

Analysis of oxyhalide disinfection by-products and other anions of interest in drinking water by ion chromatography

Daniel P. Hautman*

Technology Application Inc., 26 W.M.L. King Drive, Cincinnati, OH 45268 (USA)

Michele Bolyard

US Environmental Protection Agency, 26 W.M.L. King Drive, Cincinnati, OH 45268 (USA)

ABSTRACT

The US Environmental Protection Agency is developing regulations for various drinking water disinfection by-products (DBPs). This effort involves developing analytical methods for the DBPs formed as a result of different disinfection treatments and collecting occurrence data for these species. Ion chromatography is one method being used to analyze drinking water samples for the following inorganic DBPs: chlorite, chlorate and bromate. These anions, however, are difficult to separate from common interfering anions of chloride, carbonate and nitrate. A method is therefore presented by which tetraborate/boric acid is used to separate these anions. Method detection limits of the order of 10 µg/l, using conductivity and UV detection were obtained. Stability studies of chlorite showing the effectiveness of ethylenediamine as a preservative and summary data for an occurrence of nitrite, nitrate and the DBP precursor bromide are presented.

INTRODUCTION

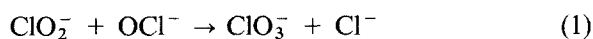
Prior to recent advances in ion chromatography (IC), studies of oxyhalide anion chemistry had been hindered by the lack of methods which could directly measure these anions. Using a recently introduced IC column, research into a reliable and practical IC method for oxyhalide anion measurement has been conducted [1]. However, when these conditions are applied to drinking water matrices, problems are often encountered in resolving low levels of bromate (BrO_3^-), nitrite (NO_2^-), and chlorate (ClO_3^-) from typical background levels of chloride (Cl^-), carbonate (CO_3^{2-}) and nitrate (NO_3^-).

Recently, the oxyhalides of chlorine and bromine have drawn much attention as inorganic disinfection by-products (DBPs). They are being considered for regulation by the US Environmental Pro-

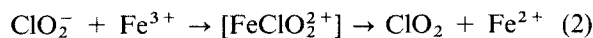
tection Agency (EPA) as part of the DBP rule (to be proposed in 1993). Depending on the disinfection process, different oxyhalide by-products can form. When chlorine dioxide (ClO_2) is used as a disinfectant, the anions chlorite (ClO_2^-) and chlorate (ClO_3^-) are formed [2]. Chlorination using hypochlorous acid (HOCl) solutions, which can contain ClO_3^- as a product of HOCl disproportionation, may contribute to ClO_3^- contamination in the treated water. When ozone is applied as a disinfectant, bromide (Br^-) in the source water initially oxidizes to hypobromous acid (HOBr), which can then further react to form BrO_3^- .

ClO_2^- and ClO_3^- have been studied as by-products of disinfection with ClO_2 [2]. Pfaff and Brockhoff [3] demonstrated ClO_3^- was stable in drinking water, but ClO_2^- was lost within a day. Research has indicated that ClO_2^- reacts with hypochlorite

(OCl^-), the aqueous form of chlorine, as follows [4]

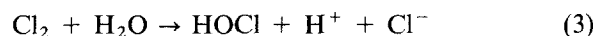


ClO_2^- has also been shown to react with Fe^{3+} by forming an intermediate [FeClO_2^{2+}] and further reacting as follows [5]



Observations made in the laboratory suggest ClO_2^- degrades upon exposure to light.

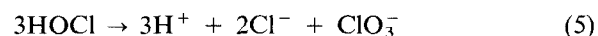
When the treatment is chlorination, the disinfectant is added to the water either as chlorine gas or as HOCl solution. Once the gas is dissolved in water it rapidly converts to HOCl by the following reaction [6]



at which point an equilibrium is established, dependent upon pH and expressed by [6]

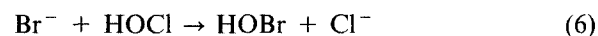


The HOCl acts as the functioning biocide, but will also readily react with fulvic and humic acids, present in the source water, to form a myriad of chlorinated organic DBPs [7]. HOCl can also decompose as is expressed in the following reaction [4]

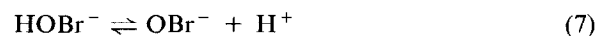


forming chlorate which EPA is also considering for regulation.

The presence of Br^- in the source water can significantly influence the distribution of DBPs in the treated water, since the following reaction occurs upon chlorination [6]

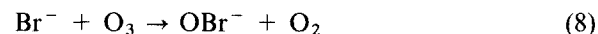


As in eqn. 4 above, an equilibrium is established dependent upon pH and expressed as [8]



HOBr will also readily react with the fulvic and humic acids to form brominated organic DBPs.

