

Determination of Sub- $\mu\text{g/L}$ Bromate in Municipal and Natural Mineral Waters Using Preconcentration with Two-Dimensional Ion Chromatography and Suppressed Conductivity Detection

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Introduction

Ozone is a powerful drinking water disinfectant that is effective in treating chlorine resistant organisms, such as *Cryptosporidia*.¹ For bottled water, ozonation is generally preferred over other available disinfection treatment methods because it does not leave a taste or residual disinfectant, due to the short lifetime of ozone.^{2,3} Ozone also improves the quality of finished drinking water by reducing filtered water turbidity and decreasing the formation of many halogenated disinfection byproducts. However, ozonation of drinking water containing bromide can result in the formation of the disinfection byproduct bromate, a potential human carcinogen even at low $\mu\text{g/L}$ concentrations.⁴ The U.S. Environmental Protection Agency (EPA) and European Commission have established a regulatory maximum contaminant level (MCL) of 10 $\mu\text{g/L}$ bromate in drinking waters.^{5,6} In the U.S., bottled water is considered a food product and is therefore regulated by the U.S. Food and Drug Administration (FDA) under the Federal Food, Drug, and Cosmetic Act.⁷ In 2001, the U.S. FDA also established an MCL of 10 $\mu\text{g/L}$ bromate in bottled drinking water.⁷ More recently, the European Commission set a lower MCL of 3 $\mu\text{g/L}$ bromate for natural mineral waters and spring waters treated by ozonation.⁸ However, these limits were based on the feasibility of detection and removal, even though studies suggest concentrations lower than 1 $\mu\text{g/L}$ pose increased lifetime cancer risks.^{4,9}

Published EPA methods for determining low concentrations of bromate in drinking waters using direct injection have focused primarily on using columns designed specifically for carbonate eluents combined with suppressed conductivity detection or postcolumn reaction

followed by UV/Vis detection.^{10–12} Application Note 167 demonstrates that the use of a high-capacity hydroxide-selective Thermo Scientific™ Dionex™ IonPac™ AS19 column, an electrolytically generated hydroxide eluent, a large loop injection, and suppressed conductivity detection can significantly reduce the bromate detection limit from 1.4 $\mu\text{g/L}$, reported in EPA Method 300.1, to 0.34 $\mu\text{g/L}$.¹³ In addition, the use of a hydroxide eluent produced a bromate MDL of <0.2 $\mu\text{g/L}$ for absorbance detection after postcolumn addition using EPA Methods 317.0 and 326.0.^{14,15}

However, determining low concentrations of bromate in high-ionic-strength matrices using suppressed conductivity detection is subject to potential interferences and loss of sensitivity. Although postcolumn reaction methods do not generally suffer from interferences by common anions, column overloading with high-ionic-strength samples can still cause peak broadening and an associated loss of response. In particular, natural mineral waters typically contain elevated levels of common anions that can significantly exceed the concentrations present in most municipal drinking water samples, presenting an additional challenge for the currently available methods to determine <1 $\mu\text{g/L}$ bromate. Natural mineral waters previously have been analyzed for trace concentrations of bromate using the the Dionex IonPac AS19 column with a hydroxide eluent or the Dionex IonPac AS23 column and a carbonate/bicarbonate eluent using a large loop injection and suppressed conductivity detection.¹⁶

In this application note, we demonstrate the use of a two-dimensional (2-D) ion chromatography (IC) system for the determination of trace concentrations of bromate in municipal and natural mineral waters with high-ionic-

strength matrices. The first dimension uses a high capacity 4 mm Dionex IonPac AS19 column to resolve the bromate from the matrix ions. The matrix ions are diverted to waste while a 2 mL plug (cut volume) containing the bromate is transferred to the second dimension for analysis. Bromate is well resolved in the second dimension using a 2 mm Dionex IonPac AS24 column. This method is fully automated using a Thermo Scientific™ Dionex™ ICS-3000 Reagent-Free™ IC (RFIC™) system. In addition, this 2-D IC method achieves bromate detection limits equivalent to or better than postcolumn addition methods. The 2-D IC method avoids the cost and disposal of the chemicals required for postcolumn configurations and simplifies the experimental setup. Additionally, it avoids potential column overload during analysis of high-ionic-strength matrices.

