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Determination of trace level bromate in drinking water by direct injection ion chromatography

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Abstract

Disinfection byproduct anions such as bromate, chlorite and chlorate pose significant health risks, even at low μg/l levels in drinking water. A direct injection, ion chromatographic method was developed using a Dionex AS9-HC anion-exchange column with a carbonate eluent and suppressed conductivity detection for the determination of these disinfection byproduct anions, and bromide, at low μg/l levels in drinking water. No additional sample pretreatment, other than filtration, is required. The method is linear for the oxyhalides and bromide over the typical concentration range expected for these analytes in drinking water; and quantitative recoveries were obtained for drinking water samples spiked at 10 μg/l. This ion chromatographic method, based on the recently developed AS9-HC column, is applicable for the quantitation of bromate in finished drinking water at the 10 μg/l maximum contaminant level currently being proposed by the US EPA.

Keywords: Trace analysis; Bromate

1. Introduction

Bromate is a disinfection byproduct (DBP) anion produced from the ozonation of source water that contains naturally occurring bromide [1]. Ozonation is becoming increasingly prevalent as a disinfection technique, as the chlorination of drinking water results in the production of carcinogens, such as trihalomethanes, which pose significant health risks [2]. Bromate itself has also been judged by both the World Health Organization (WHO) and the US Environmental Protection Agency (EPA) as a potential carcinogen, even at very low μg/l levels. The US EPA has estimated a potential cancer risk equivalent to 1 in 10^4 for a lifetime exposure to drinking water containing bromate at 5 μg/l [3].

The occurrence of bromate and other DBPs in US drinking water is currently being documented by the EPA through the comprehensive collection of data mandated by the Information Collection Rule (ICR) [4]. The EPA has proposed a maximum contaminant level (MCL) of 10 μg/l bromate in finished drinking water [5]. The ICR now requires drinking water utilities using either ozonation or chlorine dioxide for disinfection to report the concentration of bromate in finished water to levels as low as 10 μg/l [6]. The EPA also intends to convene a second regulatory negotiation on bromate in the near future, while both Germany and Japan are in the process of setting regulatory limits for bromate [7]. The recent efforts by regulatory agencies worldwide to monitor levels

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and establish regulatory limits has prompted considerable interest in the development of new analytical methods for the determination of trace level bromate.

The determination of bromate and other DBPs has traditionally been accomplished using ion chromatography (IC), as detailed in US EPA Method 300.0(B) [8]. This method specifies the use of an IonPac AS9-SC anion-exchange column with a carbonate–bicarbonate eluent and suppressed conductivity detection. However, Method 300.0 cannot meet the quantitation limit requirements of the current ICR (i.e., 10 μg/l) and modifications to the method are permitted according to the DPB/ICR Analytical Methods Manual [9]. These modifications include the use of a weaker borate eluent to improve resolution between bromate and chloride and also the use of sample pretreatment in order to minimize chloride interference [2,10]. The use of sample preconcentration with on-line matrix elimination has been demonstrated to further improve detection limits for bromate when using IC with suppressed conductivity detection [2,5,11]. This approach, while somewhat complicated, does allow sub-μg/l determination of bromate in drinking water.

Post-column derivatization IC has also been used to improve detection limits for bromate analysis. The use of IC with post-column addition of chlorpromazine, a selective reagent that does not react with chloride, can achieve an method detection limit (MDL) for bromate of 0.49 μg/l [6]. This phenothiazine derivative is readily oxidized by bromate in acid, forming an oxidized species that can be detected spectrophotometrically at 530 nm. Oxyhalide species, such as iodate, chlorite and bromate, have also been detected by post-column reaction with excess bromide under acidic conditions. This results in formation of the tribromide ion, which can be detected spectrophotometrically at 267 nm, allowing an MDL of less than 0.5 μg/l for bromate when using a large volume injection [12,13].

In addition to post-column derivatization, electrospray tandem mass spectrometry (MS–MS) and inductively-coupled plasma mass spectrometry (ICP-MS) have been used as detection techniques for the ion chromatographic analysis of bromate. The use of IC with electrospray MS–MS detection results in a limit of quantitation for bromate of approximately 0.1 μg/l after appropriate sample pretreatment followed by solid-phase extraction and elution with a water–methanol ammonium nitrate eluent [7,14]. The use of IC with ICP-MS detection requires less sample pretreatment in order to achieve an MDL of 0.8 μg/l for bromate, however the separation conditions must be carefully chosen as brominated haloacetic acids can interfere with the analysis [13,15].

