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Journal of Chromatography A, 671 (1994) 165–171

JOURNAL OF CHROMATOGRAPHY A

Trace level determination of bromate in ozonated drinking water using ion chromatography

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Abstract

Bromate is one of the disinfection by-products produced by the ozonation of drinking water. The US Environmental Protection Agency is considering regulating bromate to the low μg/l level. A method using ion chromatography has been developed which will quantify bromate at this level, even in the presence of high (mg/l) levels of common anions such as chloride and sulfate. A borate eluent system was used to improve the separation of bromate from chloride. The level of chloride in the sample was reduced by pretreating the sample using a silver-form cation-exchange resin. The lower chloride level allowed a larger sample volume and preconcentration which reduced the bromate method detection limit to 1 μg/l.

1. 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 worldwide, have been aggressively researching alternative disinfection methods which minimize the production of by-products of significant health risk. Ozonation has emerged as one of the most promising alternatives to chlorination. However, ozonation does tend to oxidize bromide, which is present naturally in source waters, to bromate. The following equations show the pathway by which bromide (Br^-) is oxidized by ozone to bromate (BrO_3^-) through the intermediate formation of hypobromite (OBr^-). These equations also show that ozone does not oxidize hypobromous acid (HOBr) to bromate. Since increased acid (H_3O^+) will favor the formation of hypobromous acid, this suggests that ozonation at a low pH will tend to minimize bromate formation. (Fig. 1)

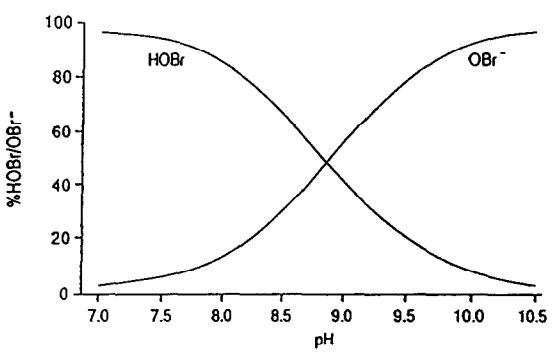

Fig. 1. Hypobromous acid equilibria in aqueous solution. Ozonating at pH 7 or lower minimizes the production of hypobromite, which in turn minimizes the formation of bromate. $pK_a = 8.8$ at 20°C.

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0021-9673/94/$07.00
SSDI 0021-9673(94)00171-5

Table 1
Bromate health risk

Risk level[a]	Trichloroethylene (μg/l)	Carbon tetrachloride (μg/l)	Bromate (μg/l)
10^{-4}	260	27	5
10^{-5}	26	2.7	0.5
10^{-6}	2.6	0.27	0.05

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

$$Br^- + O_3 + H_2O \rightarrow HOBr + O_2 + OH^-$$

$$HOBr + H_2O \rightarrow H_3O^+ + OBr^-$$

$$OBr^- + 2O_3 \rightarrow BrO_3^- + 2O_2$$

$$HOBr + O_3 \rightarrow \text{No reaction}$$

The final concentration of bromate is dependent on the amount of bromide in the source water and applied ozone. Bromate has been judged by both the US Environmental Protection Agency (EPA) and the World Health Organization as a potential carcinogen, even at the low μg/l level. Table 1 shows a comparison of health risk levels for bromate and selected chlorinated organics which are currently regulated in drinking water. Many regulatory agencies, world-wide, prefer to regulate potential carcinogens to the 10^{-5} health risk level or lower. Current EPA plans are to regulate bromate in ozonated water to < 10 μg/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.

Currently, the separation of bromate in a drinking water matrix is accomplished by using direct-injection ion chromatography (IC) with conductivity detection. The detection limit for bromate using this methodology is 7.3 μg/l [2]. Table 2 shows the method detection limits (MDLs) that were achieved by EPA researchers when using a 200-μl injected sample on a Dionex IonPac AS9-SC column using a borate-based eluent. Injecting a larger sample erodes chromatographic efficiency and does not significantly improve MDLs. The drawback to this method is that the amount of bromate present in a typical ozonated water sample is near or below the current detection limit. This paper reports the development of a modified IC method which significantly improves the MDLs for bromate.