Research has shown the oxyhalide bromate (BrO_3^-) is formed following ozone treatment of source waters containing measurable levels of Br [8]. Ozone reacts with Br^- as follows [8]



Again, as in eqn. 7, an equilibrium is established

between HOBr and OBr^- . Depending on the pH of the water, two different addition reactions can occur. In waters where the pH is slightly acidic the predominate species is HOBr. In waters where the pH is neutral or slightly basic the equilibrium shifts to the OBr^- form. This species will further react with ozone to form the oxyhalide BrO_3^- as follows [8]



This paper presents an improved method for the separation of BrO_3^- , NO_2^- and ClO_3^- from Cl^- , CO_3^{2-} and NO_3^- . In addition, we apply these analytical conditions to the analyses of NO_2^- , NO_3^- and Br^- . Application data are also included demonstrating the effectiveness of ethylenediamine (EDA) as a preservative for ClO_2^- and the relationship between source water Br^- and the formation of brominated DBPs in chlorinated and BrO_3^- in ozonated waters.

EXPERIMENTAL

Analytical conditions

Analyses were performed by direct injection using a Waters 712 WISP autosampler and a Dionex 4500i ion chromatograph. Analytical conditions are presented in Table I.

Reagents

Reagents for calibration standards and spiking solutions were purchased as follows: ClO_2^- as sodium chlorite (NaClO_2), Novatek, 99.7%; ClO_3^- as

TABLE I
ION CHROMATOGRAPHIC ANALYTICAL CONDITIONS

Guard/separation columns	Dionex Ionpac AG9/AS9
Eluent	30 mM NaOH and 120 mM H_3BO_3 in water
Eluent flow	2.0 ml/min
Detection	Dionex CDM-2 conductivity and Waters 484 UV at 195 nm in series
Suppressor	Anion micromembrane
Suppressor regenerant	25 mM H_2SO_4
Regenerant flow	10 ml/min
Sample injection volume	50 μl
Minimum R^2 value for calibration curve	0.9998

sodium chlorate (NaClO_3), Alfa, 99%; BrO_3^- as potassium bromate (KBrO_3), Alfa, ACS grade; Br^- as sodium bromide (NaBr), Alfa, ultrapure; NO_2^- as sodium nitrite (NaNO_2), Alfa, ACS grade; NO_3^- as sodium nitrate (NaNO_3), Alfa, ultrapure; Cl^- as sodium chloride (NaCl), EM Science, GR grade; SO_4^{2-} as potassium sulfate (K_2SO_4), Alfa, ultrapure; and CO_3^{2-} as sodium carbonate (Na_2CO_3), EM Science, GR grade.

Instrument calibration standards, spiking solutions, and eluents were prepared in distilled, deionized (DI) water displaying a minimum resistance of 17.8 $\text{M}\Omega$ cm.

Carbonate eluents were prepared from Na_2CO_3 (EM Science, GR grade) and sodium bicarbonate (NaHCO_3 , Alfa, ACS grade). Borate eluents were prepared from either sodium tetraborate decahydrate ($\text{Na}_2\text{B}_4\text{O}_7 \cdot 10\text{H}_2\text{O}$, Aldrich, ACS grade) and boric acid (H_3BO_3 , Aldrich, 99.999%) or sodium hydroxide (NaOH , Aldrich, ACS grade) and boric acid. The suppressor regenerant was prepared from H_2SO_4 (Baker, ULTREX ultrapure) diluted to 12.5 mM in DI water.

Data reduction

Following a sample analysis, the data were processed by the Dionex AI-450 software. Using parameters established in the instrument method of the software, the data were qualitatively and quantitatively compared, based upon retention time, peak height and external standard quantitation, to the calibration standard data.

RESULTS AND DISCUSSION

Development of analytical conditions

To demonstrate the potential problems in resolving ClO_2^- , ClO_3^- , BrO_3^- and NO_2^- , from the interferent anions of Cl^- , CO_3^{2-} and NO_3^- , a simulated drinking water matrix (SDWM) was prepared in DI water spiked with NO_3^- as N at 3 mg/l, Cl^- at 50 mg/l and CO_3^{2-} at 150 mg/l. These levels were chosen because they represent typical levels found in drinking water samples. This matrix was then spiked at trace levels of ClO_2^- , ClO_3^- and Br^- at 0.015 mg/l and NO_2^- as N at 0.0015 mg/l.

This SDWM was analyzed using an eluent of 1.8 mM Na_2CO_3 and 1.7 mM NaHCO_3 in water, as specified in ref. 1 (Other than eluent change, all of

the conditions outlined in Table I apply.) The chromatogram shown as Fig. 1 shows the poor resolution, due to the SDWM's high ionic strength as compared to that of the carbonate eluent, between ClO_2^- and the positive deflection of the baseline at the expected water dip. Before the baseline can stabilize ClO_2^- elutes and BrO_3^- begins to elute when a second dip disturbs the baseline. Also, the NO_2^- peak is unresolved from the Cl^- peak.

