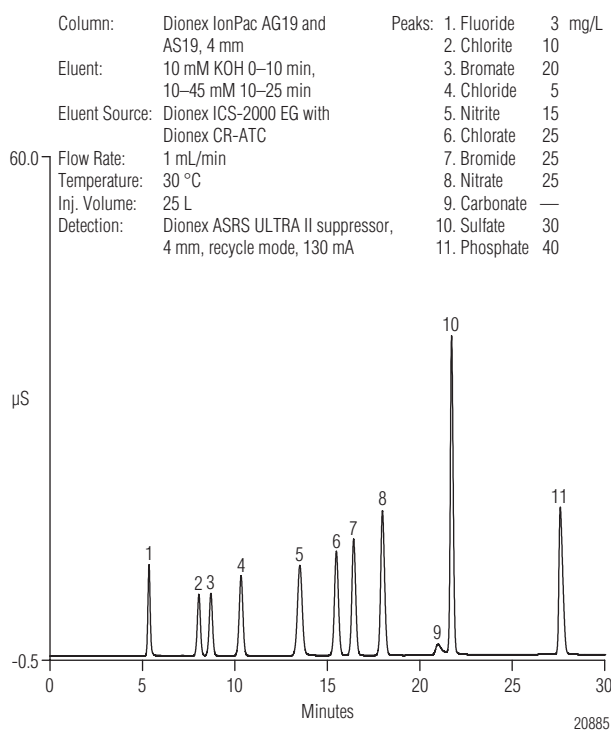


Figure 1. Separation of common anions and disinfection byproduct anions on the Dionex IonPac AS19 column.

Linearity and Method Detection Limits

Before conducting any sample analyses, the linear calibration range, MDLs, and acceptable performance of a quality control sample (QCS) should be demonstrated. Initially, a seven-point calibration range was used for chlorite, chlorate, and bromide, whereas eight calibration points were used for bromate. MDLs for each anion listed in EPA Method 300.1, Part B, were determined by performing seven replicate injections of reagent water fortified at a concentration of three to five times the estimated instrument detection limits. In addition, the MDLs were also determined by fortifying the same concentration of anions in a simulated drinking water sample. Table 2 shows typical calculated MDLs in reagent water and simulated drinking water using the Dionex IonPac AS19 column combined with an electrolytic eluent generator and a 250 μL injection. In comparing the detection limits in the two matrices, the results showed no significant difference. The only exception was the calculated MDL for bromate in simulated drinking water was only slightly greater, as expected, because increasing concentrations of chloride will affect the determination of low concentrations of bromate. The calculated MDL for bromate using this method was 0.34 $\mu\text{g/L}$, approximately 70% lower than previously reported with the Dionex IonPac AS9-HC column at comparable injection volumes.¹² The lower detection limit results from the excellent peak efficiencies of the Dionex IonPac AS19 combined with low noise and exceptionally low suppressed background conductivities obtained by using an electrolytically generated hydroxide eluent. These results demonstrate the significant advantages of using an

Column: Dionex IonPac AG19 and AS19, 4 mm Peaks: 1. Chlorite 1.0 $\mu\text{g/L}$
 Eluent: 10 mM KOH 0–10 min, 10–45 mM 10–25 min 2. Bromate 1.5
 3. Chlorate 1.3
 4. Bromide 2.0
 Eluent Source: Dionex ICS-2000 EG with Dionex CR-ATC
 Flow Rate: 1 mL/min
 Temperature: 30 $^{\circ}\text{C}$
 Inj. Volume: 250 μL
 Detection: Dionex ASRS ULTRA II suppressor, 4 mm, recycle mode, 130 mA