Equipment

- Dionex ICS-3000 Reagent-Free Ion Chromatography system*:
 - DP Dual Pump module
 - EG Eluent Generator module with a dual setup
 - DC Detector/Chromatography module (single or dual temperature zone configuration)
- Thermo Scientific Dionex AS Autosampler with a 5 mL syringe, 8.2 mL sampling needle assembly
- Two Thermo Scientific™ Dionex™ EluGen™ EGC II KOH cartridges
- Two Thermo Scientific Dionex CR-ATC Continuously Regenerated Anion Trap Columns
- Four 4 L plastic bottle assemblies for external water mode of operation
- Thermo Scientific™ Dionex™ Chromeleon™ Chromatography Data System (CDS) Software, version 6.8

Equivalent or improved results can be achieved using the Thermo Scientific Dionex ICS-5000.

Reagents and Standards

- Deionized water, Type I reagent grade, 18 MΩ-cm resistivity or better
- Bromate standard (1000 mg/L)
- Sodium bromate (NaBrO₃)
- Sodium chloride (NaCl)
- Sodium nitrate (NaNO₃)
- Sodium bicarbonate (NaHCO₃)
- Sodium sulfate (Na₂SO₄)
- Sodium phosphate, dibasic, anhydrous (Na₂HPO₄)

Conditions

First-Dimension Conditions

Columns:	Dionex IonPac AG19 Guard, 4 × 50 mm Dionex IonPac AS19 Analytical, 4 × 250 mm
Eluent:	10 mM potassium hydroxide 0–12 min, ^a step to 65 mM at 12 min, 65 mM 12–35 min ^b
Eluent Source:	Dionex EGC II KOH cartridge with Dionex CR-ATC column
Flow Rate:	1 mL/min
Temperature:	30 °C (lower compartment) 30 °C (upper compartment)
Injection Vol:	1000 µL
Detection:	Suppressed conductivity, Thermo Scientific™ Dionex™ ASRS™ ULTRA II suppressor, 4 mm, auto-suppression, external water mode (flow rate: 3–5 mL/min) Current setting: 161 mA

System
Backpressure: ~2300 psi

Expected
Background
Conductance: <0.5 µS

Noise: ~1–2 nS/min peak-to-peak

Run Time: 35 min

^aThe step change described here should occur after the valve on system #2 has switched from the load to inject position.

^bThe method equilibrates for 5 min at 10 mM KOH prior to injection.

Second-Dimension Conditions

Columns:	Dionex IonPac AG24 Guard, 2 × 50 mm Dionex IonPac AS24 Analytical, 2 × 250 mm
Eluent:	10 mM potassium hydroxide 0–24 min, step to 65 mM at 24 min, 65 mM 24–35 min ^b
Eluent Source:	Dionex EGC II KOH cartridge with Dionex CR-ATC column
Flow Rate:	0.25 mL/min
Temperature:	30 °C (lower compartment) 30 °C (upper compartment)
Cut Volume:	2 mL (on the concentrator column)
Concentrator:	Dionex IonPac TAC-ULP1, 5 × 23 mm
Detection:	Suppressed conductivity, Dionex ASRS ULTRA II suppressor, 2 mm, auto-suppression, external water mode (flow rate: 1–3 mL/min) Current setting: 41 mA

System
Backpressure: ~2400 psi

Expected
Background
Conductance: <0.8 µS

Noise: ~2–3 nS/min peak-to-peak

Run Time: 35 min

^bThe method equilibrates for 5 min at 10 mM KOH prior to injection.