Due to the poor resolution using this eluent strength, a weaker concentration (0.70 mM Na_2CO_3 /1.3 mM NaHCO_3) was investigated as a means to separate the early eluting peaks. Fig. 2 is the chromatogram generated using this weaker carbonate eluent. Again, the ionic strength of the SDWM distorts the early portion of the chromatogram causing the ClO_2^- peak to be unresolved from the baseline disturbance. The BrO_3^- peak is no longer completely obscured in the second dip and the NO_2^- is somewhat resolved from the Cl^- , however, quantitation is still difficult.

These problems, combined with the often erratic baseline and resulting high detection limits, prompted us to look for an alternate eluent. Consultation with other researchers [9], who had reported success with the borate eluent, led us to investigate it as an alternative. Initially, an eluent of 22 mM $\text{Na}_2\text{B}_4\text{O}_7$ /22 mM H_3BO_3 was prepared. Fig. 3 shows the chromatogram of the SDWM using this eluent. The resolution was a significant improvement over the carbonate eluents. Due to the high ionic strength of the borate eluent, compared to the SDWM sample, the water dip was again observed.

However, a new problem was created by the elution of the CO_3^{2-} peak following the Cl^- . With this eluent, the CO_3^{2-} eluted as a broad peak which is unresolved from NO_2^- . In drinking water samples, CO_3^{2-} can exceed 15 ppm. At such high concentrations, as demonstrated in Fig. 3, the NO_2^- peak can not be quantitated. To circumvent this problem the eluent pH was changed from 9.0 to 8.6 by adjusting the tetraborate-to-boric acid ratio. It is believed, this eluent shift converts the CO_3^{2-} to an earlier eluting bicarbonate (HCO_3^-) species [9]. By preparing an eluent of 15 mM $\text{Na}_2\text{B}_4\text{O}_7$ /60 mM H_3BO_3 the carbonate peak was resolved from the NO_2^- and coeluted with the chloride peak, an anion not of interest to us for our current studies.

After using this eluent for a few days, subtle base-

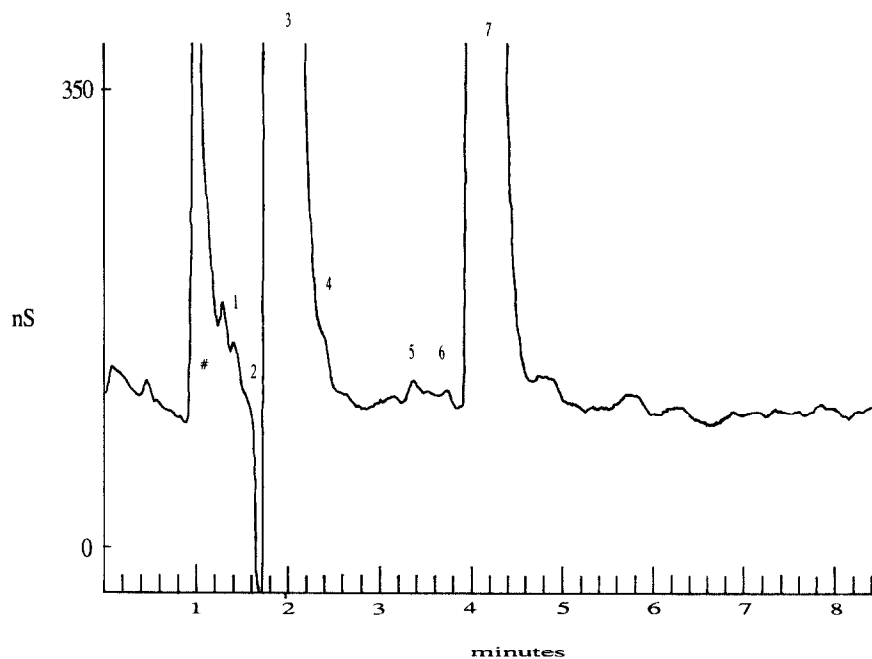


Fig. 1. Simulated drinking water matrix using eluent conditions of 1.8 mM Na_2CO_3 /1.7 mM NaHCO_3 . All other conditions as in Table I. Peaks: 1 = ClO_2^- (0.015 mg/l); 2 = BO_3^- (0.015 mg/l); 3 = Cl^- (50 mg/l); 4 = NO_2^- (0.0015 mg/l as N); 5 = Br^- (0.015 mg/l); 6 = ClO_3^- (0.015 mg/l); 7 = NO_3^- (3.0 mg/l as N). # indicates positive baseline deflection at the expected water dip.

