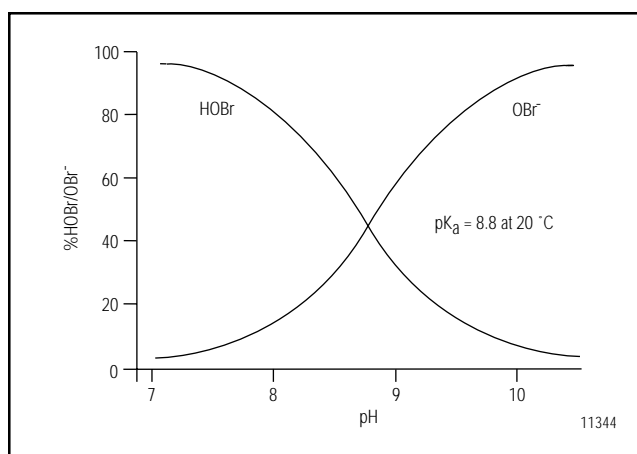
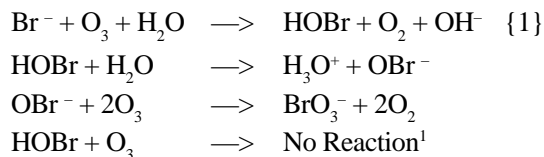


# Trace Level Determination of Bromate in Ozonated Drinking Water Using Ion Chromatography

## INTRODUCTION

During the 1970s it was discovered that the chlorination of drinking water produced carcinogens, such as the trihalomethanes. Since then environmental regulatory agencies, as well as drinking water treatment technologists, have been aggressively researching alternative disinfection methods that minimize the production of byproducts with significant health risks. Ozonation has emerged as one of the most promising alternatives to chlorination. Ozonation, however, tends to oxidize bromide to bromate, which presents a potential problem since bromide is naturally present in source waters. Bromate has been judged by both the U.S. EPA and the World Health Organization as a potential carcinogen, even at the low  $\mu\text{g/L}$  level. Many regulatory agencies prefer to regulate potential carcinogens to the  $10^{-5}$  health risk level or lower.\* The U.S. EPA has recommended that bromate in ozonated water be controlled to  $< 10 \mu\text{g/L}$  while further health risk studies are underway. Accordingly, analytical methods must be found to quantify bromate at these levels, so as to aid in researching ozonation process design options to minimize this contaminant.

The following equations show the pathway by which bromide ( $\text{Br}^-$ ) is oxidized by ozone to bromate ( $\text{BrO}_3^-$ ) through the intermediate formation of hypobromite ( $\text{OBr}^-$ ). These equations also show that ozone does not oxidize hypobromous acid ( $\text{HOBr}$ ) to bromate. Since increased acid ( $\text{H}_3\text{O}^+$ ) will favor the formation of hypobromous acid, this suggests that ozonation at a low pH will tend to minimize bromate formation (see Figure 1).



**Figure 1** A decrease in pH favors the formation of hypobromous acid.

The final concentration of bromate is dependent on the concentration of bromide in the source water, ozone concentration, and duration of contact. Currently, the separation of bromate in a drinking water matrix is accomplished by using direct injection ion chromatography (IC) with suppressed conductivity detection.

Table 1 shows the method detection limits (MDLs) for bromate and other anions of interest that were achieved by U.S. EPA researchers with a 200- $\mu\text{L}$  injected sample on a Dionex IonPac<sup>®</sup> AS9-SC column using a borate-based eluent. The detection limit for bromate using this methodology is  $7.3 \mu\text{g/L}$ .<sup>2</sup> Injecting a larger sample impairs chromatographic efficiency and does not significantly improve MDLs. The disadvantage to this method is that the amount of bromate present in a typical ozonated water sample is near or below the current detection limit.

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

This application note reports the development of a modified IC method that significantly improves the method detection limits for bromate by sample preconcentration. This method is consistent with the proposed ASTM method for bromate.<sup>3</sup>

In this method, the sample is first preserved by sparging to remove reactive gases, such as chlorine dioxide or ozone. Ethylenediamine is then added to convert any hypobromite to the corresponding bromamines, thus preventing their ongoing conversion to bromate. The preserved sample is then spiked with a magnesium chloride and a sodium carbonate reagent. This sample is then passed through three treatment cartridges in the following sequence: OnGuard-Ba, OnGuard-Ag, and OnGuard-H. This treatment reduces the concentration of sulfate, chloride, carbonate, and metals. The magnesium and carbonate ions are added to ensure reliable sulfate reduction, while maintaining high recovery of bromate.

