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Determination of bromate in drinking waters by ion chromatography with inductively coupled plasma mass spectrometric detection

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Abstract

Bromate is a disinfection by-product in drinking water, formed during the ozonation of source water containing bromide. An inductively coupled plasma mass spectrometer is combined with an ion chromatograph for the analysis of bromate in drinking waters. Three chromatographic columns are evaluated in terms of detection limits, analysis time and tolerance to potentially interfering inorganic anions. The detection limits for all columns are in the 1–2 μg/l range for the direct analysis of bromate. A 5-min analysis time was achieved using a Dionex AG10 column and 100 m*M* NaOH as the eluent. Recoveries for bromate in fortified samples containing chloride (1000 ppm) or nitrate (50 ppm) were 96–107%. Recoveries for bromate in fortified samples containing sulfate (1000 ppm) were 91–124%. The R.S.D. values for drinking water analyses are in the 2–6% range. A 1.8-ml sample was preconcentrated on a Dionex AG10 column. This system produced bromate detection limits in the 0.1–0.2 μg/l range. Coupling the AG10 preconcentrator column with an ultrasonic nebulizer produced a detection limit of 50 ppt for bromate. The precision for samples which are preconcentrated is degraded due to an adjacent peak interfering with integration of the bromate peak.

Keywords: Water analysis; Sample preparation; Inductively coupled plasma mass spectrometry; Bromate

1. Introduction

Bromate is a disinfection by-product of the ozonation of drinking water derived from source water containing bromide [1]. The bromide in the source water is oxidized to bromate by the ozone. Bromate is believed to be a cancer causing agent and has been classified by the International Agency for Research on Cancer as probably carcinogenic to humans. The United States Environmental Protection Agency (USEPA) has requested comment on setting the maximum contaminant level goal for bromate to zero based on the carcinogenic evidence [2]. Estimates of lifetime cancer risk based on an average adult's drinking water intake is 1 in 10^4 for a bromate concentration of 5 ppb [2].

Bromate is analyzed by USEPA method 300.0 using ion chromatography (IC) with conductivity detection. However, the analysis of bromate in a chloride matrix by ion chromatography with conductivity detection suffers from the chloride signal (10^3–10^4 higher concentration) enveloping the much smaller bromate signal [3,4]. Several refinements

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have been made to address the chloride interference and improve the detection limits. Hautman et al. [3] used a weaker solvent to improve the separation of the early eluting bromate and chloride. This improved the ability to tolerate a chloride matrix while improving the detection limit to 7 μg/l. Hautman et al. [5] also devised a column switching system that placed the bromate on a concentrator column. This system required the removal of the chloride and a 4-h/sample analysis time but provided sub-ppb detection limits. Joyce et al. [4,6] and Weinberg [7] used a silver containing cartridge as a sample pretreatment to remove the chloride. The cartridge removed the chloride but the silver in the sample needed to be removed prior to injection to avoid degrading the separation on the analytical column [6]. Joyce [4] preconcentrated bromate using a Dionex AG10 column and discovered an anion affinity problem when sulfate (a strongly retained anion) was present in the matrix. Gordon et al. [8] used the oxidation of chlorpromazine by bromate as the basis of a flow injection analysis. Gordon et al. [9] have combined this spectrophotometric technique with ion chromatography but still found it necessary to remove the chloride prior to analysis.

Heitkemper et al. [10,11] used IC in combination with inductively coupled plasma mass spectrometry for the analysis of bromate in bread. The chloride concentrations in bread are much higher than in drinking water so that chloride removal was still necessary [12]. The focus of this manuscript is to evaluate the IC–ICP-MS for the analysis of bromate in drinking water matrices. The ICP-MS should provide the selectivity to circumvent the co-elution of chloride and bromate in drinking waters by ion chromatography, a shortcoming of direct conductivity detection. This selectivity will be demonstrated via recoveries in a 1000 ppm chloride matrix. Because drinking waters often contain nitrate and sulfate as matrix anions, the potential interference effects of these anions are investigated and discussed with respect to the capabilities of bromate detection via IC–ICP-MS and column capacity. Detection limits for the direct analysis of drinking waters will be discussed. A preliminary evaluation of preconcentration and ultrasonic nebulization as a means of achieving lower limits of detection will be discussed.