While the post-column and MS-based detection techniques described above can all be used to achieve sub-ppb detection limits, they each add considerable complexity, and in some cases significant cost, to the analytical method. In this paper, we report on the development and application of a new anion-exchange column which allows the routine quantification of bromate at the 10 μg/l level using a direct injection, conductivity-based detection method. This column differs from that specified in US EPA Method 300.0(B) in that it has higher capacity and improved separation of the key oxyhalide anions from potential interferences. The range and MDLs which can be achieved using this method will be discussed, in addition to its suitability for determining oxyhalides and bromide in a variety of drinking water samples.

2. Experimental

2.1. Instrumentation

The ion chromatograph used for this work was a Dionex (Sunnyvale, CA, USA) DX-500 System consisting of GP40 gradient pump, AS40 automated sampler, CD20 conductivity detector and LC20 chromatography enclosure equipped with a Rheodyne (Cotati, CA, USA) Model 9126 injector. Chemical suppression was achieved using a Dionex ASRS-II, operated at 100 mA in the external water mode at a flow-rate of 8.0 ml/min. Dionex IonPac AS9-SC and AS9-HC (250×4 mm I.D.) analytical columns and respective guard columns, AG9-SC and AG9-HC (50×4.0 mm I.D.), were used for all separations. A Dionex PeakNet Chromatography Workstation was used for system control and data collection.

2.2. Reagents and procedures

All solutions were prepared from analytical-reagent grade chemicals (where possible) in 18 MΩ water, obtained from a Water Pro PS purification system (Labconco, Kansas City, MO, USA). Commercially available (Dionex) 1000 μg/ml stock standards of fluoride, chloride, nitrite, bromide, nitrate, phosphate and sulfate were used, while 1000 μg/ml stock solutions of bromate and chlorate were prepared from their analytical-reagent grade sodium salts (EM Science, Gibbstown, NJ, USA). A stock solution (1000 μg/ml) of chlorite was prepared from 80% technical grade sodium salt (Fluka, Ronkonkoma, NY, USA), as high purity sodium chlorite is not commercially available due to potential explosive instability. Stock standards were stored at 4°C and were all stable for at least two weeks. Commercially available (Dionex) 0.5 *M* sodium carbonate and 0.5 *M* sodium bicarbonate concentrates were used for all eluent preparation.

It has been previously established that preservation of drinking water samples is required to prevent oxidation of chlorite [10]. Ethylenediamine (EDA) sample preservation solution was prepared by diluting 10 ml of EDA (Fluka, 99%) to 200 ml with water. Drinking water samples were sparged with helium for 5 min to remove any reactive gases, e.g., chlorine dioxide or ozone, prior to the addition of 1.0 ml of preservation solution per liter of sample. All working standards, samples and mobile phases were prepared fresh daily.

3. Results and discussion

3.1. Column development

The IonPac AS9-HC analytical and AG9-HC guard column set used for this work were developed for the routine determination of low ppb levels of bromide and disinfection byproduct anions (chlorite, bromate and chlorate) in drinking water by IC using suppressed conductivity detection. The specific intent was to allow the quantitation of 5 μg/l bromate, and 10 μg/l each of chlorite, bromide and chlorate in drinking and treatment plant waters of relatively high ionic strength using a large loop (200–500 μl) injection, with little or no sample pretreatment.

The packing material for the AS9-HC was optimized, in terms of both capacity and selectivity, to allow improved separation of the DBP anions from common inorganic anions. The majority of the stationary phases used in suppressed IC are low capacity, pellicular resins, which consist of a monolayer of charged latex particles electrostatically attached to a surface functionalized, non-porous core particle [16,17]. The outer latex particles are generally fully functionalized and the ion-exchange capacity of the resin is typically increased by using a larger diameter latex [18]. However, the production of a high-capacity column requires the use of latex with a large diameter, which ultimately results in band broadening and decreased chromatographic efficiency. An alternative means of increasing capacity is to use a superporous resin (2000 Å pore size) which allows a thin latex layer to be coated on both the exterior and interior surfaces of the resin. This approach was used to produce the AS9-HC column and provides a simple way to increase the resin capacity by 5–10-fold using a standard diameter latex while maintaining the high chromatographic efficiency typically associated with pellicular materials.