The treated sample is then loaded into a large sample loop (e.g., 2–5 mL) and the anions remaining in the sample, including bromate, are concentrated on a high capacity concentrator column. A weak borate eluent is then used to elute the concentrated anions through the analytical column set where they are separated and through the suppressed conductivity detector where they are quantified. After bromate is eluted, a strong borate eluent is used to purge the columns of remaining ions prior to analysis of the next sample.

### EQUIPMENT

Dionex DX 500 IC system consisting of:

- GP40 Gradient Pump
- LC20 Chromatography Enclosure with Second Channel Option
- CD20 Conductivity Detector with DS3 Detection Stabilizer
- EO1 Eluent Organizer
- DXP Sample Delivery Pump
- AS40 Automated Sampler
- AC2 Power Control Accessory

PeakNet Chromatography Workstation

### REAGENTS AND STANDARDS

Deionized water, 17.8 MΩ-cm resistance or better (Type I reagent grade)

Boric acid, >99% pure (Aldrich, Milwaukee, Wisconsin, USA)

Anion	Spiking Conc. µg/L	Stats MDL <sup>a</sup> µg/L	Noise MDL <sup>b</sup> µg/L	Conservative MDL, µg/L
ClO <sub>2</sub> <sup>-</sup>	10.0	3.4	2.9	3.4
ClO <sub>3</sub> <sup>-</sup>	25.0	5.2	9.4	9.4
BrO <sub>3</sub> <sup>-</sup>	10.0	7.3	5.9	7.3
Br <sup>-</sup>	10.0	3.9	8.3	8.3

<sup>a</sup>MDL = SD (t<sub>1</sub>)

<sup>b</sup>MDL = 3 x noise

Conditions: 9 mM NaOH, 36 mM Boric acid, 1.0 mL/min, 200 µL injection

Sodium hydroxide, 50% (w/w) (Fisher Scientific, Pittsburgh, Pennsylvania, USA)

Potassium bromate (Fluka Chemie AG, Buchs, Switzerland)

Magnesium chloride (Aldrich, Milwaukee, Wisconsin, USA)

Sodium carbonate (Aldrich, Milwaukee, Wisconsin, USA)

Ethylenediamine, 99% (Aldrich, Milwaukee, Wisconsin, USA)

### SAMPLE PRETREATMENT CARTRIDGES

OnGuard™-Ba Cartridges

OnGuard-Ag Cartridges

OnGuard-H Cartridges

### CONDITIONS

Columns: IonPac AS9-SC Analytical, 4-mm i.d.  
IonPac AG9-SC Guard, 4-mm i.d.  
IonPac AG10 Guard, 4-mm i.d., or  
TAC-LP1 (Concentrator Column)

Metal Trap

Column: MetPac™ CC-1

Eluent A: 40 mM Boric acid/20 mM Sodium hydroxide

Eluent B: 200 mM Boric acid/100 mM Sodium hydroxide

Gradient:

Time (min)	Eluent A (%)	Eluent B (%)	Valve A (setting)	Valve B (setting)
0.00	100	0	Load	Inject
1.50	100	0	Inject	Load
6.50	100	0	Load	Inject
12.49	100	0	Load	Inject
12.50	0	100	Load	Inject
17.49	0	100	Load	Inject
17.50	100	0	Load	Inject

Flow Rate: 2 mL/min

Injection Volume\*: 5 mL (max.)

Concentrator Pump

Flow Rate: 2 mL/min

Detection: Suppressed conductivity

Suppressor: ASRS AutoSuppression,  
external water mode

Note: Loop volume should be checked by filling loop with water and determining actual volume by weight on an analytical balance.

\*Use 0.037-inch i.d. tubing for sample loop (1 cm = 6.9 µL)

## PREPARATION OF SOLUTIONS AND REAGENTS

### Standard Solutions

**Bromate ( $\text{BrO}_3^-$ ) 1000 mg/L**

Dissolve 1.31 g of potassium bromate ( $\text{KBrO}_3$ ) in water and dilute to 1.00 L.

