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Determination of trace concentrations of bromate in municipal and bottled drinking waters using a hydroxide-selective column with ion chromatography

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Abstract

The International Agency for Research on Cancer determined that bromate is a potential human carcinogen, even at low μg/l levels in drinking water. Bromate is commonly produced from the ozonation of source water containing naturally occurring bromide. Traditionally, trace concentrations of bromate and other oxyhalides in environmental waters have been determined by anion exchange chromatography with an IonPac AS9-HC column using a carbonate eluent and suppressed conductivity detection, as described in EPA Method 300.1 B. However, a hydroxide eluent has lower suppressed background conductivity and lower noise compared to a carbonate eluent and this can reduce the detection limit and practical quantitation limit for bromate. In this paper, we examine the effect of using an electrolytically generated hydroxide eluent combined with a novel hydroxide-selective anion exchange column for the determination of disinfection byproduct anions and bromide in municipal and bottled drinking water samples. EPA Methods 300.1 B and 317.0 were used as test criteria to evaluate the new anion exchange column. The combination of a hydroxide eluent with a high capacity hydroxide-selective column allowed sub-μg/l detection limits for chlorite, bromate, chlorate, and bromide with a practical quantitation limit of 1 μg/l bromate using suppressed conductivity detection and 0.5 μg/l using postcolumn addition of *o*-dianisidine followed by visible detection. The linearity, method detection limits, robustness, and accuracy of the methods for spiked municipal and bottled water samples will be discussed.

Keywords: Ion chromatography; Bromate; Disinfection byproduct anions; Municipal drinking water; Bottled drinking water; EPA Method 300.1B; EPA Method 317.0

1. Introduction

The presence of inorganic disinfection byproduct (DBP) anions, such as chlorite, bromate, and chlorate in drinking water is the result of using chemical disinfectants for microbiological treatment. The formation of DBPs is influenced by the treatment conditions and quality of the source water, such as the presence of natural organic matter, bromide, temperature, pH, and alkalinity. The most common treatments used to protect public water systems (PWSs) include chlorine, chlorine dioxide, chloramine, and ozone [1]. Chlorination of drinking water is known to produce trihalo methanes and other carcinogens that pose potential human health risks [2]. However, alternative disinfectant treatments such as chlorine dioxide or chloramine can generate DBP anions, such as chlorite and chlorate; that are also harmful to humans [3]. The formation of bromate from bromide by ozonation has gained considerable attention since the discovery that bromate is a potential human carcinogen [4]. In 1993, the World Health Organization (WHO) set a guideline of 25 μg/l for bromate in drinking water with an estimated excess lifetime cancer risk of 10^{-5} for 3 μg/l bromate [5]. Despite the health risks, this guideline was based on the limitations of the measurement technologies for bromate.

In the U.S., the lifetime cancer risk was estimated to be 10^{-4} for drinking water containing 5 μg/l with a potential 10^{-5} risk at 0.5 μg/l [4]. The U.S. Environmental Protection Agency (EPA) set a maximum contaminant level (MCL) for bromate at 10 μg/l under Stage 1 Disinfectants/Disinfection

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Byproducts (D/DBP) Rule in 1998 [6]. The EPA requires that PWSs serving 100,000 or more persons to report the concentration of target microorganisms present, the removal process used, and the concentration of DBPs present in their water [7]. Concerns about the health risks of bromate led the EPA to consider further reducing the MCL. However, a lower bromate MCL could potentially increase the concentration of other DBPs in drinking water and interfere with the efficiency of microbial pathogen inactivation. Therefore, the advisory committee recommended that the bromate MCL remain at 10 μg/l [8]. Based on this recommendation and other considerations, the EPA did not lower the MCL under the D/DBP Stage 2 Rule [9]. The European Union reduced their regulatory value from 50 to 10 μg/l bromate in drinking water in 1998 [10] and the WHO recently set a provisional guideline of 10 μg/l as technological advances since 1993 allowed the determination of lower bromate concentrations [11].

Bottled drinking water is a popular alternative to tap water for many consumers. Improved taste and the perception that it is a healthier choice are the primary reasons that from 1997 to 2002 bottled water sales increased from approximately 6–13% per year with growth increasing each year [12]. In the U.S., bottled water that is packaged and sold for consumption is considered a food product and therefore regulation of contaminants is the responsibility of the U.S. Food and Drug Administration (FDA). Because some bottled water products use ozone, the U.S. FDA adopted the EPA's MCL for bromate and the analytical methods used to monitor this contaminant in public drinking water [13]. The U.S. FDA also requires that bottled water manufacturers monitor their finished product for bromate and other DBPs 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).

Ion chromatography (IC) has been traditionally used for determining bromate and other DBPs in environmental waters as described in EPA Method 300.0 B [14]. This method describes the use of an IonPac AS9-SC column with a reported method detection limit (MDL) of 20 μg/l bromate. Unfortunately, this MDL does not meet the current regulatory requirement for bromate. However, modification of the method from a carbonate/bicarbonate eluent to a weaker borate eluent resulted in a significant selectivity improvement between bromate and chloride, decreasing the bromate detection limit from 20 to 5 μg/l [15]. Preconcentration followed by IC with suppressed conductivity was also investigated to reduce the MDL for bromate. Although this method could achieve an MDL at <1 μg/l, sample pretreatment was required and analysis times were long [16,17]. In 1998, the EPA promulgated Method 300.1 under the Stage 1 rule as an update to Method 300.0. This method reduced the bromate MDL to 1.4 μg/l. To achieve this MDL, EPA Method 300.1 uses an IonPac AS9-HC column, a high-capacity anion exchange column, with a carbonate eluent and a large loop injection followed by suppressed conductivity detection [18]. This method provided the simplest approach for PWS laboratories to meet the current MCL requirement.