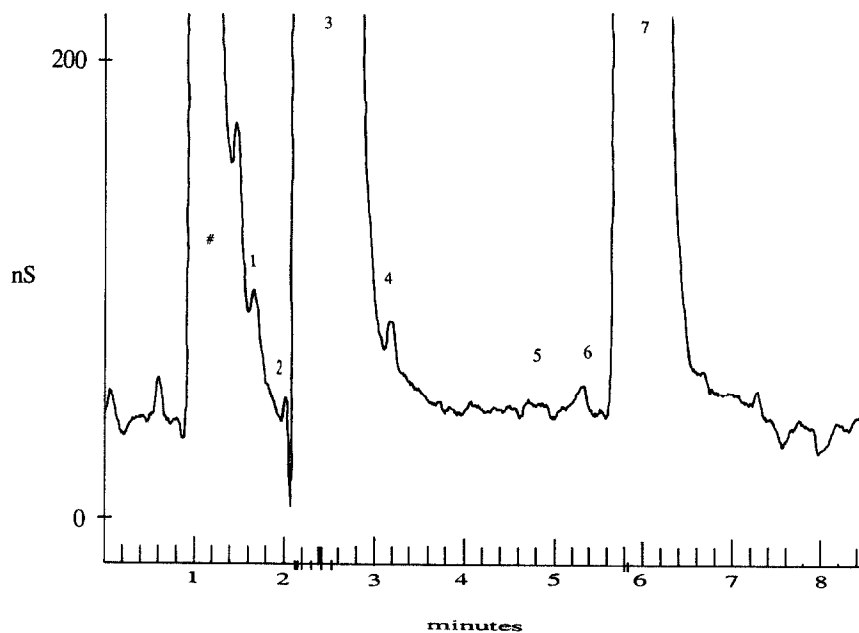


Fig. 2. Simulated drinking water matrix using eluent conditions of 0.70 mM Na_2CO_3 /1.3 mM NaHCO_3 . All other conditions as in Table I. Peaks as in Fig. 1. # indicates positive baseline deflection at the expected water dip.

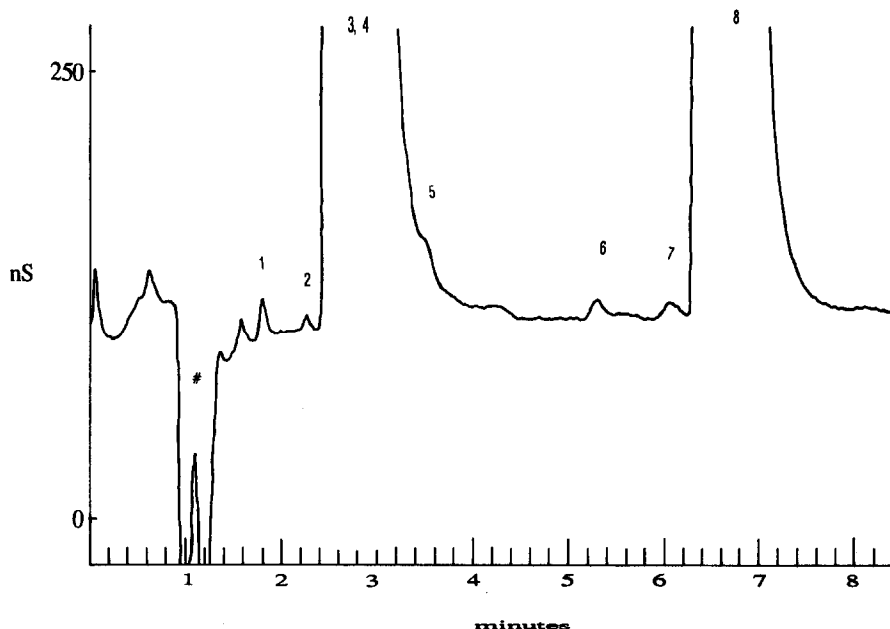


Fig. 3. Simulated drinking water matrix using eluent conditions of 22 mM $\text{Na}_2\text{B}_4\text{O}_7$ /22 mM H_3B_3 . All other conditions as in Table I. Peaks: 1 = ClO_2^- (0.015 mg/l); 2 = BrO_3^- (0.015 mg/l); 3 = Cl^- (50 mg/l); 4 = CO_3^{2-} (150 mg/l); 5 = NO_2^- (0.0015 mg/l as N); 6 = Br^- (0.015 mg/l); 7 = ClO_3^- (0.015 mg/l); 8 = NO_3^- (3.0 mg/l as N). # identifies the water dip.

line disturbances were observed. The baseline would gradually drift up approximately 20 nS at the retention time for BrO_3^- , which prevented detection of low BrO_3^- concentrations. In an attempt to eliminate this baseline drift, the preparation of the borate eluent was modified by using NaOH and H_3BO_3 [9]. By preparing the eluent from 30 mM NaOH/120 mM H_3BO_3 , nearly identical chromatographic results were achieved with a more stable baseline and lower background. It was thought the $\text{Na}_2\text{B}_4\text{O}_7$ was a source of unknown contamination, and that by using an alternative preparation, relying on the acid-base reaction of the hydroxide and boric acid, a higher-purity borate eluent could be attained. Using this eluent, the chromatogram shown in Fig. 4 was generated. The resolution, while not ideal, is acceptable considering the SDWM represents a "worst case" scenario. Due to the high ionic character of the SDWM matrix, it would be difficult to analyze under any eluent conditions. With these final conditions (Table I), it is possible to quantitatively measure trace anion concentration in the presence of interferent anions 10 000 times greater in concentration.