Table 2
Method detection limits using the AS9 column

Anion	Spiking concentration (μg/l)	Statistical MDL[a] (μg/l)	Noise MDL[b] (μg/l)	Conservative MDL (μg/l)
ClO_2^-	10.0	3.39	2.94	3.4
ClO_3^-	25.0	5.18	9.44	9.4
BrO_3^-	10.0	7.31	5.92	7.3
Br^-	10.0	3.92	8.34	8.3

Conditions: 9 m*M* NaOH–36 m*M* boric acid, 1 ml/min, 200-μl injection.
[a] Method detection limit, MDL = (S.D.)·(t_s) 99.5%, where $t_s = 3.71$ for a single sided Student's *t*-test distribution at a 99.5% confidence.
[b] MDL = 3 × noise.

2. Experimental

2.1. Chromatographic system

All chromatography was performed using a Dionex (Sunnyvale, CA, USA) DX-300 chromatograph equipped with an advanced gradient pump (AGP), a liquid chromatography module (LCM-3) and a conductivity detector (CDM-3). A Dionex automated sampler module (ASM) was utilized for sample loading. An additional inert double stack four-way slider valve was placed between the rotary injection valve and the analytical column. The rotary valve and the four-way slider valve were controlled by the AGP. A Dionex DQP single-piston pump was used to flush the sample from the sample loop onto the concentrator column. Eluents were vacuum degassed while sonicating for 15 min.

Four types of columns were used in the system. An IonPac AS9-SC was used for analyte separation. An IonPac AG9-SC and an IonPac AG10 served as concentrator columns. An IonPac AG9-SC column was utilized as a guard column. An IonPac MetPac CC-1 column was used as a metal scrubber column. Conductivity detection was carried out in the external water mode using an Anion Self Regenerating Suppressor. A chromatographic data system (AI-450; Dionex) was used for instrument control and for data collection and processing.

2.2. Chemicals

Boric acid, >99%, from Aldrich (Milwaukee, WI, USA), sodium hydroxide, 50% (w/w) from Fisher Scientific (Pittsburgh, PA, USA) and 17.8 MΩ cm deionized water were used for eluent preparation. Anion standards (1000 mg/l) were prepared from the corresponding sodium salts from Fisher Scientific. Dilute working standard solutions are prepared daily from 1000 mg/l stock standard solutions. All standard solutions were stored in polyethylene containers.

2.3. Sample pretreatment

With high levels of chloride in the sample matrix the exchange sites on the AG9/AS9-SC columns are overloaded and bromate cannot be detected as a separate peak. Chloride is removed by passing the sample through the Dionex On-Guard Ag cartridge. The cartridge packing is a silver-form high-capacity, strong-acid, cation-exchange resin, which is designed to remove chloride from the sample matrices. The cartridge capacity is 1.8–2.0 mequiv. per cartridge. Fig. 2A illustrates that, when attempting to determine bromate at the 10 μg/l level in the presence of a high chloride level (*i.e.* 64 mg/l), the resolution is not sufficient to separate bromate from chloride. Fig. 2B shows that by treating the sample with the OnGuard Ag cartridge the chloride level is reduced to approximately 0.4 mg/l which is sufficient to resolve bromate from chloride.

The lower chloride level allows a larger sample volume to be concentrated which improves the bromate response. A drawback for using the OnGuard Ag cartridges is the leaching of silver from the cartridge into the sample matrix. The accumulation of silver on the analytical and concentrator columns over time will affect column efficiency. To avoid this potential problem,