2. Experimental

2.1. Reagents

Reagent grade NaOH was used to make the 100 m*M* NaOH (Mallinkrodt, Paris, KY). The 50 ppm nitrate matrix was made from $NaNO_3$ (Reagent 99%, Baker, Phillipsburg, NJ). The 1000 ppm sulfate matrix was made from K_2SO_4 (certified, Fisher, Fairlawn, NJ). The 1000 ppm and 5000 ppm chloride matrices were made from NaCl (Baker Analyzed). The bromate standards were made from sodium bromate (Fisher). This standard was verified against a mixed anion standard (Dionex, Sunnyvale, CA). All dilutions were made using 18 MΩ water (Millipore, Bedford, MA).

2.2. Apparatus

The ICP-MS system was a Fisons (Beverly, MA) PQII which has been upgraded with a high performance interface. The data were collected in a single ion monitoring (SIM) mode using the major isotope of bromine, mass 79. The dwell time was set to 0.32 s per point. The ion chromatograph was a Dionex Model GPM2. The sample pump was a Dionex Model DQP-1. The self-regenerating suppressor (Dionex) exchanges the sodium ion in the mobile phase for hydronium ion. This exchange eliminates the deposition of sodium on the ICP-MS sampling cone and thereby provides improved long term precision. The flow-rate through the self-regenerator suppressor was 1 ml/min. The analytical columns evaluated are: IonPac AS10 with a capacity of 170 μequiv. and an alkanol quaternary ammonium functional group; IonPac AS12 with a capacity of 52 μequiv. and an alkyl quaternary ammonium functional group; IonPac AG10 which is the guard column for the AS10. The AG10 is also used as the preconcentration column. All columns were purchased from Dionex.

Fig. 1 is a system diagram for the ion chromatograph. Fig. 1 contains flow diagrams for both the direct and a preconcentration modes of analysis. The 100-μl standard injection loop allows for the injection of a bromate standard, which does not traverse the column, prior to each sample analysis.

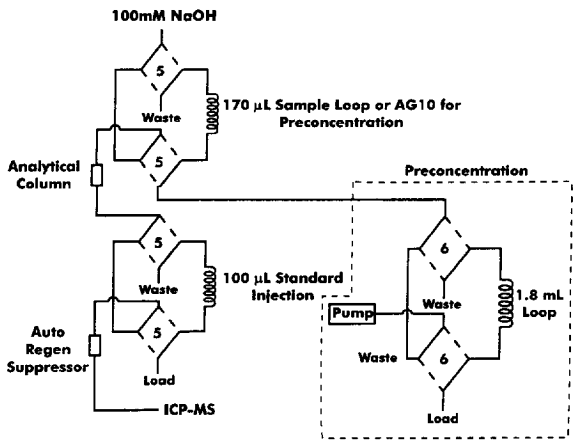

Fig. 1. Flow diagram for ion chromatographic system.

This standard is used to correct for instrumental drift during the analysis of a batch of samples. This 100-µl standard injection provides a means for synchronizing data collection from the mass spectrometer with the start of the ion chromatograph's program. This synchronization is necessary solely because the IC and ICP-MS are not connected electronically. The sample is injected using the 170-µl loop in the direct analysis mode. In the preconcentration mode, this loop is replaced with an AG10 concentrator column, and the 1.8-ml loop is loaded onto the concentrator column. The flow-rate for the 100 m*M* NaOH was 1.5 ml/min for both the direct and preconcentration work. The samples were pumped through the AG10 in the concentrator mode at 1.5 ml/min.

3. Results and discussion

3.1. Direct detection

3.1.1. Sensitivity

The ICP-MS system has been used as a detector for the analysis of bromate in bread [10–12]. The detection limits reported indicate the potential for ICP-MS to be utilized for the monitoring of bromate in ozonated drinking waters in the low µg/l concentration range. The detection limits in 18 MΩ water fortified with 5 µg/l are reported in Table 1.

Table 1
Method detection limits for bromate via direct ICP-MS detection

Column	AG10[1]	AS12[1]	AS10[1]
MDL[2] (µg/l)	1.6	1.5	1.4
R.S.D.[3] (%)	10	10	9
Analysis time (s)	300	500	1000

[1] The AG10 and AS10 columns have an alkanol quaternary ammonium functional group. The AS12 column has an alkyl quaternary ammonium functional group.
[2] MDL is determined based on 7 replicate injections of a 5 µg/l bromate standard. See Ref. [13] for the approach to defining the MDL.
[3] R.S.D. was determined using 170 µl of 5 µg/l bromate.