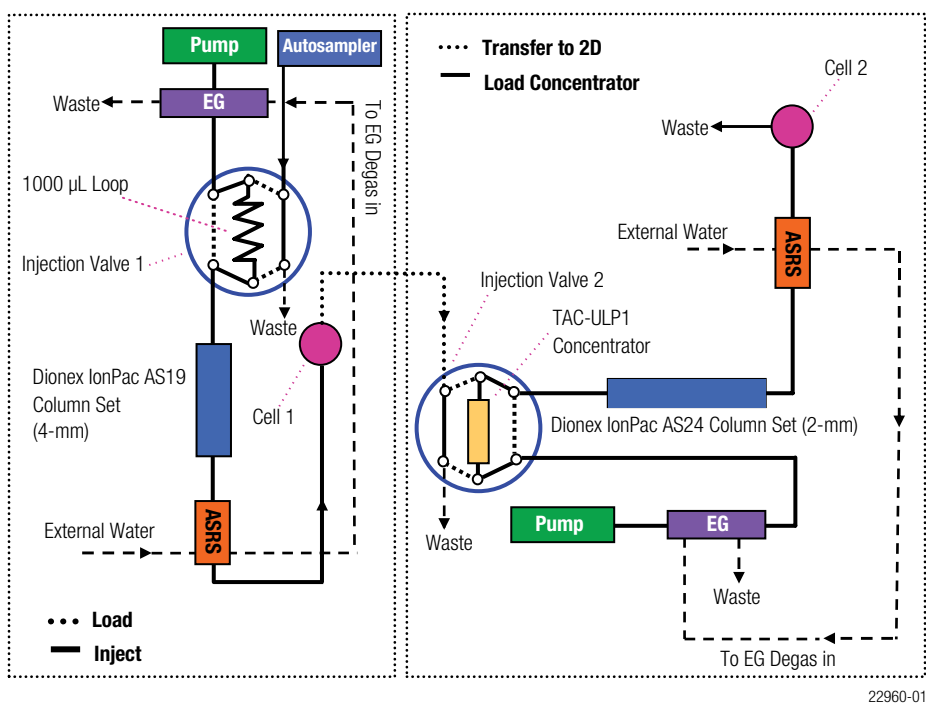


Figure 1. Schematic diagram of a Dionex ICS-3000 2-D IC system for the determination of trace concentrations of bromate.

Preparation of Solutions and Standards

Stock Bromate Standard Solution

Dissolve 0.1180 g sodium bromate in 100 mL of deionized water for a 1000 mg/L standard solution. This standard is stable for at least six months when stored at 4 °C.

Bromate Primary Dilution Standard

To prepare a 10 mg/L bromate solution, add 1 mL of the 1000 mg/L stock standard to a 100 mL volumetric flask. Bring to volume with deionized water. When stored at 4 °C, the resulting solution is stable for at least one month.

Bromate Secondary Dilution Standard

To prepare a 1 mg/L bromate solution, add 10 mL of the primary dilution standard to a 100 mL volumetric flask. Bring to volume with deionized water. When stored at 4 °C, the resulting solution is stable for at least one month.

Bromate Calibration Standards

To prepare bromate calibration standards at concentrations of 0.15, 0.25, 0.50, 1, 3, 5, 10, and 15 µg/L, add the appropriate volumes of the bromate secondary dilution standard to separate 100 mL volumetric flasks. Bring to volume with deionized water.

Common Anion Stock Solutions

Prepare 1000 mg/L each of chloride, nitrate as N, bicarbonate, sulfate, and phosphate as P. Dissolve 0.1649 g sodium chloride in deionized water and dilute to 100 mL. Dissolve 0.6068 g sodium nitrate in deionized water and dilute to 100 mL. Dissolve 0.1377 g sodium bicarbonate in deionized water and dilute to 100 mL. Dissolve 0.1479 g sodium sulfate in deionized water and dilute to 100 mL. Dissolve 0.4583 g anhydrous sodium phosphate, dibasic in deionized water and dilute to 100 mL.

Laboratory Synthetic Sample Matrix (LSSM)

The LSSM contains 100 mg/L each of chloride, bicarbonate, and sulfate and 10 mg/L each of nitrate-N and phosphate-P. Prepare this solution by adding 10 mL each of chloride, bicarbonate, and sulfate from their respective 1000 mg/L stock solutions to a 100 mL volumetric flask. Add 1 mL each of nitrate-N and phosphate-P from their respective 1000 mg/L stock solutions to the volumetric flask containing chloride, bicarbonate, and sulfate. To fortify this solution with 0.5 µg/L or 5 µg/L bromate add 0.05 mL or 0.5 mL, respectively, of the 1 mg/L bromate secondary dilution standard to the volumetric flask and bring to volume with deionized water.

System Preparation and Setup

Install a Dionex EGC II KOH cartridge for each system channel. Install backpressure tubing temporarily in place of the columns on both system channels to produce a total backpressure of 2000–2500 psi at a flow rate of 1 mL/min. Condition the cartridges by setting the KOH concentration to 50 mM at 1 mL/min for 30 min. After completing the conditioning process, disconnect the backpressure tubing. Install a Dionex CR-ATC column between the Dionex EGC II KOH cartridge and the EGC degas. Hydrate the Dionex CR-ATC column prior to use by following the instructions outlined in the Dionex EluGen Cartridge Quickstart Guide (Document No. 065037). Figure 1 shows a detailed schematic diagram of the system setup.