As is the case with the AS9-SC column, which was previously recommended for oxyhalide monitoring, the outer layer of the AS9-HC column consists of a quaternary aminated, methacrylate-based latex. This material provides significantly improved selectivity for oxyhalide species compared to the more commonly used vinylbenzyl chloride (VBC)-based resins [18]. One disadvantage of methacrylate-based polymers is that they are less pH stable than VBC-based materials. The higher capacity resulting from the use of a superporous resin for the AS9-HC column required the use of a higher ionic strength and higher pH eluent to achieve satisfactory elution times. However, the glycidyl methacrylate-based latex used for the AS9-SC column did not provide sufficient hydrolytic stability when used with the most appropriate eluent conditions. A variety of functional monomers were evaluated and a glycidoxyethyl methacrylate-based material was subsequently chosen for the AS9-HC column as the best compromise in terms of selectivity and pH stability

[19,20]. The net outcome of this development was a column which has approximately six-times the capacity (190 vs. 35 μequiv./column), improved pH stability and better overall resolution of the target DBP anions from common inorganic anions compared to the column specified in EPA Method 300.0(B). Fig. 1 shows a comparison of the AS9-SC column and the recently developed AS9-HC column for the separation of chlorite, bromate and chlorate, in addition to the seven common inorganic anions. The AS9-HC column has significantly improved overall resolution and greatly enhanced separation of the target DBP anions from common anions, particularly the critical peak pairs of fluoride/chlorite, bromate/chloride and chlorate/nitrate.

3.2. Application to drinking water analysis

The improved selectivity and increased capacity of the AS9-HC column allows the introduction of relatively large sample volumes (200–500 μl) without resolution or overloading problems. Fig. 2 shows a chromatogram of low level DBP anions and bromide in simulated drinking water sample. Despite the use of a 200-μl injection, bromate can be determined at 5 μg/l in the presence of a 10 000-fold excess of chloride. MDLs for chlorite, bromate, bromide and chlorate were determined according to US EPA guidelines [21]. Seven replicate aliquots of simulated drinking water matrix, fortified with the target analytes at a concentration of three- to five-times the estimated instrument detection limit, were injected and the MDL calculated as follows:

$$\mathrm{MDL} = tS$$

where, t = Student's t value for a 99% confidence level and a standard deviation estimate with $n-1$ degrees of freedom ($t = 3.14$ for seven replicates); and S = standard deviation of the replicate analysis. The results of the MDL study are shown in Table 1.

The results in Table 1 demonstrate that using a large loop injection with the AS9-HC column and suppressed conductivity detection can meet the quantitation requirements of the current ICR and the