The data reported in Table 1 were collected in a single ion monitoring (SIM) of mass 79 using a 170-µl injection of a 5 ppb bromate standard. The detection limits reported in Table 1 are calculated based on peak area from seven replicate injections of a 5 ppb standard [13]. The resulting detection limit for bromate using the AG10, AS12, and AS10 columns are 1.6, 1.5 and 1.4 µg/l, respectively. The relative standard deviation (R.S.D.) for the seven replicate determinations of the 5 µg/l standard are roughly 10% for all three columns. The most distinguishing factor for the three columns is the analysis time. The analysis time for the AG10 is approximately 1/3 of the time required for the AS10.

3.1.2. Selectivity

The analysis of bromate using ion chromatography with conductivity detection has an interference produced by elevated levels of chloride [3]. Fig. 2 illustrates the selectivity achievable via ICP-MS detection. Fig. 2 contains 3 SIMs using the AG10 analytical column. The first (lower, left ordinate) SIM is a 5 ppb standard while the second and third (upper two, right ordinate) SIMs are a 1000 ppm chloride and a 1000 ppm sulfate matrix, respectively, fortified with 5 ppb bromate. The large peak in the 1000 ppm chloride matrix is from the bromide contamination in the sodium chloride used to simulate the matrix. This bromide contamination is 80 ppb, based on the bromate response. The extremely high chloride concentration competes with the bromate for sites on the column, thereby allowing the bromate to traverse the column faster. This competi-

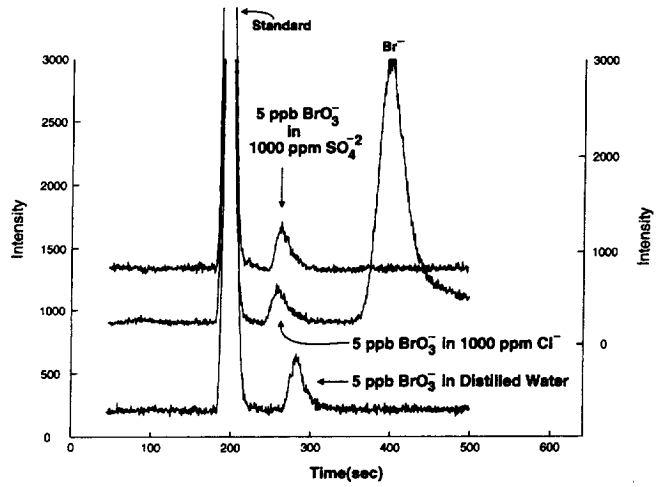

Fig. 2. Bromate recovery in the presence of common drinking water anions.

tion causes a retention time shift for bromate in the chloride matrix. In addition, the bromate peak is broadened due to the matrix anion. The shift in retention time produces added uncertainty in bromate identification based on retention time. A broader window for retention time matches will be required if a matrix contains 1000 ppm chloride. The third SIM in Fig. 2 is a 1000 ppm sulfate matrix fortified with 5 ppb bromate (upper, right ordinate). A constant has been added to this data (for graphical purposes) to offset it from the 1000 ppm chloride SIM. This SIM is collected using the AG10 analytical column. The high anionic strength of the sulfate matrix causes the peak to elute slightly earlier. Similar to chloride, high sulfate concentrations will induce some uncertainty in the positive identification of bromate.

Table 2 is a summary of the effects of 1000 ppm chloride, 1000 ppm sulfate and 50 ppm nitrate matrices on the recovery of 5 ppb bromate. The average recovery values for a 5 ppb bromate spike into a chloride matrix using the AG10, AS10, and AS12 are 96, 107 and 97%, respectively. The R.S.D. values for these recoveries are 6, 12 and 6%, respectively. The elevated recovery (107%) and higher R.S.D. (12%) occurred when bromate was spiked into a 5000 ppm chloride matrix. These results indicate that trace (5 μg/l) bromate can be

Table 2
Influence of common drinking water anions on bromate recovery

Column[4]	Chloride matrix[1]		Sulfate matrix[2]		Nitrate matrix[3]	
	Average recovery[5] (%)	R.S.D. (%)	Average recovery (%)	R.S.D. (%)	Average recovery (%)	R.S.D. (%)
AG10	96	6	91	6	96	6
AS10	107	12	103	14	100	14
AS12	97	6	124	4	104	5

[1] 1000 ppm chloride was used for the AG10 and the AS12, while 5000 ppm chloride was used for the AS10. Chloride matrices are made from NaCl.

[2] The 1000 ppm sulfate matrix was made from K_2SO_4.

[3] The 50 ppm nitrate matrix was made from $NaNO_3$.