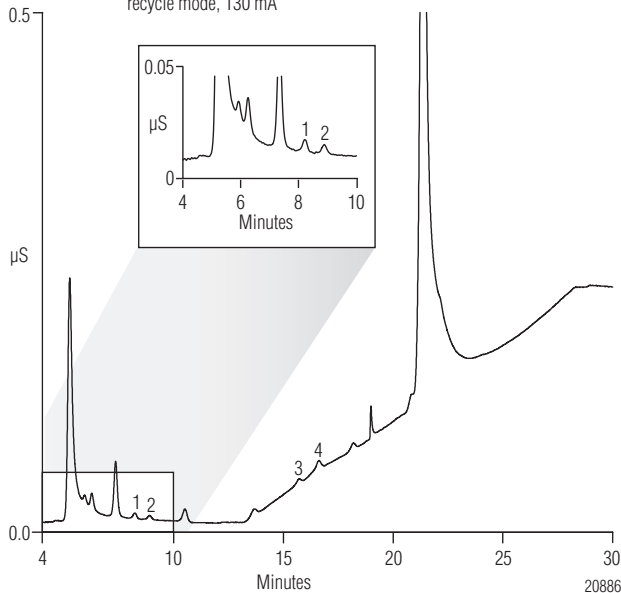


Figure 2. Separation of DBP anions and bromide method detection limit standard.

RFIC system for the determination of trace bromate. Figure 2 shows a separation of an MDL standard prepared in reagent water. As shown, bromate concentrations as low as 1.5 $\mu\text{g/L}$ are easily detected by this method.

Table 3 shows the linear concentration ranges investigated, the coefficients of determination (r^2), and the retention time and peak area precisions of a QCS based on 10 replicate injections. The excellent retention time stability and peak area precisions are consistent with results typically encountered when using an electrolytically generated high-purity potassium hydroxide eluent. The data presented in Table 3 demonstrate the advantages of using a hydroxide-selective column for routine applications, such as the determination of oxyhalides and bromide in environmental waters. The advantages of using IC with a hydroxide eluent are improved linearity, lower background conductivity, and improved method detection limits when compared with “conventional” IC columns that use carbonate eluents, such as the Dionex IonPac AS9-HC. The use of an electrolytically generated potassium hydroxide eluent further simplifies the method by eliminating the time required to manually prepare eluents and by reducing the time required for method development.

Table 2. Method detection limits for oxyhalides and bromide in reagent water and simulated drinking water using the Dionex IonPac AS19 column.^a

| Analyte | MDL Standard ($\mu\text{g/L}$) | Calculated MDL ^b in Reagent Water ($\mu\text{g/L}$) | Calculated MDL ^b Simulated Drinking Water ($\mu\text{g/L}$) |
|----------|----------------------------------|--|--|
| Chlorite | 1.0 | 0.23 | 0.26 |
| Bromate | 1.5 | 0.34 | 0.42 |
| Chlorate | 1.3 | 0.32 | 0.30 |
| Bromide | 2.0 | 0.54 | 0.52 |

^a 250 μL injection volume

^b $\text{MDL} = \sigma t_{s,99}$ where $t_{s,99} = 3.14$ for $n = 7$

Table 3. Linearity and retention time and peak area precisions obtained using the Dionex IonPac AS19 column.^a

| Analyte | Range ($\mu\text{g/L}$) | Linearity (r^2) | Retention Time Precision (RSD ^b) | Peak Area Precision (RSD) |
|----------|---------------------------|---------------------|--|---------------------------|
| Chlorite | 20–500 | 0.9997 | <0.03 | 0.44 |
| Bromate | 1–40 | 0.9995 | <0.03 | 1.09 |
| Chlorate | 20–500 | 0.9996 | <0.03 | 0.12 |
| Bromide | 20–500 | 0.9997 | <0.03 | 0.11 |

^a Dionex ICS-2000 Reagent-Free IC system with a 250 μL injection volume

^b RSD = relative standard deviation, $n = 10$

Effect of Column Overloading

The effect of sample overload on the Dionex IonPac AS19 column was evaluated as part of this study. One of the many challenges encountered when determining trace concentrations of bromate is the potential presence of a high sample chloride concentration. In addition to chloride, a high concentration of other anions can together reduce the amount of bromate recovered from a sample. For most environmental samples, chloride, sulfate, and carbonate are generally present at the greatest amounts with respect to other common anions. For this study, we chose a 250 μL sample injection for the analyses because this volume provided us the sensitivity necessary to achieve low-ppb detection of bromate and reduced the likelihood of overloading the column when analyzing high-ionic-strength samples.