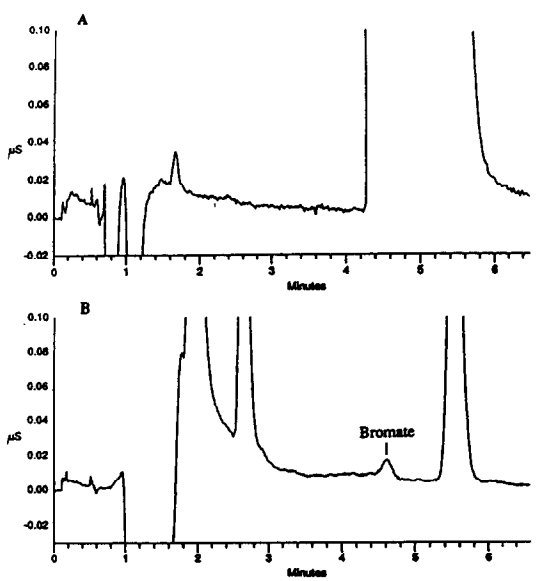

Fig. 2. Bromate determination. Direct injection (sample volume 200 μl) on a AS9-SC column, using borate eluent. (A) Sample not treated with OnGuard Ag; (B) OnGuard Ag-treated sample.

a Dionex MetPac CC-1 column is installed between the rotary injection valve and the four-way slider valve. The MetPac CC-1 column not only removes the silver but also removes any other cations which may foul the analytical column.

2.4. System operation

The chromatographic conditions are listed in Table 3. The determination of bromate utilizing this method is a three-step process as illustrated in Fig. 3: (1) loading the sample loop, (2) washing the sample onto the concentrator, (3) separating the anions of interest on the analytical column. Fig. 3A illustrates the sample being loaded into the sample loop using the auto-sampler. During this time, the AGP pumps eluent 1 to the AS9-SC column. After the loop is filled, the DQP is turned ON and it washes the sample from the sample loop onto the concentrator column using deionized water (Fig. 3B). The sample loop is rinsed two and one-half 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. Fig. 3C shows the concentrator column being switched in line with the IonPac AS9-SC, at this point the retained anions are eluted to the analytical column. After the chloride elution the remaining anions are purged off the analytical column using eluent 2.

3. Results and discussion

3.1. Concentrator columns

The performance of concentrator columns is limited by column capacity and ion-exchange competition. The column resin can trap only a certain quantity of analyte. Once the column capacity is exceeded, the trapping will not be quantitative. The processes become more complicated when concentrating ions having widely different affinities for the resin. In this case an anion such as sulfate, which has a high affinity for the resin and which is present in much higher concentration, can act as an eluent, causing displacement of bromate.

Two concentrator columns were employed for this study, an IonPac AG9-SC and an IonPac AG10 column. The AG9-SC is a low-capacity anion-exchange column which exhibits the lower recovery for 1 μg/l bromate in the presence of other ions that are of much higher concentration. Table 4 shows a decrease in recovery for bromate as the sulfate concentration increases. The AG10 is a moderate-capacity column, and it can tolerate twice (15 *vs.* 30 μg/l) the sulfate concentration compared to the AG9-SC column. Fig. 4 illustrates the results of the IC analysis of bromate after preconcentrating 5 ml of an On-Guard-treated test sample containing 30 mg/l sulfate. The AG10 concentrator column retained a high percentage (*ca.* 90–100%) of the bromate,

Table 3
Chromatographic conditions

Guard column	AG9-SC
Analytical column	AS9-SC
Concentrator column	AG9-SC or AG10
Metal trap column	MetPac CC-1
Eluents	Eluent 1: 40 m*M* boric acid–20 m*M* NaOH, eluent 2: 250 m*M* boric acid–100 m*M* NaOH
Eluent flow-rate	2.0 ml/min
Rinsing reagent	Deionized water
Rinsing flow-rate	2.0 ml/min
Sample volume	5.0 ml
Detection	Suppressed conductivity, auto suppression, external water mode