Install and configure the Dionex AS Autosampler. The most accurate and precise sample injections with the Dionex AS Autosampler are made with a calibrated sample loop, flushed with about four to five times the loop volume. Because this application requires large sample injection volumes, a sample syringe of at least 5 mL should be installed. To accommodate the larger volume, an 8.2 mL sampling needle assembly

is also required for operation. The largest injection possible with a 5 mL syringe installed on the Dionex AS Autosampler is 4000 μL . To inject 1000 μL , select the normal mode from the front panel of the autosampler. The normal mode will allow the autosampler to flush the sample loop prior to injection. Enter the correct sample loop size and sample syringe volume in the AS Plumbing Configuration screen. Instruct the Dionex AS Autosampler to inject 1000 μL with the Chromeleon (CDS) software.

Prepare a 1000 μL sample loop by measuring approximately 86.4 in. of 0.030 in. i.d. tubing. To verify the volume of the loop, first weigh the empty tubing. Fill the tube with deionized water then reweigh the filled tube and calculate the volume. The total sample volume should be $1000 \mu\text{L} \pm 5\%$. Install the sample loop on Injection Valve 1 of the DC-3000.

Because the two dimensions are working as one system, a second timebase does not need to be created. However, to allow independent control of the DC module injection valves in the timebase, the DC settings in the Chromeleon system configuration must be changed. To modify this configuration, go to the DC High Pressure Valves tab in the system configuration, double-click InjectValve_2, and change controlled by AS to DC.

Install a 4×50 mm Dionex IonPac AG19 and a 4×250 mm IonPac AS19 column on system #1 in the lower compartment of the DC module. Install a 2×50 mm Dionex IonPac AG24 and a 2×250 mm Dionex IonPac AS24 column on system #2. Connect a piece of 0.01 in. i.d. PEEK tubing from the Cell Out on system #1 to the Sample Inlet Port on Injection Valve #2. The length of this tubing should be kept to a minimum. Install a 5×23 mm Dionex IonPac TAC-ULP1 concentrator in place of the sample loop on system #2. The direction of sample loading on the Dionex IonPac TAC-ULP1 concentrator should be in the opposite direction of the analytical flow.

Make sure the pressure for both systems is from 2200–2500 psi using the operating conditions described earlier to allow the degas assembly to effectively remove electrolysis gases from the eluent. If necessary, install additional backpressure tubing between the degas assembly and the injection valve to achieve the recommended pressure setting. Monitor the pressure periodically as it can gradually rise over time. To reduce pressure, trim the backpressure tubing.

Hydrate the Dionex ASRS ULTRA II suppressors prior to installation using a disposable plastic syringe. Push 3 mL of degassed deionized water through the Eluent Out port and 5 mL of degassed deionized water through the Regen In port. Allow the suppressors to stand for 20 min to fully

hydrate the suppressor screens and membranes. Before installing the suppressors, rinse the analytical column with 65 mM KOH while diverting to waste. Install the Dionex ASRS ULTRA II suppressor for use in the external water mode by connecting the Regen Out of the suppressor to the Regen In of the Dionex CR-ATC column and connect the Regen In of the suppressor to the external water source. The Regen Out of the Dionex CR-ATC column is connected to the Regen In of the EG degasser.

Equilibrate the Dionex IonPac AS19 and AS24 columns with 65 mM KOH at their respective flow rates, shown in the Conditions section, for approximately 60 min. Analyze a matrix blank by injecting 1000 μL deionized water using 8–10 min as the default cut time. An equilibrated system has background conductances of $< 0.5 \mu\text{S}$ and $< 0.8 \mu\text{S}$ for the Dionex IonPac AS19 and AS24 columns, respectively. Determine the final cut time (preconcentration time) for the second dimension, as described in the next section, before injecting a bromate standard.

Determining the Cut Time for the Second Dimension

Because there may be slight variations in system plumbing, column capacity, and tubing lengths, individual laboratories should first determine the optimum cut time (from the first dimension) before determining bromate in the second dimension. To determine the cut time for analysis in the second dimension, we recommend performing duplicate 1000 μL injections of 15 $\mu\text{g/L}$ bromate prepared in deionized water and 15 $\mu\text{g/L}$ bromate prepared in an LSSM containing 100 mg/L each of chloride, sulfate, and bicarbonate and 10 mg/L each of nitrate-N and phosphate-P.