To determine the effect of chloride on bromate recovery, a series of increasing concentrations of chloride was added to Sunnyvale drinking water. Figure 3 illustrates the effect of increasing concentrations of chloride on the recovery of 5 $\mu\text{g/L}$ bromate. As shown, the recovery of bromate is acceptable in the presence of ~ 150 ppm chloride. Above this concentration, the bromate significantly decreases to an unacceptable recovery (e.g., $<75\%$). Based on this analysis, the Dionex IonPac AS19 column can tolerate up to ~ 150 ppm chloride, resulting in a bromate-to-chloride ratio of 1:30,000, comparable to the AS9-HC column.^{12A} A similar experiment was performed by increasing the sulfate concentration without any additional chloride added. This experiment demonstrated very little change in the bromate recovery for up to 200 ppm sulfate (results not shown). However, high concentrations of chloride and sulfate can combine to have a greater impact on reducing the bromate recovery. Equal concentrations of chloride and sulfate (up to 120 ppm each) were added to Sunnyvale drinking water, resulting in a 75% bromate

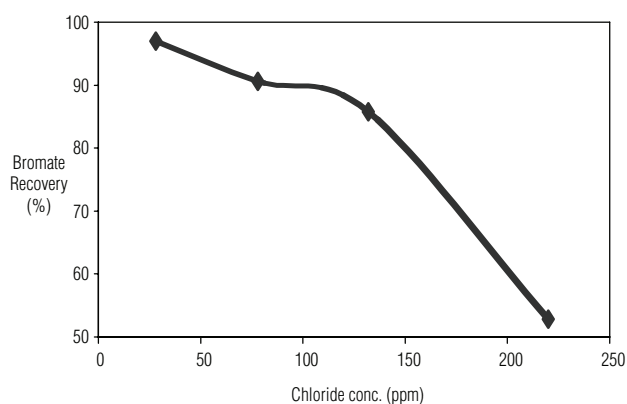


Figure 3. Effect of increasing the chloride concentration on the recovery of 5 $\mu\text{g/L}$ bromide.

recovery. However, most drinking water samples contain significantly less chloride and sulfate than the concentrations included in this study. For example, 18 of the samples examined contained chloride concentrations ranging from <0.1 to 70 ppm and sulfate from <0.1 to 60 ppm. Therefore, almost all samples can be easily analyzed using a 250 μL injection volume, while the column can tolerate 500 μL injections of low to moderate-ionic-strength samples. Figure 4 shows a chromatogram of a 500 μL injection of Sunnyvale drinking water spiked with oxyhalides and bromide. As shown, bromate was well resolved from chloride with bromate recovered at

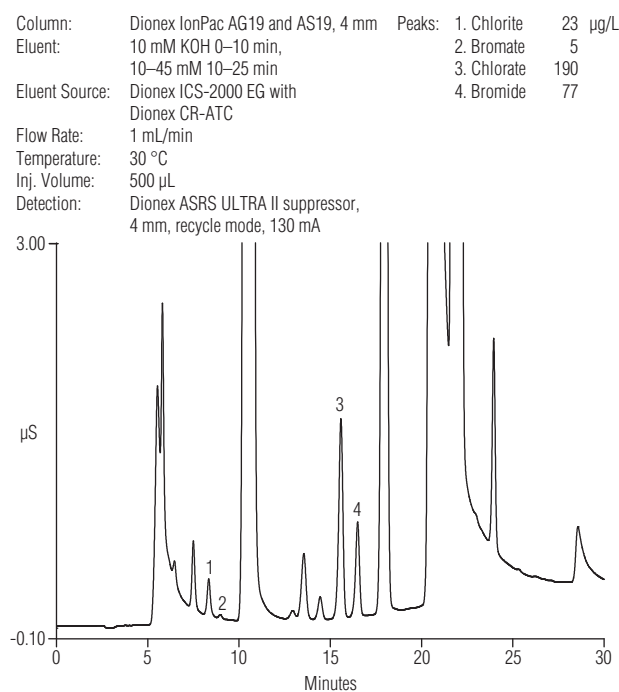


Figure 4. Determination of DBP anions and bromide spiked in drinking water A using a 500 μL injection volume.