### Preservation Solution

**Ethylenediamine Preservation Solution (45 g/L)**

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

### OnGuard-Ba Activating Reagents

**0.50 M ( $\text{MgCl}_2$ )**

Dissolve 48 g of magnesium chloride in water and dilute to 1 L.

**0.17 M ( $\text{Na}_2\text{CO}_3$ )**

Dissolve 18 g of sodium carbonate in water and dilute to 1 L.

### Chromatography Eluent (A)

**40 mM Boric Acid / 20 mM Sodium Hydroxide**

Dissolve 2.47 g boric acid in 990 mL of water, add 1.6 g of 50% sodium hydroxide, and dilute to 1.00 L.

Transfer this solution to an eluent container and vacuum degas for 10 minutes.

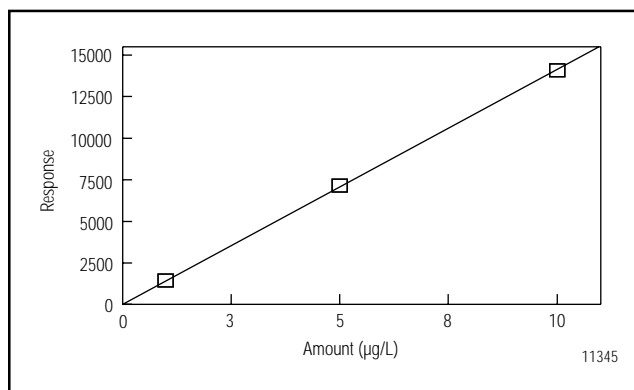


Figure 2 Linearity plot for bromate at µg/L levels.

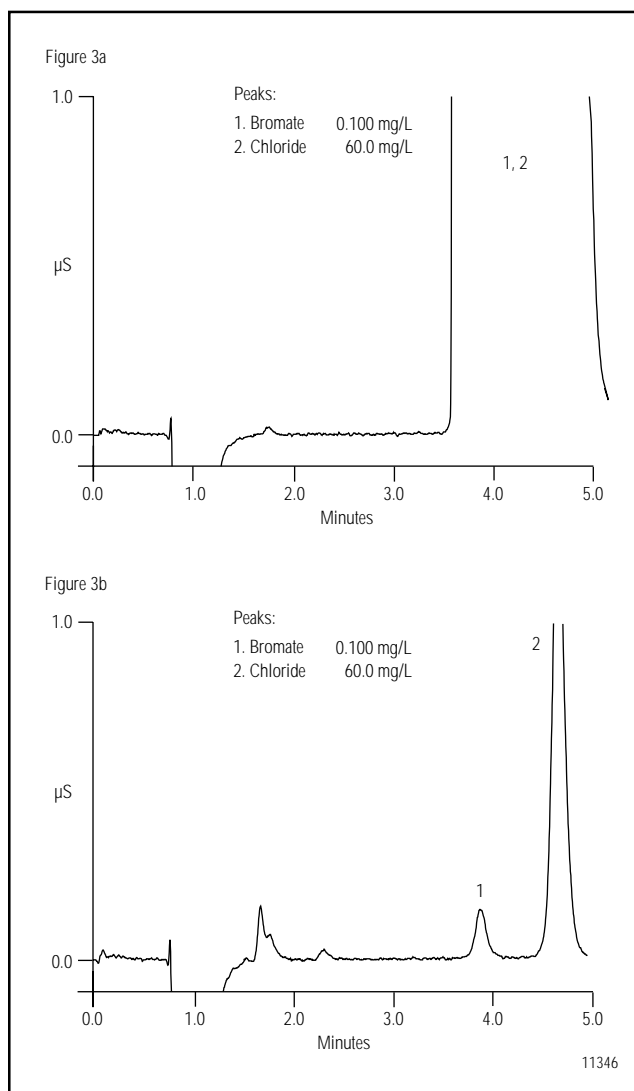


Figure 3a An untreated sample in which chloride coelutes with bromate.

Figure 3b A sample pretreated with OnGuard-Ag in which bromate is resolved from chloride.

## Purge Eluent (B)

### 200 mM Boric Acid /100 mM Sodium Hydroxide

Dissolve 12.36 g of boric acid in 900 mL of water, add 8.0 g of 50% sodium hydroxide and dilute to 1.00 L. Transfer this solution to an eluent container and vacuum degas for 10 minutes.