For this application, it is important that valve #2 on the second dimension remain in the inject position during this time to avoid any baseline disturbances that may occur in the first dimension. This can be accomplished by placing a semicolon (“;”) before the DC module inject commands in the Chromeleon program.

Determine the start time for placing valve #2 in the load position by subtracting 1 min from the retention time (RT) of bromate in the LSSM sample (in this experiment, bromate RT = 9 min – 1 min = 8 min). Determine the time for switching valve #2 to the inject position by adding 0.2 min to the time when the bromate peak in deionized water returns to the baseline (in this experiment, bromate returned to baseline = 9.8 min + 0.2 min = 10.0 min). The chromatograms used for the present experiment are shown in Figures 2A and 2B.

First-Dimension Conditions

Column: Dionex IonPac AG19, AS19, 4 mm
 Flow Rate: 1.0 mL/min
 Concentration: 10 mM KOH 0–12 min,
 65 mM 12.1–35 min
 Suppressor: Dionex ASRS ULTRA II suppressor, 4 mm,
 external water mode
 Current: 161 mA
 Inj. Volume: 1000 µL
 Temperature: 30 °C
 Matrix: A) LSSM
 B) Reagent water

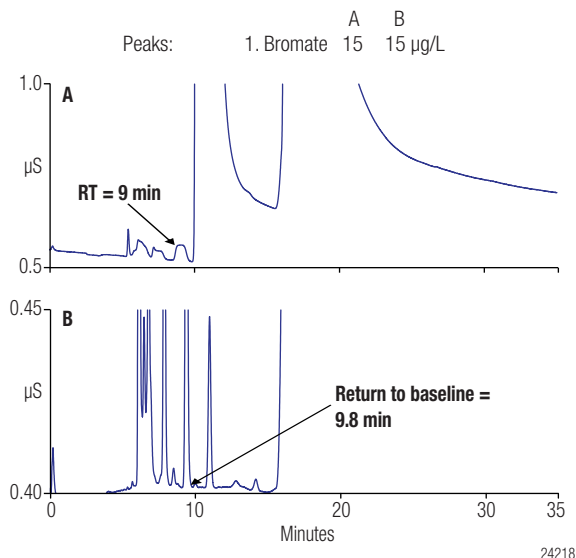


Figure 2. Determination of the cut window in the first dimension.

Note: It is important to verify the retention time of bromate on the Dionex IonPac AS19 column weekly to ensure good trapping efficiency on the Dionex IonPac TAC-ULP1 concentrator.

After the cut time has been established, enable valve #2 by removing the semicolons prior to the DC module inject commands in the Chromeleon CDS program. Perform duplicate injections of a 5 µg/L bromate standard to verify that nearly identical bromate retention times are achieved in the second dimension. Figure 3 shows an example chromatogram of 5 µg/L bromate separated on the Dionex IonPac AS24 column in the second dimension.

Results and Discussion

The bromate in the second dimension was calibrated by injecting a 1000 µL water blank and a duplicate injection of eight calibration standards in the first dimension to cover the desired concentration range. The peak area response generated by the calibration standards was tabulated against the bromate concentration using a quadratic regression curve. Table 1 summarizes the calibration data obtained from injecting standards in the range of 0.15–15 µg/L bromate. The accuracy of the calibration curve was verified by injecting a 5 µg/L bromate standard prepared from a second source, producing a calculated recovery of 97.1%.

Second-Dimension Conditions

Column: Dionex IonPac AG24, AS24, 2 mm
 Flow Rate: 0.25 mL/min
 Concentration: 10 mM KOH 0–24 min,
 10–65 mM 24.1–35 min
 Suppressor: Dionex ASRS ULTRA II suppressor, 4 mm,
 external water mode
 Current: 41 mA
 Cut Volume: 2 mL
 Concentrator: Dionex IonPac TAC-ULP1, 5 × 23 mm
 Temperature: 30 °C
 Peaks: 1. Bromate 5.0 µg/L

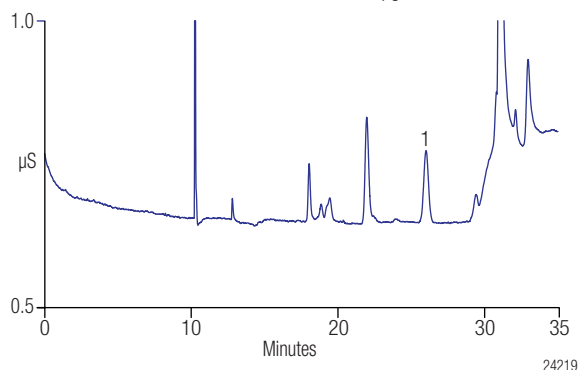


Figure 3. Chromatogram of a 5 µg/L bromate standard with the Dionex IonPac AS24 column in the second dimension.