[4] The AG10 and AS10 columns have an alkanol quaternary ammonium functional group. The AS12 column has an alkyl quaternary ammonium functional group.

[5] Average recovery and R.S.D. are based on 5 replicate injections of 5 μg/l bromate sample.

determined in a chloride matrix which is 5–6 orders of magnitude higher in concentration. Bromide which is present in the source water produces a peak which is separated from the bromate by 130, 210 and 600 s for the AG10, AS12, and AS10, respectively. These separation times are based on the time between peak maxima. This separation should only be a factor in waters containing elevated concentrations of bromide. The added analysis time (and separation from bromide) for the AS12 and AS10 may not be warranted for drinking water analysis because most drinking water supplies contain less than 1000 ppm chloride and less than 100 ppb bromide [14]. Therefore, an AG10 column, which provides adequate resolution of bromide from the bromate in 1000 ppm chloride matrix, should be adequate for drinking water analysis.

Table 2 contains the average percent recovery for a 1000 ppm sulfate matrix fortified with 5 ppb bromate. The 1000 ppm sulfate matrix was chosen based on a survey from more than 600 supplies in which the maximum sulfate concentration was 980 ppm [15]. The average recovery for the AG10 is 91%, with an R.S.D. of 6%. The average recoveries using the AS10 and the AS12 columns are 103 and 124%, respectively. The associated R.S.D. values for these recoveries are 14 and 4%, respectively. The reason for the elevated recovery observed for the AS12 is at this point unknown.

The last set of data in Table 2 is the recovery of 5 ppb bromate in 50 ppm nitrate. The 50 ppm nitrate concentration was chosen based on a survey of 600 drinking water supplies in which the maximum nitrate concentration was 38 ppm [15]. The retention time shift for the nitrate matrix is not illustrated in Fig. 2 because the relatively low ionic strength of the 50 ppm nitrate did not produce a significant retention time shift. The average recovery for 5 ppb bromate in a 50 ppm nitrate matrix using the AG10 is 96%, with an R.S.D. of 6%. The average recoveries for the AS10 and the AS12 columns are 100 and 104%, respectively. The associated R.S.D. values for these recoveries are 14 and 5%. These results indicate that each column provides adequate precision and recovery in a nitrate matrix. Overall, the limitation is not the selectivity of the detector, but rather column capacity and the influence of ionic strength on retention times.

3.2. Preconcentration/ultrasonic nebulization

Two approaches were investigated as possible means of achieving sub-ppb detection limits. The first approach utilizes a preconcentration column [6] and the second uses the increased transport efficiency of an ultrasonic nebulizer. Fig. 1 is a system diagram for preconcentration using the AG10 and a 1.8-ml sample loop. The bromate is concentrated on the AG10 and then is eluted using the 100 m*M* NaOH. Fig. 3 is a SIM chromatogram for a 0.5 ppb bromate standard using the AG10 as the analytical column. The method detection limit (MDL) based on seven replicates [13] for the AG10 is 0.2 ppb with an R.S.D. of 12%. The analysis time is just over 6 min. The MDL using the AS12 as the analytical column is 0.2 ppb with an R.S.D. of 15%. The analysis time is almost twice that of the AG10 at just over 10 min. Finally, the MDL for the AS10 column is 0.1 ppb with an R.S.D. of 7%. The analysis time for the AS10 column is almost 19 min.

The use of an ultrasonic nebulizer in combination with a concentrator column should produce the lowest detection limits. Fig. 4 is a SIM of 100 ng/l bromate which was preconcentrated on the AG10 column and then eluted off the AS12 into an ultrasonic nebulizer. The bromate concentration in this sample represents roughly the detection limit for pneumatic nebulization. The resulting MDL based on seven replicate injections is 50 ppt which is about a

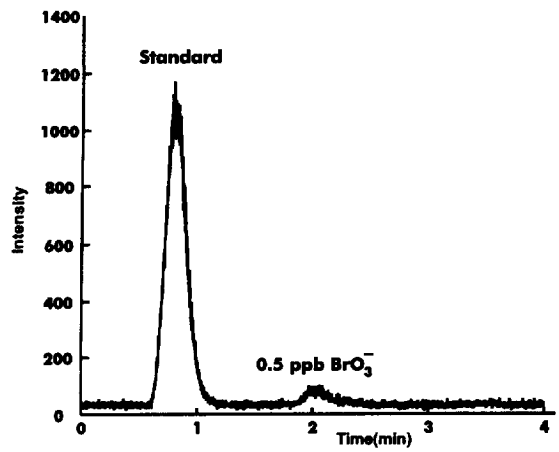

Fig. 3. Bromate preconcentration using 1.8-ml sample loop and AG10 concentrator column.