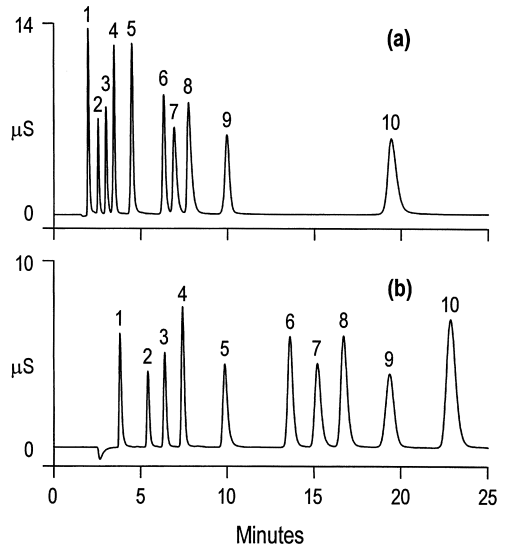

Fig. 1. Comparison of the AS9-SC and AS9-HC columns for the separation of oxyhalide anions and bromide. Conditions: guard columns, (a) Dionex IonPac AG9-SC and (b) Dionex IonPac AG9-HC; analytical columns, (a) IonPac AS9-SC and (b) IonPac AS9-HC; eluents, (a) 1.8 m*M* sodium carbonate–1.7 m*M* sodium bicarbonate and (b) 9.0 m*M* sodium carbonate; flow-rate, 1.0 ml/min; detection, suppressed conductivity with an ASRS operated at 100 mA in external water mode; injection volume, 25 μl. Solutes, 1 = fluoride (3 mg/l), 2 = chlorite (10 mg/l), 3 = bromate (20 mg/l), 4 = chloride (6 mg/l), 5 = nitrite (15 mg/l), 6 = bromide (25 mg/l), 7 = chlorate (25 mg/l), 8 = nitrate (25 mg/l), 9 = phosphate (40 mg/l), 10 = sulfate (30 mg/l).

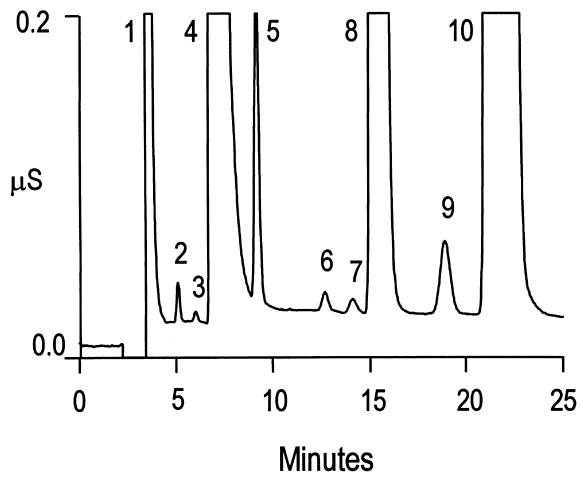

Fig. 2. Determination of low level oxyhalide anions and bromide in simulated drinking water. Conditions: as for Fig. 1b, except; injection volume, 200 μl. Solutes, 1 = fluoride (1 mg/l), 2 = chlorite (0.01 g/l), 3 = bromate (0.005 mg/l), 4 = chloride (50 mg/l), 5 = nitrite (0.1 mg/l), 6 = bromide (0.01 mg/l), 7 = chlorate (0.01 mg/l), 8 = nitrate (10 mg/l), 9 = phosphate (0.1 mg/l), 10 = sulfate (50 mg/l).

Table 1
Method detection limits for oxyhalides and bromide in simulated drinking water based on a 200-μl injection volume

Analyte	Concentration (μg/l)	σ for seven replicates (μg/l)	R.S.D. (%)	Calculated MDL[a] (μg/l)
Chlorite	10	0.76	7.99	2.38
Bromate	5	0.55	12.6	1.73
Bromide	10	0.57	5.45	1.78
Chlorate	10	0.34	4.38	1.07

[a] MDL $= \sigma t_{s,99}$ where $t_{s,99} = 3.14$ for $n = 7$.

proposed MCL of 10 μg/l for bromate in finished drinking water [5]. Method linearity was then established using a 200-μl injection volume for seven points over the anticipated concentration range of the target analytes. The results, shown in Table 2, demonstrate that excellent linearity was obtained for bromate between 5–40 μg/l, and for chlorite, chlorate and bromide between 20–500 μg/l, i.e., over the typical concentration range for these analytes in drinking water. Both the MDL and linearity studies were repeated with addition of EDA preservation solution to the standards and synthetic samples. This required the addition of 1.0 ml of the EDA preservation solution to 1.0 l of standard or sample to give a final EDA concentration of 50 mg/l [22]. No statistically significant differences were observed in calculated MDLs or method linearity upon preservation with EDA.

The effects of injection volume and excessive anion concentration on simulated drinking water analysis were investigated to test the robustness of the AS9-HC method for DBP anion analysis. Acceptable chromatography, in terms of peak shape and resolution, was obtained using a 500-μl injection of the simulated drinking water, which was shown in Fig. 2, however a 750-μl injection of this same sample resulted in column overloading and co-elution of the bromate and chloride peaks. Increasing the concentration of chloride and sulfate in the simulated drinking water sample, from 50 to 200 μg/ml, still allowed complete resolution of bromate from chloride when using a 200-μl injection. Hence, bromate can be determined at the 5 μg/l level in the presence of as much as 200 μg/ml of chloride, a 40 000-fold concentration difference. This level of chloride is significantly higher than would routinely be present in finished drinking water.