Table 1. Calibration data and method detection limits for bromate.

Analyte	Range (µg/L)	Linearity* (r ²)	MDL Standard (µg/L)	SD (µg/L)	Calculated MDL (µg/L)
Bromate	0.15–15	0.9995	0.20	0.012	0.036

*Quadratic fit.

During the initial development of the 2-D method for determining trace concentrations of bromate, the lowest concentration minimum reporting level (LCMRL) was determined. The U.S. EPA has developed a statistical approach for determining a single-laboratory LCMRL using linear regression and prediction intervals and has found this to be a more systematic procedure for determining the minimum reporting level (MRL).¹⁷ The MRL is the lowest analyte concentration that demonstrates known quantitative quality, whereas the LCMRL is the lowest true concentration at which the future recovery is predicted to fall with a 99% confidence between 50% and 150% recovery. The LCMRL can be used to determine the MRL for a particular analyte by either using a multiplying factor or by combining results from a multi-laboratory study. Although the EPA encourages all laboratories to determine the LCMRL to aid in evaluating the performance of spiked recoveries at or below the MRL, it does not mandate LCMRL determinations.

In this study, the LCMRL was determined to be 0.15 µg/L bromate by preparing and analyzing seven individual replicate injections of 0.15, 0.20, 0.30, 0.40, and 0.50 µg/L bromate. The data from these replicate injections were then inserted into the statistical program

provided on the EPA website (approved methods are described at <http://www.epa.gov/OGWDW/methods/sourcalt.html>) to determine the LCMRL. The target MRL for this application was established at 0.50 µg/L bromate, which is just over three times the calculated LCMRL.

EPA Method 314.2, also using 2-D IC, does not require the determination of the detection limit for validation of the method. However, some laboratories may require this determination due to the various regulatory bodies associated with compliance monitoring. The limit of detection (LOD) of the 2-D method was determined for bromate by performing seven replicates of reagent water fortified with 0.20 µg/L bromate and using the following equation:

$$\text{LOD} = \text{St}_{(n-1, 1-\alpha=0.99)}$$

where:

$t_{(n-1, 1-\alpha=0.99)}$ = student's t-value for a 99% confidence level with n-1 (t=3.14 for seven replicate injections)

n=number of replicates

S=standard deviation of replicate analyses

A calculated LOD of 0.036 µg/L bromate was determined as shown in Table 1. The bromate LOD using 2-D IC is significantly lower than the bromate detection limits of 0.12 µg/L and 0.17 µg/L reported in EPA Methods 317.0 and 326.0, using postcolumn addition and absorbance detection.^{11,12}

The performance of the 2-D bromate method was evaluated through a single-operator precision and accuracy study using fortified municipal and natural mineral water samples. The recovery of bromate was evaluated by analyzing eight different matrices, including reagent water, LSSM, two municipal drinking waters from different sources, and four natural mineral waters from different countries (France, Japan, Switzerland, United Kingdom). Each sample was fortified with 0.5 and 5 µg/L bromate. To ensure the accuracy of the calibration curve, quality control standards prepared at 0.5, 5, and 15 µg/L bromate were analyzed at the beginning, middle, and end of each sample analysis batch.

Table 2 summarizes the performance of the method for determining trace concentrations of bromate in municipal drinking waters using 2-D IC. As shown, trace concentrations of bromate were detected in both municipal drinking water samples, well below the current regulatory limit of 10 µg/L. The most likely source of bromate in these samples is the hypochlorite solution used for disinfection treatment, as ozonation is not used at either of the tested drinking water treatment facilities.

For the municipal drinking waters fortified with 0.5 µg/L bromate, the calculated recoveries were between 98 and 99%. For the same samples fortified with 5 µg/L bromate, the recovery was approximately 105%. Figure 4 shows chromatograms of drinking water B, unfortified and

Table 2. Bromate recoveries from fortified reagent water, LSSM, and municipal drinking water matrices.