Further developments allow laboratories to achieve sub-μg/l detection limits for bromate. The EPA promulgated two postcolumn derivatization procedures for bromate under the Stage 2 D/DBP rule [9]. EPA Method 317.0 adds capability to Method 300.1 B by allowing simultaneous suppressed conductivity and absorbance detection in order to achieve a sub-μg/l bromate MDL. This method uses a postcolumn addition of *o*-dianisidine followed by visible detection at 450 nm to achieve a bromate MDL of 0.1 μg/l with a practical quantitation limit (PQL of 0.5 μg/l [4,19]. Alternatively, bromate can be determined by postcolumn reaction with excess iodide under acidic conditions resulting in MDLs similar to those reported in Method 317.0 [20]. More sophisticated detection techniques, such as mass spectrometry (MS) and inductively-coupled plasma mass spectrometry (ICP-MS), have been used to determine bromate in environmental waters with reported bromate MDLs of 0.5 and 0.8 μg/l, respectively [21,22]. However, these approaches add considerable complexity and cost to each analysis.

Most promulgated EPA methods have used an AS9-HC column with a carbonate eluent. Although hydroxide eluents provide considerable advantages for this application over carbonate eluents, hydroxide has not been used due to the lack of a hydroxide-selective anion exchange column with a suitable selectivity for bromate and other oxyhalides. In this paper, we report the determination of low μg/l bromate in environmental waters using a large volume direct injection followed by separation with a new hydroxide-selective column with suppressed conductivity detection using EPA Method 300.1 (B) and combined suppressed conductivity and visible detection using EPA Method 317.0. The linear range, method detection limits, and method robustness will be discussed. In addition, the suitability of the column for the determination of bromate and other oxyhalides in a variety of municipal and bottled drinking water samples is described.

2. Experimental

2.1. Instrumentation

A Dionex ICS-2000 Reagent-Free Ion Chromatograph (Dionex Corporation, Sunnyvale, CA, USA) was used for EPA Method 300.1 (B). The ICS-2000 is an integrated ion chromatograph that incorporates an electrolytic eluent generator, dual piston pump with vacuum degas, six-port injection valve fitted with a 250 μl injection loop, heated conductivity cell, and column heater set at 30 °C. A Dionex ICS-2500 Reagent-Free Ion Chromatograph was used for EPA Method 317.0. The ICS-2500 consisted of a GP50 gradient pump, an EG50 eluent generator, an AS50 thermal compartment with conductivity cell, and a CD25A conductivity detector. A pressurized postcolumn delivery module (PC 10, Dionex) was used to deliver the postcolumn reagent at a flow rate of 0.54 ml/min. The flow rate of the postcolumn reagent was adjusted to a lower flow rate to maintain the same analyt-

ical flow to PCR flow ratio as described in Method 317.0. A 500 μl knitted reaction coil was placed in a postcolumn heater (PCH-2, Dionex), set at 60 °C, to mix the effluent and postcolumn reagent. An AS50 autosampler was used for sample processing with both systems. A Dionex IonPac AS19 (250 mm × 4 mm i.d.) analytical column and its respective guard column, AG19 (50 mm × 4 mm i.d.) were used for all analytical separations. An EluGen EGC-KOH cartridge and continuously regenerated anion trap column (CR-ATC) were used with the AS19 column. All analytes were detected by suppressed conductivity with an ASRS ULTRA II (4 mm) self-regenerating suppressor operating at 130 mA current in the recycle mode for EPA Method 300.1 (B) and the external water mode for Method 317.0. Chromeleon 6.6 chromatography management software was used for system control and data processing.

2.2. Reagents and samples

All solutions were prepared in deionized water with a specific resistance of at least 18 MΩ cm or better (Labconco, Kansas City, MO, USA). Commercially available 1000 mg/1 stock standards of fluoride, chloride, and sulfate (Dionex) and nitrite, bromide, nitrate, and phosphate (VWR Scientific, San Francisco, CA, USA) were used to prepare working standards. Stock solutions (1000 mg/1) of bromate and chlorate were prepared from analytical-grade sodium salts (EM Science, Gibbstown, NJ, USA). The chlorite stock solution (1000 mg/1) was prepared from 80% technical grade sodium salt (Fluka Chemical Co, Ronkonkoma, NY, USA) because high purity sodium chlorite is not commercially available due to its potential explosive instability. Stock standards for most anions are stable for at least 1 month when stored at 4 °C, except chlorite, which is stable for only 2 weeks when stored protected from light at 4 °C.

A stock solution of ethylenediamine (EDA) was prepared by diluting 2.8 ml EDA (99%, Sigma–Aldrich, St. Louis, MO, USA) to 25 ml of deionized water. Samples were preserved by adding 50 μl of the stock EDA to 100 ml of sample. This is primarily used as a preservative for chlorite because chlorite is susceptible to degradation through catalytic reactions with dissolved iron salts and is reactive towards free chlorine that exists as hypochlorous acid/hypochlorite ion in most drinking waters [18]. Although calibration standards do not require preservation, the same amount of EDA was added to each standard solution to minimize any potential bias between samples and standards.

The *o*-dianisidine postcolumn reagent was prepared as described in section 7.6 of Method 317.0 [19] by combining 40 ml of 70% redistilled nitric acid (Sigma–Aldrich) to approximately 300 ml of deionized water in a 500 ml volumetric flask and adding 2.5 g of potassium bromide (VWR Scientific). In a separate 250 ml volumetric flask, 250 mg *o*-dianisidine, dichloride salt (Sigma–Aldrich) was dissolved in 100 ml methanol (Spectrophotometric grade, Sigma–Aldrich). After dissolution, the *o*-diansidine was added to the 500 ml volumetric flask and diluted to the mark with deionized water. This solution was allowed to stand overnight until the slight champagne color faded and was then filtered through a 0.45 μm filter before use.

The municipal drinking waters analyzed for the presence of DBP anions and bromide were obtained from five cities in Northern California, including Sunnyvale, Palo Alto, Union City, Vacaville, and Twain Harte Valley. The surface water was collected from a lake in Twain Harte Valley and the well water was obtained from two different private sources in Brentwood, CA, USA. Ten bottled drinking water samples (bottled water #s 1–10) were randomly purchased from a local grocery store and two samples (bottled water #s 11 and 12) were obtained from water dispensers. The types of bottled water samples analyzed in this study included spring water (bottled water #s 1, 3, 6–10), purified water (bottled water #s 2, 5, 11, 12), and mineral water (bottled water # 4). Bottled waters 1, 4, 7, and 9 did not provide treatment processes used, other than filtration (bottled water #7). All samples were included for the evaluation of EPA Method 300.1 (B) whereas randomly selected samples were used to evaluate Method 317.0.