Fig. 3 shows the application of the AS9-HC

Table 2
Linear concentration range established for oxyhalides and bromide based on a 200-μl injection volume

Analyte	Concentration range (μg/l)	Correlation coefficient (r^2)
Bromate	5-40	0.9998
Chlorite	20-500	0.9999
Bromide	20-500	0.9991
Chlorate	20-500	0.9999

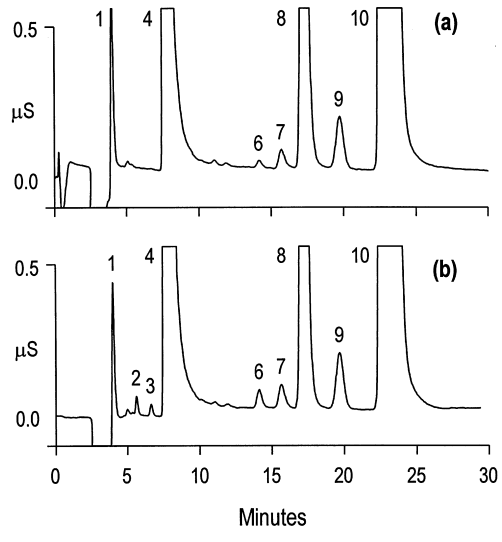

Fig. 3. Determination of oxyhalide anions and bromide in Sunnyvale drinking water. Conditions: as for Fig. 2, except; sample (a) drinking water and (b) drinking water spiked with 0.01 mg/l of oxyhalide anions and bromide. Solutes, (a) 1=fluoride (0.05 mg/l), 4=chloride (19 mg/l), 6=bromide (0.004 mg/l), 7=chlorate (0.03 mg/l), 8=nitrate (1.7 mg/l), 9=phosphate (0.25 mg/l), 10=sulfate (30 mg/l) and (b) 1=fluoride (0.05 mg/l), 2=chlorite (0.008 g/l), 3=bromate (0.012 mg/l), 4=chloride (19 mg/l), 6=bromide (0.013 mg/l), 7=chlorate (0.041 mg/l), 8=nitrate (1.7 mg/l), 9=phosphate (0.25 mg/l), 10=sulfate (30 mg/l).

method to the determination of DBP anions in drinking water from Sunnyvale, California. The water in this municipality is disinfected using hypochlorite, hence chlorate appears in the drinking water matrix, shown in Fig. 3a. A chromatogram of Sunnyvale drinking water spiked with 10 μg/l each of chlorite, bromate, bromide and chlorate is shown in Fig. 3b. The DBP anions are clearly resolved from the common inorganic anions (and bromide) present in drinking water. The recoveries obtained for the spiked anions were 80, 120, 93 and 103% for chlorite, bromate, bromide and chlorate, respectively.

4. Conclusions

An improved methacrylate-based column has been developed for the ion chromatographic analysis of trace bromate and other oxyhalide anions in drinking water. A method based on the IonPac AS9-HC column with a carbonate eluent and suppressed conductivity detection permits quantitation of low-μg/l levels of bromate, chlorite, bromide and chlorate in drinking waters when using a 200-μl injection. No additional sample pretreatment, other than filtration, was required. Method detection limits were calculated to be 2.38, 1.73, 1.78 and 1.07 μg/l for chlorite, bromate, bromide and chlorate, respectively. The method was linear for the oxyhalides and bromide over the typical concentration range expected for these analytes in drinking water; and acceptable recoveries (80–120%) were obtained for these anions spiked at the 10 μg/l level in Sunnyvale drinking water.

The method based on the AS9-HC column and suppressed conductivity detection described in this paper meets the quantitation requirements of the current ICR and the MCL being proposed by the US EPA of 10 μg/l for bromate in finished drinking water. The AS9-HC column forms the basis of EPA Method 300.1(B), which is shortly to be promulgated for regulatory monitoring of bromate and other DBP anions in drinking waters.

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