Matrix	Amount Found (µg/L)	Amount Added (µg/L)	Replicates	Average Recovery (%)	Peak Area Precision (RSD)
Reagent Water	—	0.5	7	101.5	1.98
		5.0	7	105.6	0.66
LSSM ^a	—	0.5	7	96.1	5.75
		5.0	7	106.7	1.66
Drinking Water A	0.45	0.5	7	98.2	6.06
		5.0	7	104.5	1.71
Drinking Water B	1.19	0.5	7	98.7	2.51
		5.0	7	105.6	1.91

^aLSSM = Laboratory synthetic sample matrix containing 100 mg/L each of chloride, sulfate, and bicarbonate and 10 mg/L each of nitrate-N and phosphate-P

Second-Dimension Conditions

Column: Dionex IonPac AG24, AS24, 2 mm
 Flow Rate: 0.25 mL/min
 Concentration: 10 mM KOH 0–24 min,
 65 mM 24.1–35 min
 Suppressor: Dionex ASRS ULTRA II suppressor,
 2 mm, external water mode
 Current: 41 mA
 Concentrator: Dionex IonPac TAC-ULP1, 5 × 23 mm
 Cut Volume: 2 mL
 Temperature: 30 °C
 Sample: A) Unfortified drinking water B
 B) Fortified drinking water B

Peaks: 1. Bromate 1.19 1.69 µg/L

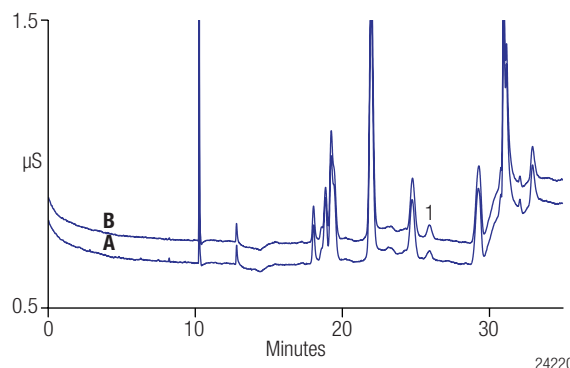


Figure 4. Chromatogram of (A) drinking water B and (B) drinking water B fortified with 0.5 µg/L bromate.

fortified with 0.5 µg/L bromate, using the combined Dionex IonPac AS19/AS24 columns with 2-D IC. As shown, bromate is well-resolved from any potential inference on the Dionex IonPac AS24 column, and therefore produces an excellent recovery of 98.7%.

Some drinking water samples may contain elevated concentrations of chloride, sulfate, and bicarbonate that can increase peak broadening of bromate, and therefore lower recovery. To determine whether the 2-D IC method can analyze these types of samples, an LSSM was prepared and fortified with 0.5 and 5 µg/L bromate. The excellent recoveries shown in Table 2 for this sample and system configuration indicate that bromate was not influenced by the increased concentrations of common anions.

In general, the ionic strength of natural mineral waters significantly exceeds the concentrations found in typical municipal drinking water samples. Determining low concentrations of bromate in these matrices using currently available methods is a challenging analytical problem because of column overloading. In some cases, sample dilution is required, increasing the MRL in proportion to the dilution factor. Alternatively, samples can be treated with Thermo Scientific™ Dionex™ OnGuard™ cartridges to remove most of the chloride, carbonate, and sulfate in the sample. However, this requires additional time and increases the cost of each analysis. One of the primary advantages of 2-D IC is that most samples can be injected directly without any sample pretreatment, thereby simplifying analysis.

In this study, four different natural mineral water samples were analyzed for bromate. Table 3 summarizes the ionic properties of three of the investigated samples according to the manufacturers' specifications. As shown, the ionic strength of the mineral waters analyzed in this study varied significantly. None of the bottled mineral waters indicated that ozonation was used as a disinfection treatment method; therefore, the detection of bromate was not anticipated.

Table 3. Concentrations (mg/L) of cations and anions of the investigated mineral water samples.