Method detection limits (MDLs) [10] under these final method conditions were determined through the analyses of 8 replicate reagent water spikes at approximately 3 times the baseline noise. A statistical MDL was calculated by multiplying the student's t value for 7 degrees of freedom, 99% confidence interval (2.998) by the standard deviation. In addition, a noise MDL was estimated by calculating the concentration of an analyte which would generate a peak response equal to 3 times the baseline noise. An actual MDL was reported as the higher value of the statistical MDL or the noise MDL. The results from this MDL calculation showing the statistical MDL, the noise MDL and actual MDL, for each anion of interest, are shown in Table II for the conductivity and UV detectors.

Precision data for the conductivity detector were generated by performing an initial demonstration of capabilities (IDC) where 20 replicate DI water spikes were analyzed over 4 days, 5 samples per day. These data (Table III) represent a maximum relative standard deviation (R.S.D.) of less than 6% and are used to construct control charts to monitor instrument performance. With each set of samples

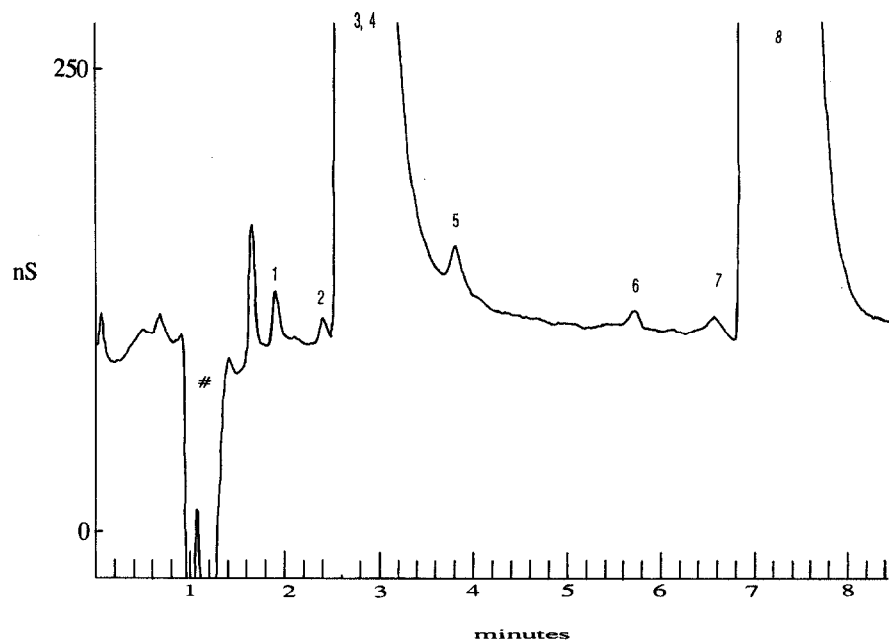


Fig. 4. Simulated drinking water matrix using eluent conditions of 30 mM NaOH/120 mM H₃BO₃. All other conditions as in Table I. Peaks as in Fig. 3. # identifies the water dip.

TABLE II

METHOD DETECTION LIMITS (MDLs) FOR SIX ANIONS OF INTEREST BY IC: CONDUCTIVITY AND UV DETECTORS IN SERIES

Analytical conditions as in Table I. Spiked DI water was used for replicate analyses and signal-to-noise determinations. The actual MDL was the higher value of the noise MDL or the statistical MDL.

Anion	Spiking concentration (μg/l)	MDL (μg/l)		
		Statistical ^a	Noise	Actual ^b
<i>Conductivity detection</i>				
ClO ₂ ⁻	10.0	3.39	2.94	3.4
BrO ₃ ⁻	10.0	7.31	5.92	7.3
N — NO ₂ ⁻	2.0	1.44	0.86	1.4
Br ⁻	10.0	3.92	8.34	8.3
ClO ₃ ⁻	25.0	5.18	9.44	9.4
N — NO ₃ ⁻	2.0	2.41	1.42	2.4
<i>UV detection at 195 nm</i>				
ClO ₂ ⁻	10.0	6.53	9.44	9.4
BrO ₃ ⁻	10.0	6.51	10.3	10.3
N — NO ₂ ⁻	2.0	2.06	0.74	2.1
Br ⁻	10.0	7.58	3.48	7.6
N — NO ₃ ⁻	2.0	2.14	0.66	2.1

^a Student's *t* value of 2.998 for 8 replicates at 99% confidence level.

^b Calculated as 3 times baseline noise.

TABLE III

PRECISION RESULTS FROM AN INITIAL DEMONSTRATION OF CAPABILITY

Analytical conditions as in Table I. Replicates (20) were analyzed over 4 days, 5 samples per day, to generate the following statistical data.