Table 4. Recoveries of trace oxyhalides and bromide spiked into environmental waters.

| Analyte | Drinking Water A | | | Drinking Water B | | | Drinking Water C | | | Drinking Water D | | |
|----------|---------------------|---------------------|-------------------|---------------------|---------------------|--------------|----------------------------------|---------------------|--------------|----------------------------------|---------------------|--------------|
| | Amount Found (µg/L) | Amount Added (µg/L) | Recovery (%) | Amount Found (µg/L) | Amount Added (µg/L) | Recovery (%) | Amount Found (µg/L) | Amount Added (µg/L) | Recovery (%) | Amount Found (µg/L) | Amount Added (µg/L) | Recovery (%) |
| Chlorite | 8.8 | 10.0 | 95.3 | <MDL | 21.0 | 105.6 | 11.6 | 10.0 | 95.7 | <MDL | 20.0 | 108.0 |
| Bromate | <MDL | 5.0 | 92.2 | <MDL | 5.1 | 95.6 | <MDL | 5.0 | 96.8 | 1.3 | 4.9 | 93.9 |
| Chlorate | 81.9 | 106.0 | 96.9 | 120 | 144.0 | 104.4 | 85.3 | 90.7 | 97.6 | 73.6 | 79.4 | 98.2 |
| Bromide | 26.3 | 30.0 | 99.6 | 202 | 200.0 | 99.8 | 1.2 | 25.0 | 94.2 | 9.7 | 10.0 | 107.4 |
| Analyte | Drinking Water E | | | Surface Water | | | Shallow Well Water ^b | | | Well Water ^b | | |
| | Amount Found (µg/L) | Amount Added (µg/L) | Recovery (%) | Amount Found (µg/L) | Amount Added (µg/L) | Recovery (%) | Amount Found ^c (µg/L) | Amount Added (µg/L) | Recovery (%) | Amount Found ^c (µg/L) | Amount Added (µg/L) | Recovery (%) |
| Chlorite | 4.6 | 14.0 | 93.4 | <MDL | 20.0 | 95.7 | <MDL | 21.0 | 103.1 | <MDL | 20.0 | 101.4 |
| Bromate | <MDL | 5.0 | 100.5 | <MDL | 5.0 | 94.7 | 16.0 | 9.8 | 101.1 | <MDL | 5.0 | 86.5 |
| Chlorate | 136.0 | 151.0 | 99.9 | <MDL | 20.0 | 96.8 | <MDL | 30.0 | 96.8 | 10.6 | 20.0 | 93.0 |
| Bromide | <MDL | 20.0 | 24.8 ^a | <MDL | 20.0 | 103.3 | 381.0 | 200.0 | 104.0 | 452.0 | 230.0 | 100.7 |

^a Suspect/matrix

^b Sample diluted 1:1

^c Calculated amounts

nearly 100%. Figure 5 compares 250 to 500 µL injection volumes for a simulated drinking water sample. The 500 µL injection volume caused some column overloading, and therefore a lower bromate recovery of ~74%. However, a 250 µL injection of the same sample significantly improved the recovery of bromate to 92%. Therefore, a 250 µL injection is recommended for most sample analyses. The effect of column overloading is most prevalent on early-eluting peaks, observed by increased peak broadening and lower recoveries, as demonstrated in this example.

Accuracy and Precision

The performance of the Dionex IonPac AS19 was also evaluated through a single-operator precision and bias study using spiked municipal and bottled water samples. Table 4 shows typical recoveries for single-operator data obtained using the Dionex IonPac AS19 column for trace concentrations of DBPs and bromide in environmental waters. Most anions demonstrated acceptable recoveries (i.e., 75–125%) according to the criteria outlined in EPA Method 300.1. However, drinking water E resulted in an exceptionally lower recovery for bromide, regardless of the amount of bromide spiked in the sample. Section 9.4.1.5 of EPA Method 300.1 states, “If the recovery of any analyte falls outside the LFM [Laboratory Fortified Matrix] recovery range and the laboratory performance for that analyte is shown to be in control, the recovery problem encountered with the LFM is judged to be either matrix or solution related, not system related.” Therefore, the sample was labeled as “suspect/matrix” to indicate that the poor recovery of bromide was sample related and not system related.