Note: Care must be taken to minimize air contact with hydroxide reagent as absorbed carbon dioxide will change eluent characteristics. Keep eluent containers pressurized with an inert gas to prevent atmospheric carbon dioxide from entering.

## Preparation of Calibration Standards

### Calibration Standards

Prepare calibration standards at a minimum of three concentrations in deionized water from the stock standard solution. The lowest concentration of the bromate standard should slightly exceed 1 µg/L, the method detection limit (MDL). The other concentrations of the calibration curve should correspond to the expected range of concentrations found in the samples of interest. A typical calibration curve is shown in Figure 2.

## SAMPLE PREPARATION

Samples should be sparged for 5 minutes to remove any reactive gases. Next, preserve samples with ethylenediamine to prevent oxidation of chlorite or formation of bromate from hypobromite by adding 1 mL of ethylenediamine preservation solution per liter of sample. Now add the OnGuard-Ba activating reagents: 1 mL of the 0.5 M magnesium chloride reagent and 1 mL of the sodium carbonate reagent to 100 mL of sample. All samples should be filtered through a 0.45-µm filter prior to injection. With high levels of sulfate, chloride, and carbonate in the sample matrix, the exchange sites on the AG10/AS9-SC columns are overloaded and bromate cannot be detected as a separate peak (Figure 3a). Sulfate is removed by passing the sample through the Dionex OnGuard-Ba cartridge. This cartridge removes sulfate by forming the precipitate barium sulfate.

Chloride is removed by passing the sample through the Dionex OnGuard-Ag cartridge. Chloride precipitates as silver chloride. Next, the sample is passed through the Dionex OnGuard-H cartridge. It minimizes the carbonate in the sample by converting it to carbonic acid, which is removed by sparging the sample with helium for 2–3 minutes.

**Table 2 Determination of bromate in drinking water, 5 mL preconcentrated**

Sample	Bromate Present (µg/L)	Bromate Added (µg/L)	Bromate Found <sup>a</sup> (µg/L)	n	SD (µg/L)	MDL <sup>b</sup> (µg/L)
Raw Water A	ND <sup>c</sup>	1.0	1.1	7	0.09	0.3
	ND	5.0	5.1	6	0.29	0.9
	ND	10.0	10.0	7	0.58	1.7
Raw Water B	1.1	0.0	1.1	7	0.04	0.1
Raw Water B (Ozonated)	1.1	1.0	1.2	7	0.11	0.3
	1.1	5.0	4.7	7	0.70	2.1
	1.1	10.0	10.0	5	1.52	5.1