Anion	Spiked concentration $\mu\text{g/l}$	Mean recovery (%)	Precision (R.S.D., %)
ClO_2^-	250	101.8	3.09
BrO_3^-	100	96.6	3.87
N — NO_2^-	500	98.7	2.55
Br^-	100	99.0	5.91
ClO_3^-	250	99.3	3.13
N — NO_3^-	1000	98.2	2.90

analyzed, one DI water spike, at the same levels of the IDC, is analyzed. To confirm the instrument is in control, recoveries must fall within ± 3 times the R.S.D. of the mean. Over time these data are used to rate the performance of the method and can be used to calculate confidence limits.

Chlorite stability

Experiments were conducted to study the stability of ClO_2^- in solution with the reactive species OCl^- and Fe^{3+} . A 15-day storage study was conducted using three matrices of deionized water, all containing 2.0 mg/l ClO_2^- . One matrix contained 1.0 mg/l Fe^{3+} , the second 2.4 mg/l OCl^- , and the third was free of any reactive species. The matrices were divided into two groups, preserved with 50 mg/l EDA and unpreserved. Currently, no preservation technique is identified for ClO_2^- as part of EPA Method 300.0 [1], therefore, EDA was studied as a preservative due to its ability to chelate metal ions and because of experimental evidence indicating its ability to remove OCl^- [11]. Analyses were conducted on days 0, 1, 2, 8 and 15. All samples were stored in opaque, brown, high-density polyethylene bottles.

The stability studies involving chlorite demonstrated the effectiveness of EDA as a preservative. In Fig. 5, the results from the stability study of the unpreserved (Fig. 5A) and preserved (Fig. 5B) matrices are presented. These figures graphically illustrate ClO_2^- losses in both the unpreserved Fe^{3+} and OCl^- matrices of 85 and 50%, respectively. No losses were observed in the unpreserved matrix with no reactive species present or in any matrix preserved with EDA.

 NO_2^- , NO_3^- and Br^- survey summary

Thirty-nine community system drinking water wells were sampled for the occurrence of NO_2^- , NO_3^- and Br^- [12]. Sites were chosen which reflected a total $\text{NO}_2^-/\text{NO}_3^-$ greater than 3.0 mg/l as N based upon occurrence data gathered in the National Pesticide Survey [13]. NO_2^- and NO_3^- are regulated anions with maximum contaminant levels (MCL) of 10 mg/l and 1.0 mg/l in drinking water, respectively [14]. Table IV presents a summary of the analytical results from the analyses of these samples. Every site sampled contained measurable concentrations of both NO_3^- and Br^- , however, only one site contained detectable concentrations of NO_2^- .

The performance of this analytical procedure for ground water samples was illustrated through these results. Table V shows the precision of duplicate sample analyses and the low relative standard deviation attained.

 Br^- as a DBP precursor

As an illustration of the importance of monitoring Br^- in source water, six sites were chosen to demonstrate the effect of Br^- on the distribution of trihalomethanes. For three sites, Br^- was not present above the detection limit (At the time of analyses the MDL for Br^- was 20 η/l), while the other three had measurable Br^- concentrations in the source water. This study was conducted prior to the change to a borate eluent, using the 0.7 mM $\text{Na}_2\text{CO}_3/1.3$ mM NaHCO_3 , which gave a higher background conductance resulting in a noisier baseline and higher detection limits. Other than eluent change, all of the conditions in Table I apply. Trihalomethanes was determined by liquid-liquid extrac-