3. Results and discussion

3.1. Column development

It is well known that hydroxide eluents provide significantly lower suppressed background conductivity, lower baseline noise, and therefore lower detection limits than "conventional" carbonate eluents [23]. Therefore, our initial goal was to develop a column with a suitable hydroxide selectivity that would improve the sensitivity for the DBP anions, chlorite, bromate, and chlorate, in typical environmental waters. To achieve this goal, the column had to meet the following characteristics: (1) good bromate/chloride resolution, (2) good resolution of chlorite, chlorate, and bromide from other potentially interfering ions, and (3) high ion exchange capacity to tolerate large sample injection volumes (200–500 μl). The IonPac AS19 met these goals. The IonPac AS19 is a high capacity, hydroxide-selective column, capable of tolerating at least a 250 μl injection for the determination of trace concentrations of DBP anions and bromide in typical environmental waters.

The AS19 stationary phase is based on a novel hyperbranched anion exchange condensation polymer that is electrostatically attached to the surface of a wide pore polymeric substrate. The resin of the AS19 contains alternating treatments of epoxy and amines that produce a coating that grows directly off the surface of the sulfonated substrate. The number of alternating coating cycles allows a carefully controlled ion exchange capacity with a polymer that is extremely hydrophilic and therefore has excellent selectivity for a hydroxide eluent. The high hydroxide selectivity allows relatively low hydroxide concentrations to be used, despite the high

column capacity. The hyper-branched anion exchange polymer of the AS19 compared to the methacylate-based latex used for the AS9-HC column provides significantly better pH stability, allowing the use of hydroxide as an eluent. The AS19 column also has a slightly greater anion exchange capacity of 240 μeq/column compared to 190 μeq/column for the AS9-HC and an improved selectivity between bromate and chloride (AS19 R_s = 4.6 versus AS9-HC R_s = 3.4), which is important for the analysis of matrices containing excess amounts of chloride (e.g., wastewaters) and other potentially interfering ions. Fig. 1 compares the AS9-HC column specified in EPA Method 300.1 to the AS19 hydroxide-selective column for the separation of seven common inorganic anions and DBP anions. The selectivity for chlorate and bromide is reversed on the AS19 compared to the AS9-HC column. Also, phosphate elutes last on the AS19 column due to the higher eluent pH that results in a greater charge on the polyprotic acid species. The AS19 also has an overall improved resolution between other important peaks pairs, such as fluoride/chlorite (AS19 R_s = 9.8 versus AS9-HC R_s = 6.2) and chloride/nitrite (AS19 R_s = 7.4 versus AS9-HC R_s = 6.8).

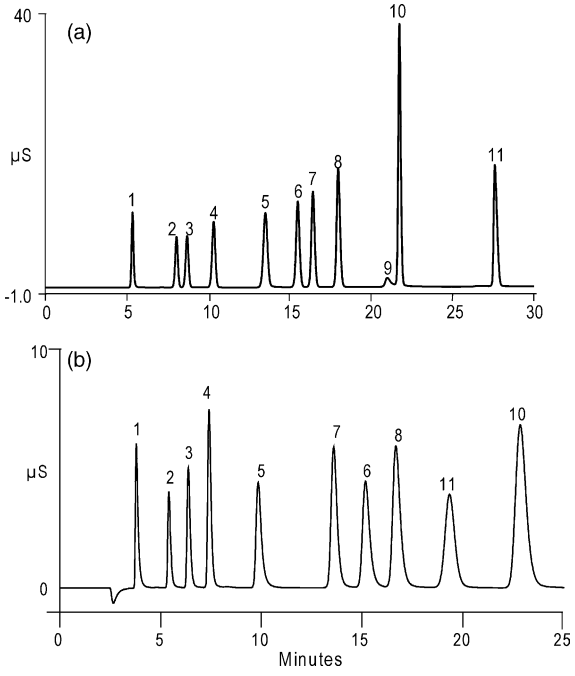

Fig. 1. Comparison of the IonPac AS9-HC to the AS19 column for the separation of DBP anions and bromide. Conditions: (a) column, IonPac AS19; eluent source, ICS-2000 EG with CR-ATC; eluent, 10 mM potassium hydroxide 0–10 min, 10–45 mM 10–25 min; column temperature, 30 °C; flow rate, 1.0 ml/min; detection, ASRS ULTRA II operated at 130 mA in the recycle mode; injection volume, 25 μl; (b) column, IonPac AS9-HC; eluent, 9 mM sodium carbonate; flow rate, 1.0 ml/min; detection, ASRS ULTRA operated in the external water mode; injection volume, 25 μl; analytes, 1-fluoride (3 mg/l), 2-chlorite (10 mg/l), 3-bromate (20 mg/l), 4-chloride (5 mg/l), 5-nitrite (15 mg/l), 6-chlorate (25 mg/l), 7-bromide (25 mg/l), 8-nitrate (25 mg/l), 9-carbonate, 10-sulfate (30 mg/l), 11-phosphate (40 mg/l).

3.2. Method performance using a hydroxide-selective column

The initial performance criteria, according to Section 9.2 of EPA Method 300.1, was assessed by determining the method linearity, MDLs, and the precision and recovery of a quality control sample (QCS). Because hydroxide produces an exceptionally low suppressed background conductivity (<1 μS), compared to 9 mM sodium carbonate (~22 μS), a lower PQL of 1 μg/l bromate was achieved using the hydroxide-selective column (250 μl injection).