Column: Dionex IonPac AG19 and AS19, 4 mm Peaks: 1. Fluoride 1.0 mg/L
 Eluent: 10 mM KOH 0–10 min, 2. Chlorite 0.02
 10–45 mM 10–25 min 3. Bromate 0.005
 Eluent Source: Dionex ICS-2000 EG with 4. Chloride 50.0
 Dionex CR-ATC 5. Nitrite 0.1
 Flow Rate: 1 mL/min 6. Chlorate 0.02
 Temperature: 30 °C 7. Bromide 0.02
 Inj. Volume: (A) 250 µL 8. Nitrate 10.0
 (B) 500 µL 9. Carbonate 100.0
 Detection: Dionex ASRS ULTRA II suppressor, 10. Sulfate 50.0
 4 mm, recycle mode, 130 mA 11. Phosphate 0.1

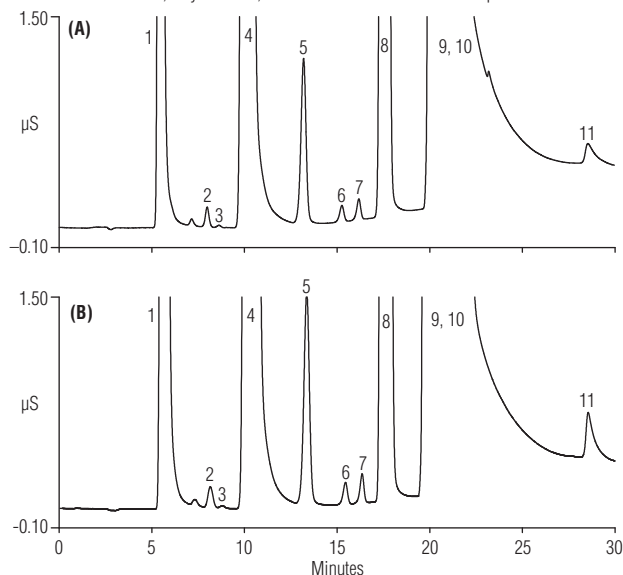


Figure 5. Comparison of simulated drinking water using (A) 250 µL injection and (B) 500 µL injection.

Due to the high ionic strength of the well water samples, both were diluted 1:1 to avoid column overloading. The estimated chloride and sulfate concentrations were 160 and 270 ppm, respectively, for the shallow well water, and 150 and 170 ppm, respectively, for the well water prior to dilution. These concentrations exceed the limits determined for this column during the sample overload study. Section 4.1.2 in EPA Method 300.1 states that “sample dilution will alter your Minimum Reporting Limit (MRL) by a proportion equivalent to that of the dilution.” In this study, dilution of the well water samples increased the bromate MRL from 1 to 2 µg/L. However, the adjusted MRL was still sufficient to report the 8 µg/L bromate detected in the diluted sample. Because this well water sample is not known to be treated, the presence of bromate was unexpected. The detection of bromate in the well water may result from contamination by a nearby site that originally contained a high concentration of the anion. Figure 6A shows a chromatogram of diluted shallow well water. Figure 6B shows the same well water sample spiked with 10–20 µg/L of DBP anions and 200 µg/L of bromide. As shown, bromate was well resolved from the high concentration of chloride, resulting in a recovery of 101.1%.

Figure 7 shows chromatograms of an unspiked and spiked drinking water B. This sample also demonstrates the excellent resolution and accuracy of analysis for the determination of trace DBP anions and bromide using an RFIC system. The calculated recoveries of the target analytes ranged from 96 to 106%.

Column: Dionex IonPac AG19 and AS19, 4 mm
 Eluent: 10 mM KOH 0–10 min, 10–45 mM 10–25 min
 Eluent Source: Dionex ICS-2000 EG with Dionex CR-ATC
 Flow Rate: 1 mL/min
 Temperature: 30 °C
 Inj. Volume: 250 µL
 Detection: Dionex ASRS ULTRA II suppressor, 4 mm, recycle mode, 130 mA
 Sample Prep: 1:1 dilution

Peaks: (A) 2. Bromate 8 µg/L, 3. Chlorate 24, 4. Bromide 190
 (B) 1. Chlorite 18 µg/L, 2. Bromate 18, 3. Chlorate 51, 4. Bromide 400