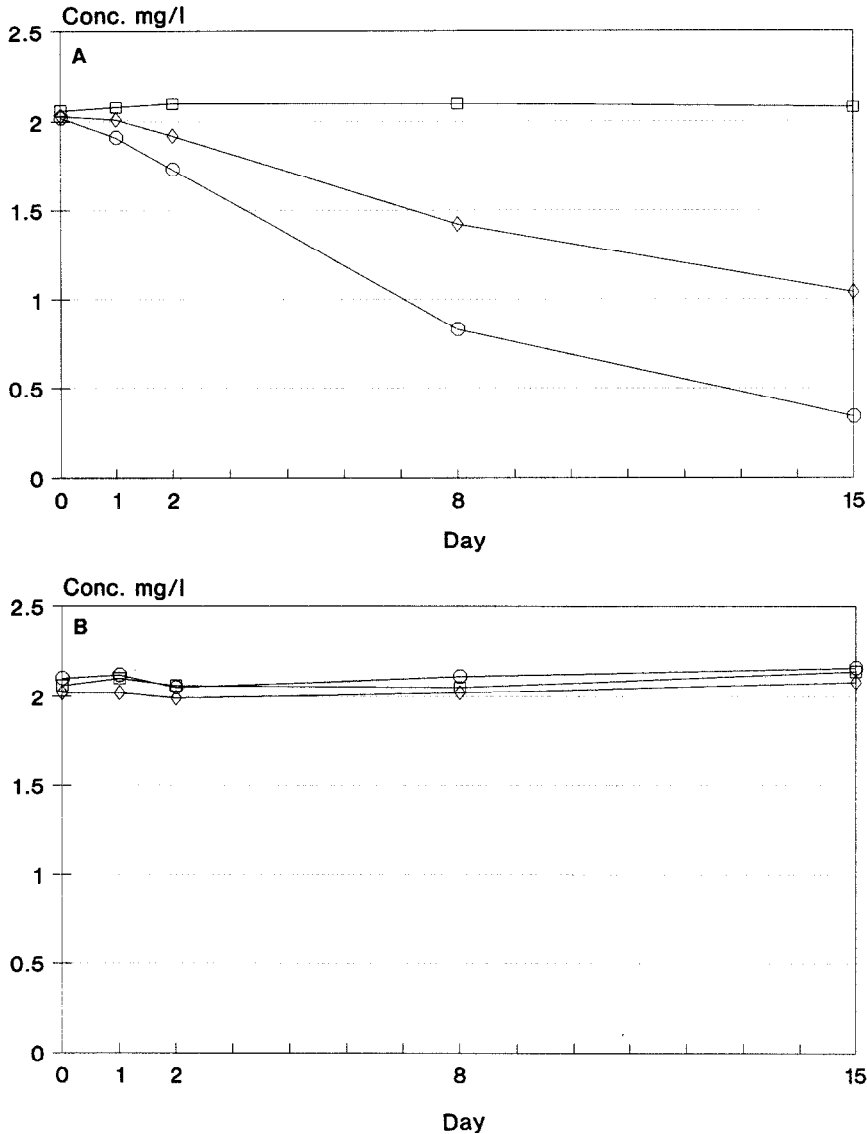


Fig. 5. (A) Results from the ClO_2^- stability study showing degradation in unpreserved matrices when reactive species are present. All matrices initially were spiked with 2.0 mg/l ClO_2^- . □ = Unpreserved with no reactive species present; ◇ = unpreserved and spiked with 2.4 mg/l OCl^- ; ○ = unpreserved and spiked with 1.0 mg/l Fe^{3+} . (B) Results from the ClO_2^- stability study showing no degradation in any matrices preserved with 50 mg/l EDA. All matrices initially were spiked with 2.0 mg/l ClO_2^- . □ = EDA preserved with no reactive species present; ◇ = EDA preserved and spiked with 2.4 mg/l OCl^- ; ○ = EDA preserved and spiked with 1.0 mg/l Fe^{3+} .

tion following EPA method 551 [15] on a gas chromatograph equipped with an electron-capture detector. Table VI presents data showing the relationship between Br^- levels in the source water and the distribution of trihalomethanes in the treated water. As shown in the table, the presence of Br^- in the

source water contributes to proportionately higher concentrations of CHClBr_2 and CHBr_3 in the treated water. It should be pointed out, the levels for chlorinated and brominated DBPs in treated water is additionally effected by various parameters of source water quality.

TABLE IV
SUMMARY OF THE NO_2^- , NO_3^- AND Br^- SURVEY

Analytical conditions as in Table I. Thirty-nine community system drinking water wells were sampled for the occurrence of the anions NO_2^- , NO_3^- and Br^- .

Analyte	No. of positive samples	Minimum (mg/l)	Maximum (mg/l)	Mean (mg/l)
N — NO_2^-	1	<0.001	0.015	<0.001
N — NO_3^-	39	0.49	13	5.3
Br^-	39	0.006	1.0	0.13

TABLE V
PRECISION OF DUPLICATE SAMPLE ANALYSES FOR THE NO_2^- , NO_3^- AND Br^- SURVEY

Analytical conditions as in Table I. Of the 39 community drinking water wells sampled, 18 were analyzed in duplicate.

Analyte	No. of duplicate samples	Precision (R.S.D., %)
N — NO_3^-	18	1.5
N — NO_2^-	18	0 ^a
Br^-	18	2.5

^a 17 out of 18 were non-detects.

When the treatment is ozonation, Br^- in the source water can react with the disinfectant to form DBPs. Samples were analyzed from an EPA pilot treatment plant experimenting with ozonation. The source water had a Br^- concentration of 0.037 mg/l

TABLE IV
EFFECTS OF HIGH Br^- IN SOURCE WATER ON TRIHALOMETHANE DISTRIBUTION IN CHLORINATED DRINKING WATER

Analytical conditions as in Table I except the eluent was 0.7 mM Na_2CO_3 /1.3 NaHCO_3 . This study was conducted prior to a change to the borate eluent. Anions were determined by IC and trihalomethanes were determined by liquid-liquid extraction following EPA Method 551 on a gas chromatograph equipped with an electron-capture detector.