<sup>a</sup>Reference to 10 µg/L fortification of matrix

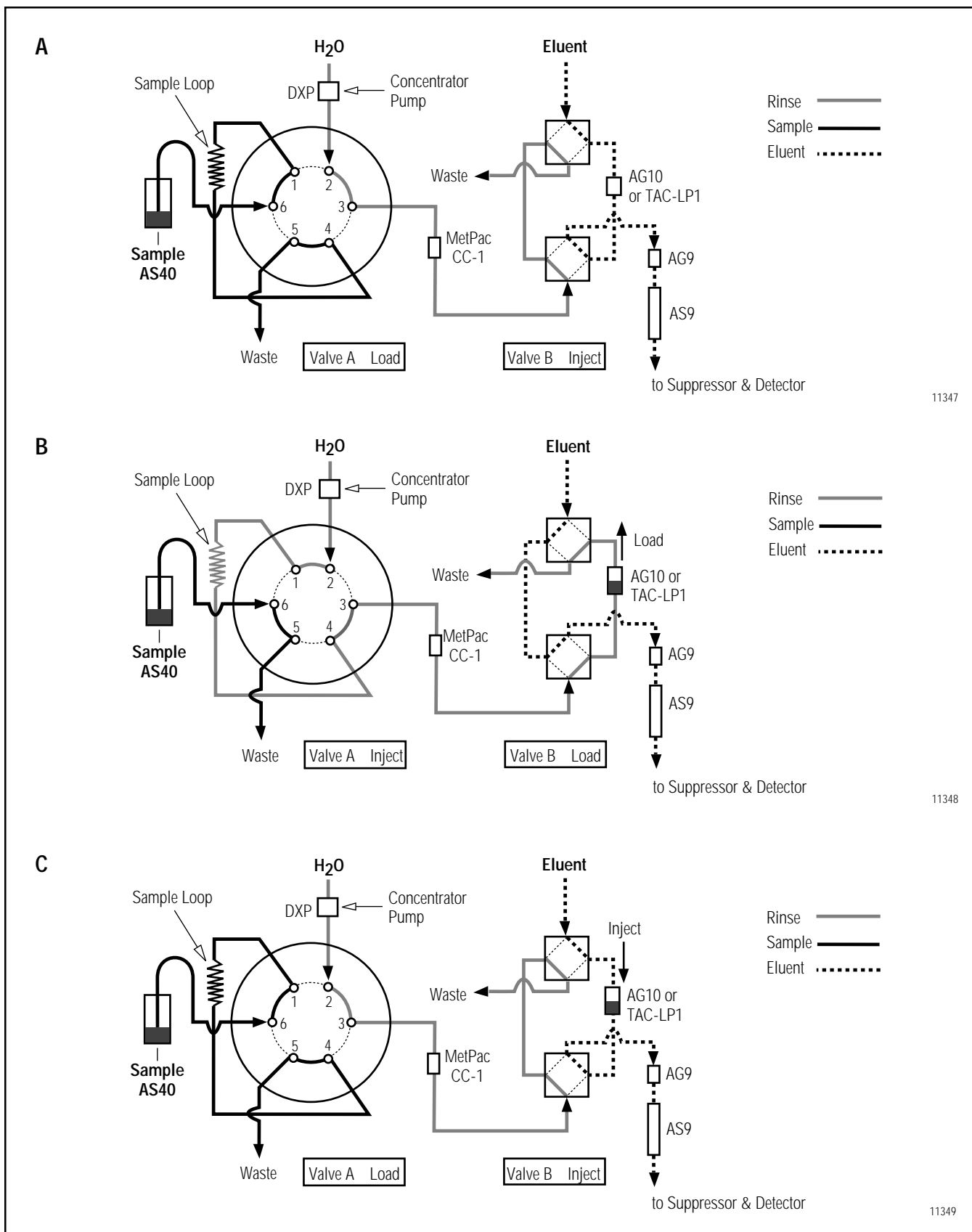
<sup>b</sup>MDL = SD × (t)<sub>99%</sub>

<sup>c</sup>ND = Not Detected (< 0.1 µg/L)

## DISCUSSION AND RESULTS

Traditionally, a cation resin in the barium-form has been used to remove sulfate from the sample matrices by forming a barium sulfate precipitate ( $K_{sp} = 1.1 \times 10^{-10}$ ). Using this method, however, the sulfate removal varies considerably. Our studies indicate that for consistent sulfate removal, a sample must have a sufficient amount of a divalent cation to displace the divalent barium from the resin so that it can react with sulfate.<sup>4</sup> Some samples have sufficient calcium and magnesium to initiate the barium displacement; whereas, others do not contain sufficient levels of calcium and magnesium. Therefore, to ensure consistent sulfate removal a divalent cation such as magnesium must be added. It has been determined that at least 120 mg/L in magnesium from magnesium chloride will provide sufficient barium displacement from a cation resin in the barium form (OnGuard-Ba) for removal of sulfate up to 500 mg/L. Furthermore, it has been found that a minimum level of carbonate is required to ensure high bromate recovery when sulfate is being removed by the OnGuard-Ba cartridge. The excess chloride can be removed with OnGuard-Ag treatment, which is also required for removing chloride that is normally present in the sample.

The OnGuard-Ag cartridge packing is a silver form, high capacity, strong acid, cation exchange resin that is designed to remove chloride from the sample matrices. The cartridge capacity is 1.5–1.8 meq per cartridge. By treating the sample with the OnGuard-Ag cartridge, the chloride level is reduced to approximately 0.4 mg/L; this level is sufficient to resolve bromate from chloride (see Figure 3b).