Therefore, bromate was calibrated from 1 to 40 μg/l using an eight-point calibration curve by tabulating peak area versus concentration. Chlorite, chlorate, and bromide were each calibrated from 20 to 500 μg/l using a seven-point calibration curve. A second calibration data set was acquired for the DBP anions and bromide using the procedure described in Method 317.0. For this method, the calibration range for chlorite, chlorate, and bromide spanned two orders of magnitude from 5 to 500 μg/l. The addition of a postcolumn reagent (PCR) and visible detection reduces the bromate PQL from 1 to 0.5 μg/l. Therefore, bromate was calibrated over the range of 0.5–15 μg/l, as recommended by Method 317.0. Part of the quality control procedure for Method 300.1 includes the analysis of a quality control sample (QCS) where the stated recoveries must be ±15%. However, Method 317.0 requires an initial demonstration of precision and accuracy to qualify the instrument and laboratory performance prior to performing analyses. Table 1 summarizes the calibration data and the results of the quality control requirements using

Table 1
Linearity and quality control data obtained using the hydroxide-selective AS19 column

Analyte	EPA Method 300.1 B					EPA Method 317.0				
	Range (μg/l)	Linearity (r^2)	Recovery of QCS[a] (%)	Retention time precision (% RSD[b])	Peak area precision (% RSD)	Range (μg/l)	Linearity (r^2)	Recovery of QCS[a] (%)	Retention time precision (% RSD[b])	Peak area precision (% RSD)
Chlorite	20–500	0.9997	94.8	<0.03	0.44	5–500	0.9982	98.2	0.11	3.64
Bromate (conductivity)	1–40	0.9995	97.4	<0.03	1.09	1–40	0.9997	94.2	0.17	2.37
Bromate (UV–vis)	–	–	–	–	–	0.5–15	0.9996	98.5	0.35	1.76
Chlorate	20–500	0.9996	95.9	<0.03	0.12	5–500	0.9999	102.6	0.09	1.92
Bromide	20–500	0.9997	96.0	<0.03	0.11	5–500	0.9997	96.9	0.03	0.92

[a] QCS: quality control sample contained 100 μg/l each of chlorite, chlorate, and bromide and 15 μg/l bromate for EPA Method 300.1 B and 10 μg/l each of chlorite, chlorate, and bromide and 5 μg/l bromate for EPA Method 317.0.

[b] RSD: relative standard deviation, n = 10 for Method 300.1 B and n = 7 for Method 317.0.

Table 2
Comparison of method detection limits for disinfection byproduct anions and bromide

Analyte	Hydroxide-selective IonPac AS19 column[a]			Carbonate-selective IonPac AS9-HC column	
	EPA Method 300.1 B MDL[b] (μg/l)	EPA Method 300.1 B MDL in simulated drinking water[c] (μg/l)	EPA Method 317.0 MDL (μg/l)	EPA Method 300.1 B MDL[d] (μg/l)	EPA Method 317.0 MDL[e] (μg/l)
Chlorite	0.23	0.26	0.26	1.15	0.80
Bromate (conductivity)	0.34	0.42	0.32	1.06	0.64
Bromate (UV–vis)	–	–	0.14	–	0.11
Chlorate	0.32	0.30	0.38	2.04	0.56
Bromide	0.54	0.52	0.52	0.78	0.62

[a] 250 μl injection volume.
[b] MDL: $\sigma t_{s,99}$ where $t_{s,99} = 3.14$ for $n = 7$.
[c] The simulated drinking contained 1 mg/l F^-, 50 mg/l Cl^-, 0.1 mg/l NO_2^-, 10 mg/l NO_3^-, 100 mg/l CO_3^{2-}, 50 mg/l SO_4^{2-}, 0.1 mg/l PO_4^{3-}.
[d] MDLs adjusted for differences in injection volumes (200–250 μl).
[e] MDLs adjusted for differences in injection volumes (225–250 μl).

suppressed conductivity detection without postcolumn addition (EPA Method 300.1 B) and with postcolumn addition (EPA Method 317.0). The results show excellent linearity for all target analytes and the addition of the PCR equipment did not influence the results obtained using conductivity detection. Both methods exhibited excellent recoveries of the target DBP anions and excellent retention time and peak area precisions as shown in Table 1. These results demonstrate that the use of a hydroxide eluent combined with a hydroxide-selective column successfully meet EPA's quality control criterion.

MDLs for chlorite, bromate, chlorate, and bromide were determined by performing seven replicate injections of the target analytes fortified at concentrations of three to five times the estimated instrument detection limits in reagent water. The MDLs were calculated according to section 9.2.3 of Method 300.1 by multiplying the standard deviation of the replicate analyses by the Student's *t*-value for a 99% confidence level and standard deviation estimate with $n - 1$ degrees of freedom ($t = 3.14$ for seven replicates). Table 2 compares the calculated MDLs in reagent water and simulated drinking water (EPA Method 300.1 B only) for EPA methods 300.1 B and 317.0 using a hydroxide-selective column to the reported values using a carbonate-selective AS9-HC column [18,19]. An electrolytically generated hydroxide eluent system combined with an appropriate hydroxide-selective column produced a bromate detection limit between 0.32 and 0.34 μg/l using a 250 μl large loop injection. The results in Table 2 demonstrate that a hydroxide eluent improves the sensitivity of bromate and other oxyhalides in environmental waters by 50–75% compared to using a carbonate eluent. In comparing the detection limits in reagent water to simulated drinking water, the calculated MDLs for chlorite, chlorate, and bromide were not significantly different. However, increasing concentrations of chloride can influence the detection of low concentrations of bromate. The presence of 50 mg/1 chloride in the simulated drinking water resulted in a slight increase (∼20%) in the detection limit of bromate from 0.34 to 0.42 μg/l. However, the observed increase in the bromate MDL is still significantly less than the detection limit reported in Method 300.1 B using the AS9-HC column and more than adequate to meet current regulatory requirements.