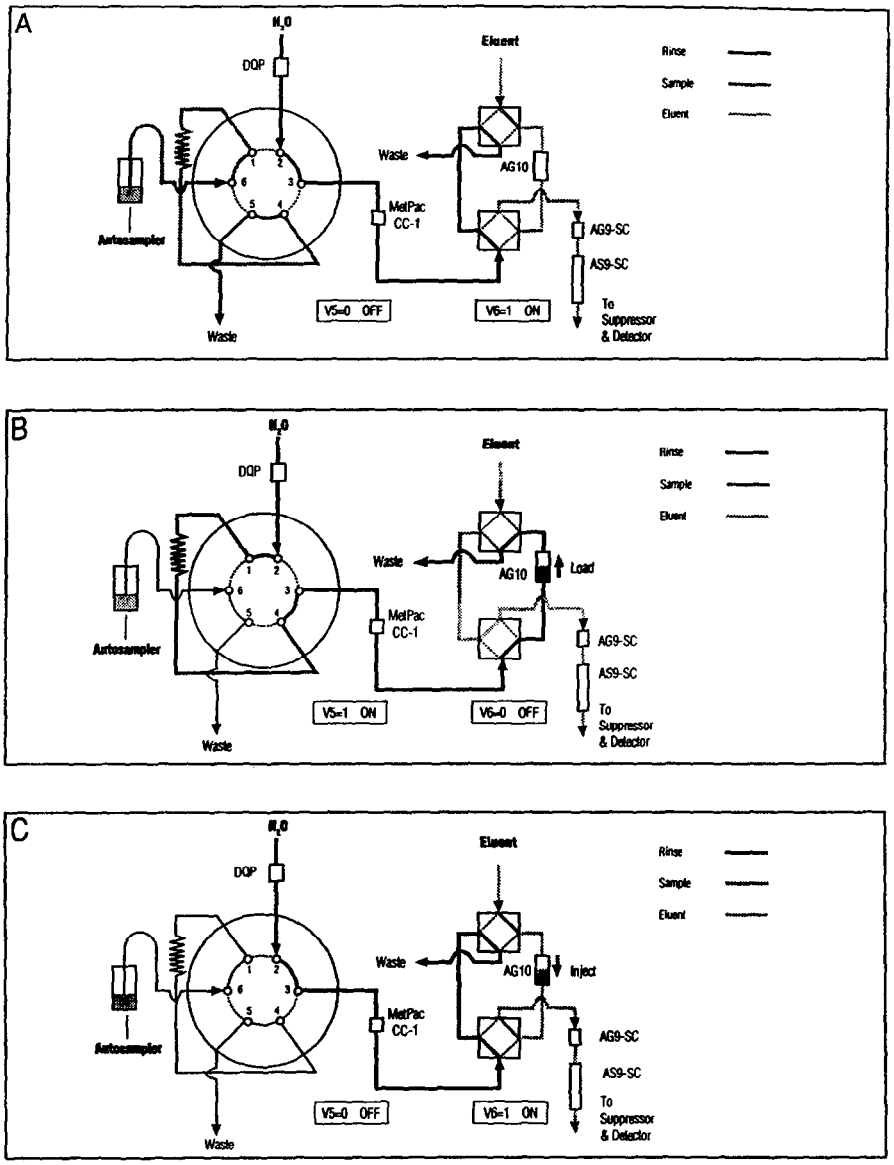

Fig. 3. Preconcentration suppressed IC system configuration. (A) Loading sample loop; (B) sample washed onto concentrator column; (C) retained anions eluted to AS9-SC analytical column.

while the bromate was eluted from the AG9-SC column by the sulfate.

Since the EPA plans to regulate bromate in ozonated water to <10 μg/l, 3–5 ml sample volume must be concentrated. Analyte anions such as bromate, chloride and sulfate are retained on the concentrator column as the sample loop is rinsed with deionized water. The anions are then eluted from the concentrator column and separated on the AS9-SC analytical column. Later-eluting anions such as sulfate are purged from the analytical column using 250 m*M* boric acid–100 m*M* sodium hydroxide eluent. After purging for 5 min, the AS9-SC column is equili-

Table 4
Effect of sulfate on recovery (%) of 1 μg/l bromate

Sulfate (mg/l)	Recovery (%)	
	AG9-SC (7 μequiv./column)	AG10 (34 μequiv./column)
5	98.5	99.7
10	96.2	99.3
15	94.5	99.3
20	0	98.7
25	0	96.5
30	0	92.3
35	0	0

Sample volume: 5 ml; test matrix: fluoride 2 mg/l, bromate 0.001 mg/l, chloride 64 mg/l (reduced to *ca.* 0.4 mg/l using OnGuard Ag), nitrate 20 mg/l, sulfate as listed.

brated with the chromatography eluent for 7–10 min. The equilibration time is placed at the beginning of the analysis as the sample loop is being filled and the sample is flushed onto the concentrator column. The total analysis time for this method is 25 min. Table 5 shows the bromate MDLs that have been achieved when preconcentrating a raw water sample both before and after ozonation. Using this method, a bromate MDL of 1 μg/l or less can be achieved.