Mineral Water	Na ⁺	K ⁺	Mg ²⁺	Ca ²⁺	F ⁻	Cl ⁻	NO ₃ ⁻	HCO ₃ ⁻	SO ₄ ²⁻
A	5.5	0.7	9.5	50.8	— ^a	5.9	<3	190	5.8
B	9.0	0.6	3.4	147.3	0.12	21.5	18	390	33
C	4.2	— ^a	117	510	1.8	3.0	<0.1	278	1445

^a Not specified

The samples were fortified with 0.5 and 5 µg/L bromate to evaluate the accuracy of the 2-D method for determining bromate in natural mineral waters (Table 4). As shown, recoveries were in the range of 95–105% with peak area precisions for seven replicate injections in the range of 0.6–7.2%. Previously, a 250 µL direct injection of mineral water C was analyzed with the Dionex IonPac AS19 column followed by suppressed conductivity detection.¹⁶ Using the method parameters described in Application Note 184 required a 1:5 sample dilution to reduce the 1445 mg/L sulfate in the sample to avoid column overloading. This would result in an increase in the MRL by a factor of five. However, because the 2-D method removes most of the interfering matrix ions in the first dimension, the sample can be injected directly without any sample preparation steps, thereby maintaining the method's MRL of 0.5 µg/L bromate. However, the increased sulfate concentration did shift the retention time of bromate in the first dimension, resulting in a lower bromate recovery than expected. To improve the bromate recovery, the cut window was increased from 8–10 min to 7–10 min to account for the shift in retention time on the

Table 4. Bromate recoveries from fortified natural mineral water samples.

Matrix	Amount Found (µg/L)	Amount Added (µg/L)	Replicates	Average Recovery (%)	Peak Area Precision (RSD)
Mineral Water A	<MDL ^b	0.5	7	95.2	3.37
		5.0	7	103.9	1.22
Mineral Water B	<MDL	0.5	7	95.2	5.85
		5.0	7	105.5	0.62
Mineral Water C ^a	<MDL	0.5	7	95.6	7.23
		5.0	7	103.8	1.22
Mineral Water D	<MDL	0.5	7	96.5	4.00
		5.0	7	103.8	1.35

^a Cut time changed from 8–10 min to 7–10 min due to the increased amount of sulfate (1445 mg/L) that shifted retention times on the first-dimension column

^b <MDL = less than the method detection limit

Second-Dimension Conditions

Column: Dionex IonPac AG24, AS24, 2 mm
 Flow Rate: 0.25 mL/min
 Concentration: 10 mM KOH 0–24 min,
 65 mM 24.1–35 min
 Suppressor: Dionex ASRS ULTRA II suppressor,
 2 mm, external water mode
 Current: 41 mA
 Cut Volume: 2 mL
 Concentrator: Dionex IonPac TAC-ULP1, 5 × 23 mm
 Temperature: 30 °C
 Sample: A) Unfortified mineral water C
 B) Fortified mineral water C

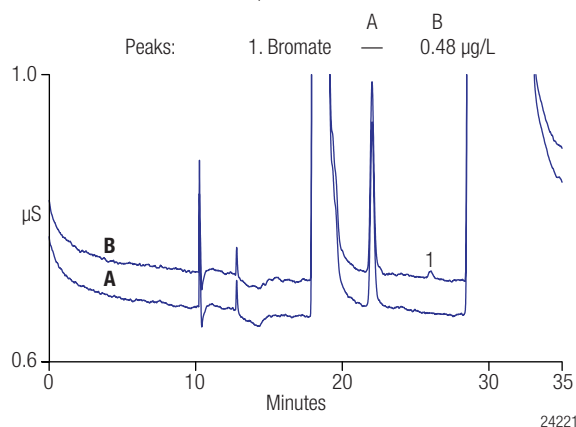


Figure 5. Chromatogram of (A) mineral water C and (B) mineral water C fortified with 0.5 µg/L bromate.

Dionex IonPac AS19 column. This minimal change in cut time resulted in a significant improvement in recovery from <50% to ~96%. Figure 5 shows example chromatograms of unfortified and fortified mineral water C. As shown in these chromatograms, a significant amount of chloride was transferred to the Dionex IonPac AS24 column due to the shift in retention times on the AS19 column. The Dionex IonPac AS24 column is a high-capacity anion-exchange column that provides an excellent bromate/chloride resolution as demonstrated in this example, and thereby allowed good quantification of bromate from the sample.

Conclusion

This application note describes a 2-D IC system for the determination of ≥ 0.5 $\mu\text{g/L}$ bromate in municipal and natural mineral waters. The method provides an improvement to existing EPA methods for bromate by providing lower detection limits and improved recoveries of bromate in high-ionic-strength matrices. In addition, samples can be injected directly without requiring the use of Dionex OnGuard cartridges, sample dilution, or sample degassing for carbonate removal prior to analysis. The elimination of time-consuming off-line sample preparation improves consistency between different analysts and laboratories. The method also allows the determination of trace concentrations of bromate in a wide range of sample matrices.

References

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