Published IC methods that use postcolumn addition provide improved selectivity and sensitivity for the determination of trace concentrations of bromate in environmental waters [4,19]. Initially, we confirmed that the presence of bromate in a suppressed hydroxide eluent (e.g., water) did not influence the reaction of the *o*-dianisidine reagent compared to the procedure described in Method 317.0 where the suppressed eluent is a weak carbonic acid. The calculated bromate MDLs shown in Table 2 demonstrate comparable detection limits as reported in Method 317.0 using a carbonate eluent. The addition of a postcolumn reagent followed by visible detection improved the bromate detection limit by more than 50% compared to using suppressed conductivity detection with a hydroxide eluent.

3.3. Method robustness

The effects of sample injection volume and increasing concentrations of chloride and sulfate in Sunnyvale, CA, USA drinking water were investigated to examine the robustness of the hydroxide-selective AS19 column for trace bromate determinations. A high concentration of chloride is the primary contributor to influencing an accurate quantification of bromate. The most commonly observed symptoms of chloride interference include reduced retention time, reduced peak efficiency, and peak overlapping that typically lead to low bromate recoveries. Although chloride is a primary contributor to these effects, excessive concentrations of other anions can combine to produce the same results. The most commonly observed high concentration anions in environmental samples include chloride, sulfate, and carbonate. Injection volumes of 250 and 500 μl were evaluated to determine the most appropriate volume to achieve the required sensitivity for the methods, but that could also tolerate the ionic strengths typically found in most environmental samples. An ideal test mixture was a simulated high inorganic water (HIW) sample, as described in Method 300.1 B, containing 100 mg/1 each of chloride, sulfate, and carbonate. Although these concentrations are higher than in most drinking water samples,

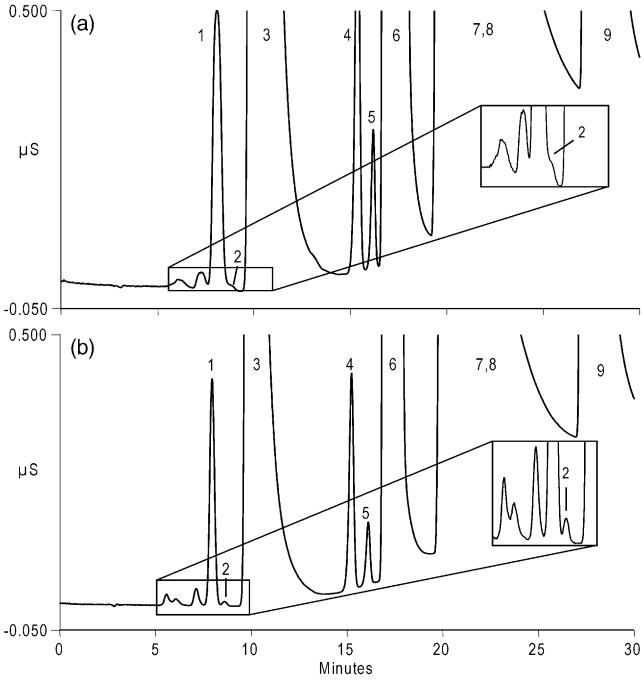

Fig. 2. Comparison of injection volumes for the analysis of simulated high inorganic water. Conditions: same as Fig. 1a except; injection volume, (a) 500 μl, (b) 250 μl; analytes, 1-chlorite (0.1 mg/l), 2-bromate (0.005 mg/l), 3-chloride (100 mg/l), 4-chlorate (0.1 mg/l), 5-bromide (0.025 mg/l), 6-nitrate (10 mg/l-N), 7-carbonate (100 mg/l), 8-sulfate (100 mg/l), 9-phosphate (10 mg/l-P).

the concentrations are not unusual for some ground water samples. Fig. 2 compares 500 and 250 μl injections of a HIW sample. As illustrated in this example, 5 μg/l bromate was no longer visible using the larger injection volume, however, a 250 μl injection resulted in an acceptable recovery of 84.6%. Therefore, a 250 μl sample injection was determined to be an appropriate volume for tolerating most environmental samples while still providing an improved sensitivity for bromate.

To assess the effect of the chloride concentration on the quantification of bromate, increasing chloride concentrations were added to a Sunnyvale, CA, USA drinking water sample. Because EPA methods routinely use analyte recovery to properly evaluate laboratory performance, the recovery of bromate was used as the primary characteristic to estimate the tolerable chloride concentration for the hydroxide-selective AS19 column. EPA Method 300.1 considers 75–125% analyte recovery to be acceptable for concentrations ranging from the MRL to 10×MRL (i.e., 1–10 μg/l with the AS19 column). Therefore, this criterion was used as the determining factor in these experiments. The Sunnyvale, CA drinking water contained a native concentration of 30 mg/1 chloride and chloride was added up to 200 mg/1 (i.e., total chloride concentration = 230 mg/1). From 130 to 230 mg/1 of chloride added, the recovery of 5 μg/l bromate decreased from an acceptable 85.8% to an unacceptable level of 52.8%. However, increasing concentrations of sulfate had very little influence on the recovery of bromate. The addition of

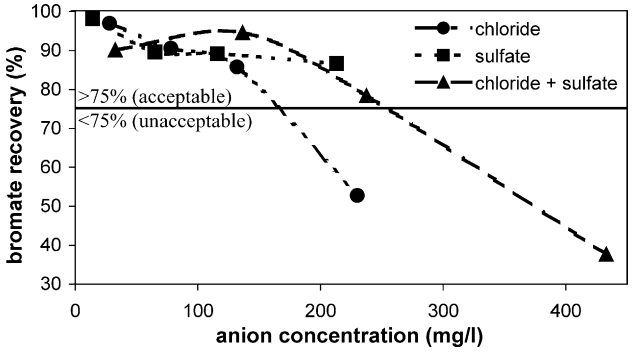

Fig. 3. Effect of increasing concentrations of chloride and sulfate on the recovery of 5 μg/l bromate. Conditions: column, IonPac AS19; eluent source, ICS-2000 EG with CR-ATC; eluent, 10 mM potassium hydroxide 0–10 min, 10–45 mM 10–25 min; column temperature, 30 °C; flow rate, 1.0 ml/min; detection, ASRS ULTRA II operated 130 mA in the recycle mode; injection volume, 250 μl.