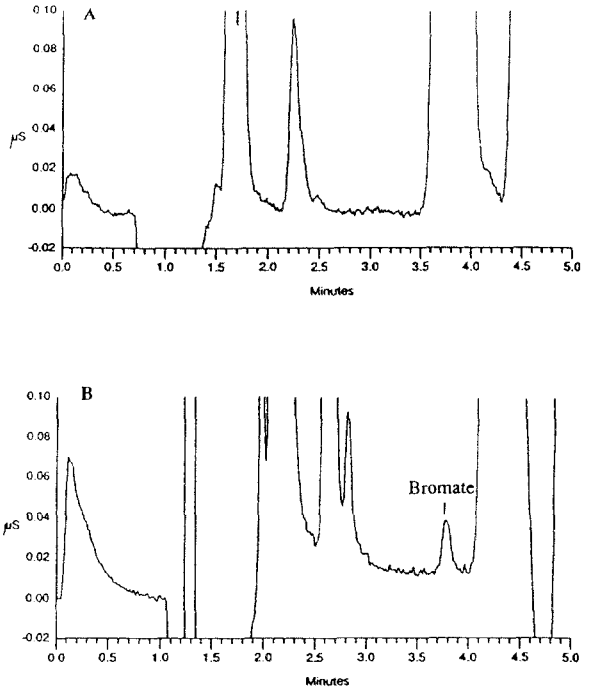

Fig. 4. Evaluation of concentrator columns for bromate analysis by preconcentrating 5 ml of sample. Sample concentration: bromate (0.001 mg/l); chloride [64 mg/l (reduced to *ca.* 0.4 mg/l using OnGuard Ag)]; bromide (2 mg/l); nitrate (20 mg/l); phosphate (10 mg/l); sulfate (30 mg/l). (A) AG9-SC column bromate shows no recovery of 1 μg/l bromate; (B) AG10 column shows 92.3% recovery.

Table 5
Determination of bromate in drinking water, 5 ml, preconcentrated

Sample	Bromate present (μg/l)	Bromate added (μg/l)	Bromate found (μg/l)[a]	*n*	S.D. (μg/l)	MDL (μg/l)[b]
Raw water	ND[c]	1	1.05	7	0.09	0.27
	ND	5	5.1	6	0.29	0.91
	ND	10	10.0	7	0.58	1.74
Raw water (ozonated)	1.1	0	1.1	7	0.04	0.12
	1.1	1	1.2	7	0.11	0.33
	1.1	5	4.7	7	0.70	2.10
	1.1	10	10.0	5	1.52	5.11

[a] Reference to 10 μg/l fortification of matrix.
[b] Method detection limit, MDL = (S.D.)·(t_s) 99.5%, where t_s = 3.71 for a single sided Student's *t*-test distribution at a 99.5% confidence.
[c] ND = Not detected (< 0.1 μg/l).

Table 6
Method detection limits for bromate analysis of ozonated drinking water using chemically suppressed IC

Sample volume injected	Inject mode	MDL (μg/l)
200 μl	Direct	5
5 ml	Preconcentrated	1

4. Conclusions

An improved method for the determination of trace level bromate has been developed. As summarized in Table 6 low-level, bromate MDLs can be achieved on the AS9-SC column using a borate eluent and chemically suppressed conductivity detection. Reduction of the chloride concentration in the sample matrix combined with preconcentration are the major modifications to the existing method.

5. Acknowledgements

The authors are grateful to Dr. Howard Weinberg, University of North Carolina and James N. Scott, Santa Clara Valley Water District for providing ozonated water samples. They would also like to thank Edward Kaiser, Dionex Corporation, for his assistance in preparing this manuscript.

6. References

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