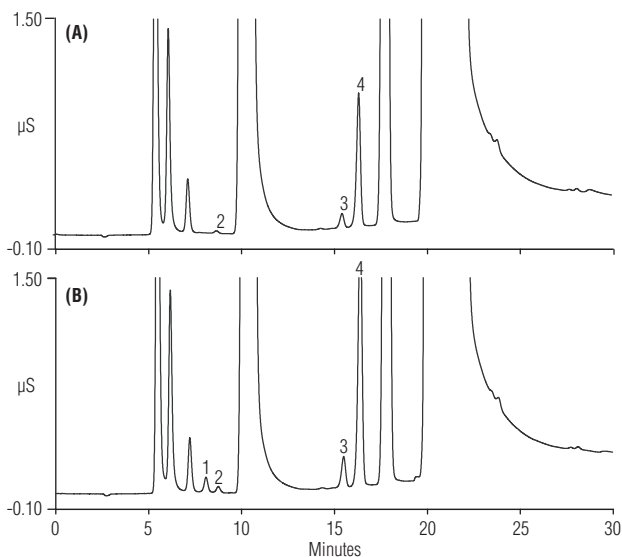


Figure 6. Determination of DBP anions and bromide in (A) shallow well water and (B) spiked shallow well water using the Dionex IonPac AS19 column.

This study also included the analysis of a variety of bottled water samples randomly obtained from a local supermarket. A previous study conducted from 1997–1998 in Canada found many bottled waters contained bromate, some at concentrations greater than 25 µg/L.¹⁷ These results in combination with the increasing popularity of bottled water, led us to examine the presence of bromate in several different brands of bottled waters. More than half of the bottled waters tested in this study reported using ozonation as a form of treatment according to the bottle’s label or company’s web site (Table 5).

Column: Dionex IonPac AG19 and AS19, 4 mm
 Eluent: 10 mM KOH 0–10 min, 10–45 mM 10–25 min
 Eluent Source: Dionex ICS-2000 EG with Dionex CR-ATC
 Flow Rate: 1 mL/min
 Temperature: 30 °C
 Inj. Volume: 250 µL
 Detection: Dionex ASRS ULTRA II suppressor, 4 mm, recycle mode, 130 mA

Peaks: (A) 3. Chlorate 118 µg/L, 4. Bromide 200
 (B) 1. Chlorite 19 µg/L, 2. Bromate 5, 3. Chlorate 270, 4. Bromide 403

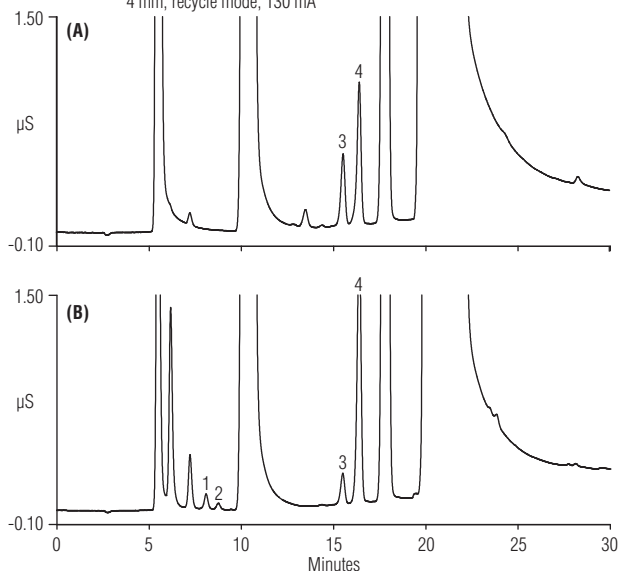


Figure 7. Determination of DBP anions and bromide in (A) drinking water B and (B) spiked drinking water B using the Dionex IonPac AS19 column.

Table 5. Treatments used for different bottled waters.

| Bottled Water | Treatment |
|---------------|--|
| 1 | Natural spring water (no treatment) |
| 2 | UV light, RO ^a , ozonation |
| 3 | Ozonation |
| 4 | Natural mineral water (no treatment) |
| 5 | RO |
| 6 | Microfiltration, UV light, ozonation |
| 7 | Filtration |
| 8 | Microfiltration, ozonation |
| 9 | Natural spring water (no treatment) |
| 10 | Microfiltration, ozonation |
| 11 | Microfiltration, RO, DI ^b , ozonation |
| 12 | Ozonation |

^a RO = reverse osmosis

^b DI = deionization

Table 6. Recoveries of trace oxyhalides and bromide spiked into bottled waters.