200 mg/1 sulfate (total sulfate concentration = 214 mg/1) to the drinking water sample produced a recovery of 87% compared to 98% with no sulfate added. A combination of chloride and sulfate added in equal concentrations produces a greater influence on the bromate recovery than chloride alone. Equal concentrations of 200 mg/1 chloride and sulfate (total concentration = 430 mg/1) were added to the Sunnyvale, CA drinking water containing 5 μg/l bromate. Bromate recovery decreased significantly from 78 to 38% for total chloride and sulfate concentrations of 240 and 430 mg/1, respectively. Fig. 3 summarizes the influence of increasing concentrations of chloride, sulfate, and an admixture of the two. From this graphical representation, we estimated that the total tolerable chloride concentration was 150 mg/1, representing a 1:30,000 bromate to chloride ratio. However, this was slightly reduced to 120 mg/1 upon the addition of an equal concentration of sulfate. Typically, most drinking water samples contain significantly less than the tolerable concentrations determined in this study.

3.4. Application to municipal drinking waters

Chlorination has been commonly used for more than a century to disinfect public drinking waters. However, chlorination of drinking water can produce trihalomethanes and other suspected carcinogenic DBPs that can endanger human health. Therefore, many Northern California counties have converted from chlorination to chloramination as a safer alternative to disinfecting drinking water. Drinking water samples from five different municipalities in Northern California and untreated surface water and well water samples were analyzed for the presence of DBP anions and bromide. Table 3 demonstrates typical single-operator recovery data obtained using the AS19 column with suppressed conductivity detection for the determination of trace concentrations of DBP anions and bromide in typical environmental waters. Table 4 shows the same data collected for a drinking water and a surface water sample using combined suppressed conductiv-

Table 3
Single operator recovery results for DBP anions and bromide spiked in environmental and bottled drinking waters using Method 300.1 B with the IonPac AS19 column

Sample	Chlorite			Bromate			Chlorate			Bromide		
	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 (%)
Drinking water A	8.8	10.0	95.3	<MDL	5.00	92.2	81.9	106	96.9	26.3	30.0	99.6
Drinking water B	<MDL[a]	21.0	105.6	<MDL	5.10	95.6	120	144	104.4	202	200	99.8
Drinking water C	11.6	10.0	95.7	<MDL	5.00	96.8	85.3	90.7	97.6	1.2	25.0	94.2
Drinking water D	<MDL	20.0	108.0	1.3	4.90	93.9	73.6	79.4	98.2	9.7	10.0	107.4
Drinking water E	4.6	14.0	93.4	<MDL	5.00	100.5	136	151	99.0	<MDL	20.0	24.8[b]
Surface water	<MDL	20.0	95.7	<MDL	5.00	94.7	<MDL	20.0	96.8	<MDL	20.0	103.3
Shallow well water[c]	<MDL	21.0	103.1	16.0	9.80	101.1	<MDL	30.0	96.8	381	200	104.0
Well water[c]	<MDL	20.0	101.4	<MDL	5.00	86.5	10.6	20.0	93.0	452	230	100.7
Bottled water 1	<MDL	20.0	108.1	<MDL	5.00	96.1	2.4	20.0	107.7	7.5	20.0	105.0
Bottled water 2[d]	<MDL	20.0	102.9	<MDL	5.00	100.7	<MDL	20.0	106.5	<MDL	20.0	106.5
Bottled water 3[d]	<MDL	20.0	99.8	10.2	9.80	104.6	<MDL	20.0	102.8	19.4	20.0	92.9
Bottled water 4	<MDL	20.0	90.2	<MDL	5.00	83.5	10.2	20.0	103.0	95.5	105	97.7
Bottled water 5	<MDL	20.0	101.2	<MDL	5.00	95.9	1.6	20.0	108.6	1.2	20.0	95.6
Bottled water 6[d]	<MDL	20.0	101.5	9.2	9.80	106.6	375	150	97.3	2.5	20.0	100.9
Bottled water 7	<MDL	20.0	106.7	<MDL	5.00	92.3	<MDL	25.0	90.6	31.8	30.0	98.9
Bottled water 8[d]	<MDL	20.0	102.2	<MDL	5.00	93.7	<MDL	20.0	105.4	18.7	20.0	93.8
Bottled water 9	<MDL	20.0	106.1	<MDL	5.00	98.4	<MDL	20.0	105.7	2.7	20.0	104.1
Bottled water 10[d]	<MDL	20.0	98.2	4.4	5.00	101.1	<MDL	20.0	107.7	<MDL	20.0	105.3
Bottled water 11[d]	<MDL	20.0	104.8	<MDL	5.00	96.4	<MDL	23.0	98.3	6.3	23.0	94.5
Bottled water 12[d]	<MDL	20.0	95.2	0.98	5.00	102.1	4.2	20.0	98.5	<MDL	20.0	99.2

[a] <MDL indicates less than the method detection limit.
[b] Suspect/matrix.
[c] Sample diluted 1:1.
[d] Manufacturer used ozonation as part of the disinfection treatment.

ity and postcolumn addition with ODA followed by visible detection.

The data in these tables demonstrate acceptable recoveries (i.e., 80–120%) for most inorganic DBP anions and bromide using either EPA methods. However, the unusually low recovery of bromide (i.e., <30%) in drinking water E was an exception. Increasing the spiked bromide concentration from 20 to 250 μg/l did not produce any improvement in the recovery. Section 9.4.1.5 of EPA Method 300.1 states "If the recovery of any analyte falls outside the designated laboratory fortified matrix recovery range and the laboratory performance for that analyte is shown to be in control (Section 9.3), the recovery problem encountered with the laboratory fortified matrix is judged to be either matrix or solution related, not system related." Based on successfully meeting all quality control requirements, the low recovery was judged to be sample related and was therefore labeled as "suspect/matrix." A bromate concentration of 1.3 μg/l was detected in drinking water D using the hydroxide-selective column (Table 3). The determination of this low bromate concentration in a typical drinking water sample further demonstrates the improved sensitivity achieved using a hydroxide eluent. The bromate concentration measured in this sample is less than the PQL of 5 μg/l bromate using the AS9-HC column. Although, this value is significantly lower than the regulatory limit, the maximum contaminant level goal for bromate in drinking waters is zero. However, this same drinking water source collected 6 months later resulted in the detection 2.5 μg/l bromate by suppressed conductivity with a comparable concentration confirmed with postcolumn addition (Table 4). Fig. 4 shows chromatograms obtained for this sample using EPA Method 317.0. Fig. 4a demonstrates that 2.5 μg/l bromate is easily resolved from other potentially interfering ions (e.g., chloride) present in the sample and Fig. 4b shows an enhanced response for bromate using postcolumn addition with *o*-dianisidine. Fortification of the drinking water with 3 μg/l bromate resulted in calculated recoveries of approximately 103 and 96% by suppressed conductivity and visible detection, respectively.