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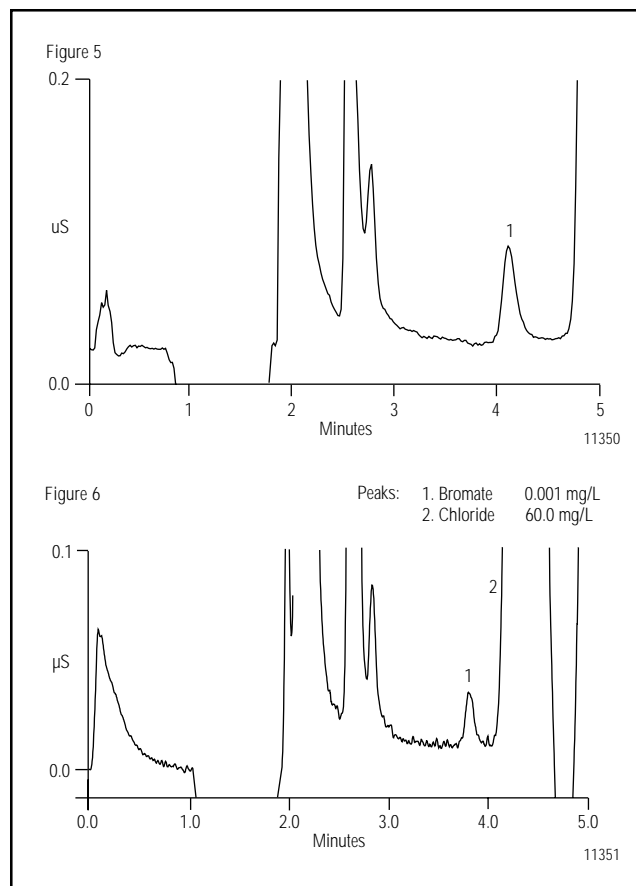
**Figure 4** Preconcentration suppressed IC system configuration. (A) sample loaded into loop; (B) sample washed onto concentrator column; (C) retained anions eluted to AG9/AS9-SC analytical column set.

The lower sulfate and chloride levels allow for a larger sample volume to be concentrated, which improves the bromate response. The OnGuard-H sample pretreatment cartridge is a hydrogen-form cation resin. Its use followed by helium sparging minimizes the carbonate in the sample, which further improves preconcentration efficiency. The use of the OnGuard-Ag leaches a small amount of silver from the cartridge into the sample matrix. The accumulation of silver on the analytical column and concentrator column will affect column performance over time. The OnGuard-H cartridge also removes metal ions such as silver. To further avoid metal contamination, a Dionex MetPac CC-1 column is installed between the two injection valves (see Figure 4). The MetPac CC-1 metal chelating column not only removes the silver, but it also removes other metal cations that may foul the analytical column.

The determination of bromate utilizing this method is a three step process as illustrated in Figures 4a–4c: Step 1 loads the sample loop, Step 2 washes the sample onto the concentrator, Step 3 separates the anions of interest on the analytical column. Figure 4a illustrates the sample being loaded into the sample loop using an autosampler. During this first step, the GP40 pumps Eluent A to the AS9-SC column. After the loop is filled, the DXP Pump is turned “ON” and it washes the sample from the sample loop onto the concentrator column using deionized water (see Figure 4b). The sample loop is then rinsed 2.5 times its volume to ensure that all of the sample is transferred onto the concentrator. The concentrator column strongly retains anionic species such as bromate, chloride, and sulfate. Figure 4c shows the concentrator column being switched in-line with the IonPac AG9/AS9-SC columns. At this step, the retained anions are eluted to the analytical column. After the chloride elution, the remaining anions are purged off the analytical column using the purge eluent.

After purging for 5 minutes, the AG9/AS9-SC columns are equilibrated with the chromatography eluent for 7–10 minutes. The equilibration time is placed at the beginning of the analysis sequence, during which the sample loop is being filled and the sample is flushed onto the concentrator column. The total analysis time for this method is 25 minutes. Table 2 lists the bromate MDLs that have been achieved when preconcentrating raw water samples, obtained before and after ozonation.

Using this method, bromate (at the low  $\mu\text{g/L}$  level) can be measured in a matrix containing as much as 200 mg/L of chloride, carbonate, and sulfate as shown in Figure 5. Figure 6 shows the analysis of an ozonated drinking water sample spiked with 1  $\mu\text{g/L}$  bromate.



**Figure 5** Bromate in the presence of 200 mg/L of chloride, carbonate, and sulfate.

**Figure 6** An ozonated drinking water sample is spiked with 1.0  $\mu\text{g/L}$  of bromate.

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3. American Society for Testing and Materials. Proposed ASTM Method “Determination of Oxyhalides and Bromide in Water by Chemically Suppressed Ion Chromatography,” under review by the ASTM D-19 Committee on Water.
4. Patent filed.



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