| Analyte | Bottled Water 1 | | | Bottled Water 2 | | | Bottled Water 3 | | | Bottled Water 4 | | |
|----------|---------------------|---------------------|--------------|---------------------|---------------------|--------------|---------------------|---------------------|--------------|---------------------|---------------------|--------------|
| | Amount Found (µg/L) | Amount Added (µg/L) | Recovery (%) | Amount Found (µg/L) | Amount Added (µg/L) | Recovery (%) | Amount Found (µg/L) | Amount Added (µg/L) | Recovery (%) | Amount Found (µg/L) | Amount Added (µg/L) | Recovery (%) |
| Chlorite | <MDL | 20.0 | 108.1 | <MDL | 20.0 | 102.9 | <MDL | 20.0 | 99.8 | <MDL | 20.0 | 90.2 |
| Bromate | <MDL | 5.0 | 96.1 | <MDL | 5.0 | 100.7 | 10.2 | 9.8 | 104.6 | <MDL | 5.0 | 83.5 |
| Chlorate | 2.4 | 20.0 | 107.7 | <MDL | 20.0 | 106.5 | <MDL | 20.0 | 102.8 | 10.2 | 20.0 | 103.5 |
| Bromide | 7.5 | 20.0 | 105.0 | <MDL | 20.0 | 106.5 | 19.4 | 20.0 | 92.9 | 95.5 | 105.0 | 97.7 |
| Analyte | Bottled Water 5 | | | Bottled Water 6 | | | Bottled Water 7 | | | Bottled Water 8 | | |
| | Amount Found (µg/L) | Amount Added (µg/L) | Recovery (%) | Amount Found (µg/L) | Amount Added (µg/L) | Recovery (%) | Amount Found (µg/L) | Amount Added (µg/L) | Recovery (%) | Amount Found (µg/L) | Amount Added (µg/L) | Recovery (%) |
| Chlorite | <MDL | 20.0 | 101.2 | <MDL | 20.0 | 101.5 | <MDL | 20.0 | 106.7 | <MDL | 20.0 | 102.2 |
| Bromate | <MDL | 5.0 | 95.9 | 9.2 | 9.8 | 106.6 | <MDL | 5.0 | 92.3 | <MDL | 5.0 | 93.7 |
| Chlorate | 1.6 | 20.0 | 108.6 | 375.0 | 150.0 | 97.3 | <MDL | 25.0 | 90.6 | <MDL | 20.0 | 105.4 |
| Bromide | 1.2 | 20.0 | 95.6 | 2.5 | 20.0 | 100.9 | 31.8 | 30.0 | 98.9 | 18.7 | 20.0 | 93.8 |
| Analyte | Bottled Water 9 | | | Bottled Water 10 | | | Bottled Water 11 | | | Bottled Water 12 | | |
| | Amount Found (µg/L) | Amount Added (µg/L) | Recovery (%) | Amount Found (µg/L) | Amount Added (µg/L) | Recovery (%) | Amount Found (µg/L) | Amount Added (µg/L) | Recovery (%) | Amount Found (µg/L) | Amount Added (µg/L) | Recovery (%) |
| Chlorite | <MDL | 20.0 | 106.1 | <MDL | 20.0 | 98.2 | <MDL | 20.0 | 104.8 | <MDL | 20.0 | 95.2 |
| Bromate | <MDL | 5.0 | 98.4 | 4.4 | 5.0 | 101.1 | <MDL | 5.0 | 96.4 | 0.98 | 5.0 | 102.1 |
| Chlorate | <MDL | 20.0 | 105.7 | <MDL | 20.0 | 107.7 | <MDL | 23.0 | 98.3 | 4.2 | 20.0 | 98.5 |
| Bromide | <MDL | 20.0 | 104.1 | <MDL | 20.0 | 105.3 | 6.3 | 23.0 | 94.5 | <MDL | 20.0 | 99.2 |