Because the shallow well water sample is not known to be treated, it was surprising to find bromate in excess of the EPA's MCL. The reason for this is unclear. This sample also contained estimated chloride and sulfate concentrations of 160 and 280 mg/1, respectively. Although bromate is well resolved from the excess chloride, the bromate recovery fell below 80%, outside the 80–120% EPA specifications (concentration > 10 × MRL). Therefore, a 50% dilution was used to improve the bromate recovery. Section 4.1.2 of EPA Method 300.1 states ". . . sample dilution will alter your minimum reporting limit (MRL) by a proportion equivalent to that of the dilution." The presence of 8 μg/l bromate in the diluted sample was still well above the 2 μg/l adjusted MRL and therefore could be reported for compliance monitoring.

Table 4
Single operator recovery results for DBP anions and bromide spiked in environmental and bottled drinking waters using Method 317.0 with the IonPac AS19 column

Sample	Chlorite			Bromate (conductivity)			Bromate (UV–vis)			Chlorate			Bromide		
	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 (%)	Amount found (μg/l)	Amount added (μg/l)	Recovery (%)
Drinking water D	<MDL	5.00	97.0	2.50	3.00	103.3	2.20	3.00	96.3	64.0	73.0	94.2	18.8	20.0	98.1
Surface water	<MDL	5.00	104.5	<MDL	1.00	103.4	<MDL	1.00	97.4	<MDL	5.00	103.7	<MDL	5.00	102.0
Bottled water 3	<MDL	5.00	94.6	9.98	10.0	95.7	10.1	10.0	102.8	<MDL	5.00	99.0	18.0	20.0	97.5
Bottled water 5	<MDL	5.00	97.5	<MDL	1.00	110.5	<MDL	1.00	106.9	1.60	5.00	104.0	0.90	5.00	111.5

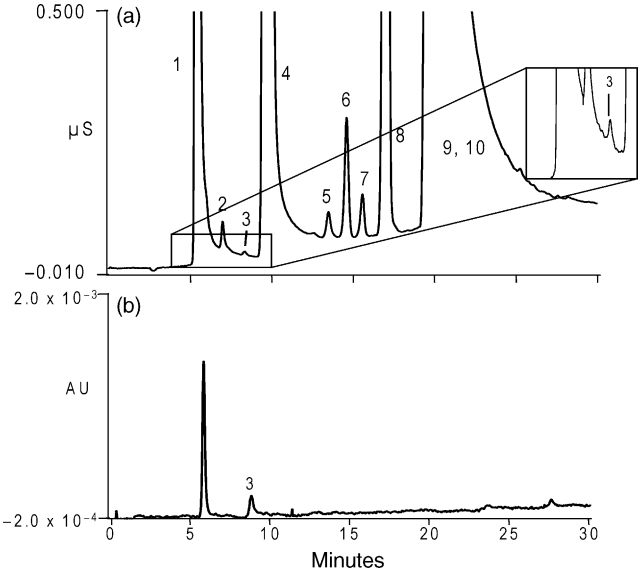

Fig. 4. Analysis of drinking water D for DBP anions and bromide using EPA Method 317.0. Conditions: column, IonPac AS19; eluent source, EG50 with CR-ATC; eluent, 10 mM potassium hydroxide 0–10 min, 10–45 mM 10–25 min; column temperature, 30 °C; flow rate, 1.0 ml/min; detection: (a) suppressed conductivity with ASRS ULTRA II operated at 130 mA in the external water mode; (b) visible detection at 450 nm after post-column reaction with *o*-dianisidine; PCR flow rate, 0.54 ml/min; PCR temperature, 60 °C; injection volume, 250 μl; analytes: (a) 1-fluoride (0.75 mg/l), 2-formate, 3-bromate (0.0025 mg/l), 4-chloride (35.7 mg/l), 5-nitrite (0.04 mg/l), 6-chlorate (0.064 mg/l), 7-bromide (0.019 mg/l), 8-nitrate (1.4 mg/l), 9-carbonate, 10-sulfate (45 mg/l); (b) 3-bromate (0.0022 mg/l).

Recoveries of the target analytes in the sample ranged from 96.8 to 104%.

3.5. Application to bottled drinking waters

Many consumers have a strong preference for bottled drinking water based on a better taste compared to chlorinated tap water. There also appears to be a widely held perception that bottled water is healthier and safer than the water provided by local municipalities. However, bottled water is not entirely free of potential health risks. For the twelve bottled waters randomly selected for this study, the treatment processes included filtration, reverse osmosis, deionization, UV light, and ozonation. Four bottled water manufacturers reported using no treatment other than filtration. Tables 3 and 4 shows single-operator spiked recovery data for DBP anions and bromide in bottled waters. Bromate was found in four of the bottled drinking waters tested. The concentrations ranged from 1 μg/l for the purified drinking water (bottled water #12) to 10.2 μg/l for the natural spring water (bottled water #3). All bottled water samples where bromate was detected reported using ozonation as a disinfection treatment. However, ozonation was also reportedly used for bottled waters 2, 8, and 11, but no bromate was detected. It is generally assumed that ozonation of source water containing bromide will result in the formation of bromate. Furthermore, two of the

three ozonated bottled waters where no bromate was detected also contained bromide concentrations of 6.3 and 18.7 μg/l, respectively. However, bromide concentrations varied from <MDL to 19.4 μg/l in samples containing bromate. Though we do not know the bromide concentrations of the bromate-containing waters prior to ozonation, this study observed no correlation between the presence of naturally occurring bromide and the formation of bromate in the bottled drinking water samples. The formation of bromate from bromide is based on several factors, such as the presence of natural organic matter, pH, temperature, and the ozone dosage used and therefore these variables could contribute to the results observed.