Site No.	Source water Br^- concentration (mg/l)	Trihalomethane concentration ($\mu\text{g/l}$)			
		CHCl_3	CHCl_2Br	CHClBr_2	CHBr_3
34	<0.02	18.3	4.00	0.40	<0.20
36	<0.02	40.6	10.2	2.04	<0.20
52	<0.02	30.4	5.84	0.58	<0.20
41	0.058	23.8	12.9	5.09	0.96
43	0.108	33.5	23.5	13.8	5.92
46	0.180	20.3	22.5	20.1	4.72

and a pH of 7.5 to 8.1. Source water was dosed with O_3 at 0.29 mg/l, 1.08 mg/l, 1.94 mg/l, and 3.97 mg/l. Table VII displays the results of the analyses and shows the formation of BrO_3^- at measurable concentrations once the applied ozone dose reaches 1.95 mg/l. The BrO_3^- found in the treated water accounts for the loss of Br^- , relative to the level present in the source water, on a mass balance basis, within the confidence limits of the data. This demonstrates BrO_3^- is a possible DBP of ozone treatment. Further studies are planned to better understand the parameters involved in the formation of this DBP.

CONCLUSIONS

Depending on the type of disinfection employed for drinking water, various inorganic DBPs can be formed. Whether the treatment is with chlorine, chlorine dioxide or ozone, there is a potential for formation of oxyhalide anions of chlorine and bromine. Because these anions are being considered for regulation, a method for monitoring these anions by IC has been refined and is currently being used to collect occurrence data. A borate eluent was shown to provide improved separation over the carbonate eluent for resolving trace levels of ClO_2^- , ClO_3^- , BrO_3^- and NO_2^- in the presence of high concentrations of Cl^- , CO_3^{2-} and NO_3^- . The effectiveness of EDA to preserve ClO_2^- concentrations from the reactive species of OCl^- and Fe^{3+} was illustrated. IC has been shown to be an effective analytical tool for

TABLE VII

EFFECTS OF HIGH Br^- IN SOURCE WATER FOLLOWING OZONATION: FORMATION OF BrO_3^-

Analytical conditions as in Table I.

Sample	O_3 Dose		Br^- ($\mu\text{g/l}$)	BrO_3^- ($\mu\text{g/l}$)
	Applied (mg/l)	Dissolved (mg/l)		
Source	0.00	0.00	37	<7
No. 1	0.29	0.03	36	<7
No. 2	1.08	0.47	36	<7
No. 3	1.94	1.13	23	15
No. 4	3.97	2.13	12	35

monitoring inorganic DBPs as well as the presence of NO_2^- , NO_3^- and Br^- in drinking water.

REFERENCES

- 1 Method 300.0: The Determination of Inorganic Anions in Water by Ion Chromatography. US Environmental Protection Agency, Cincinnati, OH, December 1989.
- 2 L. W. Condie, J. —*Am. Water Works Assoc.*, 78 (1986) 73.
- 3 J. D. Pfaff and C. A. Brockhoff, J. —*Am. Water Works Assoc.*, 82 (1990) 195.
- 4 G. Gordon and S. Tachiyashiki, *Environ. Sci. Technol.*, 25 (1991) 468.
- 5 I. Fabian and G. Gordon, *Inorg. Chem.*, submitted for publication.
- 6 J. C. Morris, in R. L. Jolley (Editor), *Water Chlorination: Environmental Impact and Health Effects*, Proc. Conf. on Environmental Impact of Water Chlorination, Oak Ridge, TN, Oct. 1975, Vol. 1, Ann Arbor Sci. Publ. 1978, p. 22.
- 7 J. M. Symons, A. A. Stevens, R. M. Clark, E. E. Geldreich, O. T. Love and J. Demargo, *Treatment Techniques for Controlling Trihalomethanes in Drinking Water*, Office of Research and Development, US Environmental Protection Agency, Cincinnati, OH, September 1981, p. 10.
- 8 W. R. Haag and J. Hoigne, *Environ. Sci. Technol.*, 17 (1983) 161.
- 9 R. Joyce and M. Harrold, Dionex Corp., personal communication.
- 10 J. A. Glaser, D. L. Forest, G. D. McKee, S. A. Quave and W. L. Budde, *Environ. Sci. Technol.*, 15 (1981) 1426.
- 11 D. P. Hautman, *Investigations in reactivity of HOCl Internal report*, Drinking Water Quality Assessment Branch, US Environmental Protection Agency, Cincinnati, OH, May 1991; working for Technology Applications Inc. under EPA Contract No. 68-03-3352.
- 12 D. J. Munch, L. C. Shadix, M. Bolyard, D. P. Hautman, C. Frebis, *A Study of the Occurrence of Nitrate, Nitrite, Bromide, and Bacteriological Parameters in Community System Drinking Water Wells*, in preparation.
- 13 National Survey of Pesticides in Drinking Water Wells, Phase I Report, EPA 57079-90-015, US Environmental Protection Agency, Cincinnati, OH, November 1990.
- 14 *Fed. Reg.*, Jan. 30 (1991) 3526-3597.
- 15 *Methods for the Determination of Organic Compounds in Drinking Water, Supplement I*, EPA 600/4-90/020, US Environmental Protection Agency, Washington, DC, July, 1990, p. 169.