Table 6 shows the amount found and the recoveries obtained using the Dionex IonPac AS19 column for trace concentrations of DBP anions and bromide spiked in the bottled waters. All target analytes demonstrated acceptable recoveries according to U.S. EPA Method 300.1. Only four bottles tested contained some amount of bromate, with two of these near or slightly above the bromate MCL of 10 µg/L. No correlation was observed between the concentrations of bromide in the samples versus the amount of bromate detected. For example, bottled water #10 contained approximately 4 µg/L bromate, but no bromide was detected in the sample. However, the conversion of bromide to bromate upon ozonation is affected by several factors, such as the presence of natural organic matter, pH, temperature, and other variables.² As expected, most bottled waters analyzed contained appreciably less chloride and sulfate than tap water with estimated maximum concentrations of 8 and 30 ppm, respectively. The low ionic content of most bottled waters allows the use of larger injection volumes (500 µL or more). Figure 8 shows a 250 µL injection of an unspiked and spiked bottled water sample. The disinfection treatment used for this bottled water was UV radiation and ozonation. An unusually high amount of chlorate was detected in the sample, indicating that some form of chlorination may also be used for treatment. Bromate was detected at a slightly lower concentration than the EPA's MCL, possibly indicative of elevated levels of bromide in the source water. The recoveries for oxyhalide DBPs and bromide spiked in the sample ranged from ~97 to 107%, well within EPA Method 300.1 specifications.

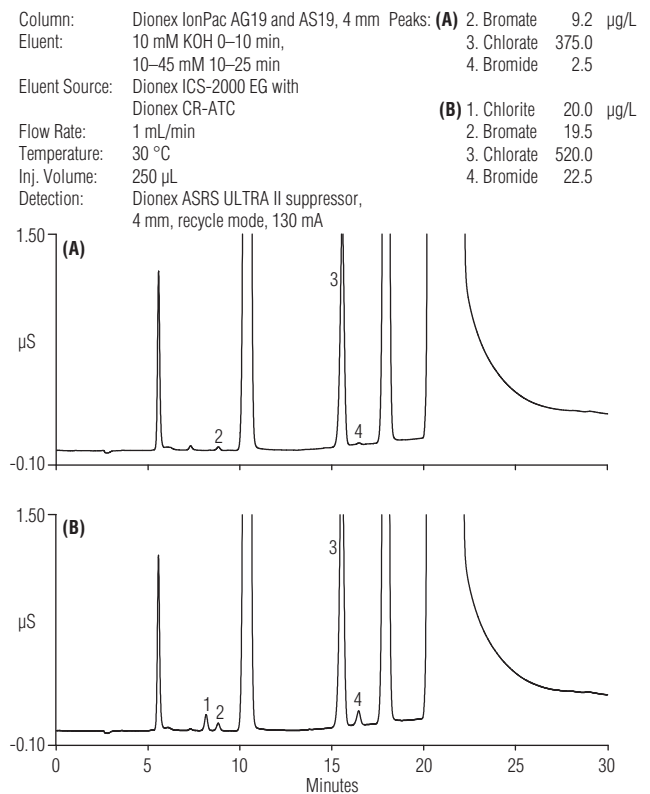


Figure 8. Determination of DBP anions and bromide in (A) bottled water 6 and (B) spiked bottled water 6 using the Dionex IonPac AS19 column.

The precision of the method using the Dionex IonPac AS19 column in combination with an electrolytic eluent generation was determined by performing 10 replicate injections of randomly selected samples spiked with trace concentrations of DBPs and bromide. Overall, the calculated peak area precisions varied from 0.21 to 1.78% with retention time precisions <0.04% for most target analytes. For bromate, the worst peak area precision observed was 1.78%. This number represents a deviation of only ± 0.09 $\mu\text{g/L}$ based on a sample containing 5 $\mu\text{g/L}$ bromate. The high precision of this method is consistent with results typically found with an RFIC system.

Conclusion

IC with a hydroxide-selective Dionex IonPac AS19 column and an electrolytic eluent generator is an improved approach for determining trace concentrations of DBP anions and bromide in municipal and bottled water samples. The high-capacity Dionex IonPac AS19 column can be used with large-volume injections to detect low-ppb concentrations of bromate, a potential human carcinogen, in many municipal and bottled waters. In addition, electrolytic generation of an ultrapure potassium hydroxide eluent, combined with the Dionex IonPac AS19 column, improves linearity, MDLs, precision, and resolution between bromate and chloride compared to the AS9-HC column described in EPA Method 300.1. This approach also eliminates the need to manually prepare eluents and thereby increases the automation, ease of use, and reproducibility between analysts and laboratories. The U.S. EPA, Office of Water, has determined that the use of hydroxide eluents in EPA Method 300.1 is acceptable for compliance monitoring under the Clean Water Act and Safe Drinking Water Act.¹⁸

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