To determine the accuracy of the methods using the AS19 column, samples were spiked with known amounts of the target analytes. For samples in which the target analyte concentrations were <MDL, spiked concentrations were 20 μg/l chlorite, chlorate, and bromide and 5 μg/l bromate when using the procedure described in Method 300.1 B. For samples determined with Method 317.0, spiked concentrations were 5 μg/l chlorite, chlorate, and bromide and 1 μg/l bromate. For bottled waters containing bromate, recoveries ranged from 101.1 to 106.6% using Method 300.1 B and 95.7–102.8% for bottled water #2 using Method 317.0. Overall, recoveries ranged from 83.5 to 111.5% for the analysis of the spiked bottled water samples, well within EPA's specifications. Fig. 5a shows a chromatogram of an ozonated bottled water containing about 1 μg/l bromate, 4 μg/l chlorate, and no bromide. The improvement in method sensitivity using a hydroxide eluent allowed the detection of a low concentration of bromate in the sample. The concentrations of common anions (e.g., chloride, sulfate, etc.) are also relatively low compared to most tap water samples, therefore permitting the use of larger sample injection volumes (e.g., 500 μl). Fig. 5b shows the same bottled water sample spiked with 20 μg/l each of chlorite, chlorate, and bromide and 5 μg/l bromate with calculated recoveries between 95.2 and 102.1%.

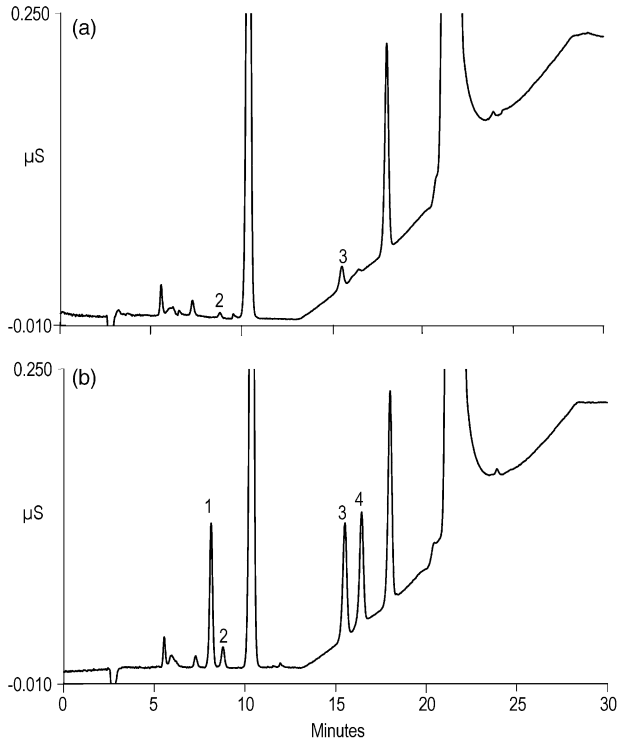

Fig. 5. Analysis of bottled drinking water #12 using EPA Method 300.1 B. Conditions: same as Fig. 3 except; sample: (a) bottled water and (b) spiked bottled water. Analytes: (a) 2-bromate (0.00098 mg/l), 3-chlorate (0.0042 mg/l); (b) 1-chlorite (0.022 mg/l), 2-bromate (0.0049 mg/l), 3-chlorate (0.022 mg/l), 4-bromide (0.022 mg/l).

The precision of the method using a hydroxide-selective column with an electrolytically generated eluent was evaluated by performing 10 replicate injections of most bottled water samples spiked with trace concentrations of DBP anions and bromide. For samples spiked with 5 μg/l bromate (bottled waters 1, 2, 5, 7, 9, 11), we obtained retention time and peak area precisions of <0.1 and <1.8%, respectively. A 1.8% peak area precision calculates to ±0.09 μg/l bromate, a relatively insignificant difference. Overall, retention time precisions were <0.04% for most target analytes while peak area precisions varied from 0.21 to 1.78%. In general, electro lytically generating the eluent online improves the method's precision by avoiding common errors and potential contamination encountered from the manual preparation of eluents offline. Furthermore, this simplifies the method and eliminates the time required to prepare eluents, particularly for a system operating 24 h a day as is common for trace analysis.

4. Conclusion

A novel polymeric anion exchange column was specifically developed for the determination of trace bromate and other oxyhalides in drinking water. The use of an electrolytically generated hydroxide eluent combined with a hydroxide-selective IonPac AS19 column permits a practical quantitation limit of 1 μg/l bromate using a 250 μl injection with suppressed conductivity detection and 0.5 μg/l using postcolumn addition with *o*-dianisidine followed by visible detection. The hydroxide eluent produced significantly lower suppressed background conductivity; compared to the carbonate eluent described in Method 300.1 B, enabling sub-μg/l detection limits of chlorite, bromate, chlorate, and bromide. Both methods were linear for the DBP anions and bromide over the concentration range investigated and acceptable recoveries in the range 83.5–111.5% were obtained for the target analytes spiked in typical municipal and bottled drinking water samples.

The described method based on a hydroxide-selective AS19 column improves the determination of trace bromate in environmental waters by exceeding the 5 μg/l MRL for bromate reported in EPA Method 300.1 B [9]. All quality control requirements were successfully fulfilled to comply with EPA Methods 300.1 B and 317.0. Electrolytically generated hydroxide eluents further enhance the performance

of both methods by eliminating the time and potential errors from manually preparing the eluent offline.

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