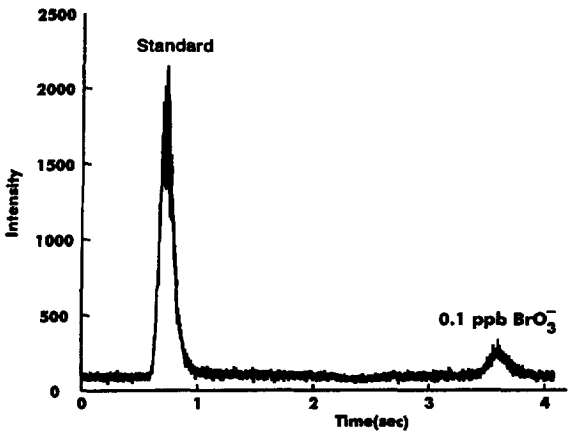

Fig. 4. Bromate preconcentration using an AG10 with ultrasonic nebulization and AS12 analytical column.

factor of four lower than those reported for the AG10 column.

3.3. Analysis of drinking water samples

Four ozonated drinking waters from four independent sources were analyzed in order to evaluate the direct and preconcentration system shown in Fig. 1. The AG10 was chosen as the analytical column because of its performance in the synthetic chloride, nitrate and sulfate matrices and its relatively short analysis time. The results from this analysis are in Table 3. These waters were analyzed as received. They were fortified with the concentrations reported in Table 3 for the precision and recovery data reported. Waters labelled 1 and 2 were analyzed using the direct system while waters labelled 3 and 4 were analyzed using the preconcentration system. The average recoveries for the direct system were 90 and 113% with R.S.D. values of less than 6%. The precision indicates that the two recoveries are near the 95% confidence bounds. Waters labelled 3 and 4 were analyzed using the indirect (or preconcentration) system and the AG10 as the analytical column. The determined concentration for these two waters were both less than 3 ppb with R.S.D. values of 18 and 27%, respectively. The average percent recoveries for a 2 ppb spike were 79 and 96% with R.S.D. values of 9 and 7%, respectively. The relatively poor precision obtained for the unfortified preconcentrated samples can be attributed to the poor precision induced by an adjacent peak interfering with the bromate peak integration. This adjacent peak is believed to have multiple components with the major constituent being bromide. The identity of the other constituents and a means of eliminating its interference is currently being investigated. This poor precision could also be caused by elevated concentrations of sulfate which have been shown to interfere with this preconcentration technique [4].

4. Conclusion

The selectivity of ICP-MS detection allows for the determination of bromate in a 1000 ppm chloride matrix. The recoveries of bromate in the chloride matrix range from 96–107% for the three columns evaluated. The recoveries of bromate in a 1000 ppm sulfate matrix were 91, 103 and 124% for the AG10, AS10 and the AS12 respectively. Recoveries in a 50

Table 3
Precision and recovery data for bromate[1]

Sample	Determined concentration (μg/l)	R.S.D. (%)	Fortified concentration (μg/l)	Average[2] recovery (%)	R.S.D.[3] recovery (%)
Water 1[4]	28	5	20	113	5
Water 2[4]	108	2	100	90	4
Water 3[5]	1.3	18	2	79	7
Water 4[5]	2.8	27	2	96	9

[1] All reported values based on $n=5$, except Water 1, $n=4$.
[2] Average recovery of the fortified concentration.
[3] R.S.D. of the percent recovery.
[4] Sample analyzed without preconcentration.
[5] Sample analyzed after preconcentration.

ppm nitrate matrix were 96–104%. These recoveries indicate that chloride, sulfate and nitrate, the major anions in drinking waters, do not interfere with IC–ICP-MS detection of bromate. Two ozonated drinking waters were analyzed and the resulting average recoveries were 90% and 113%.

The MDL for direct analysis is 1.6 ppb with an analysis time of 5 min. The preliminary preconcentration results using an AG10 concentrator column reduced the MDL to 0.1–0.2 ppb for the three columns evaluated. The preconcentration of two drinking waters using the AG10 produced recoveries of 79 and 96%. These samples after preconcentration produced a broad peak which interfered with the integration of the bromate peak. The source of this unidentified broad peak is currently being evaluated.

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