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Eliminating the chlorite interference in US Environmental Protection Agency Method 317.0 permits analysis of trace bromate levels in all drinking water matrices

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Abstract

A post-column reagent (PCR) method for bromate analysis in drinking water with a method detection limit (MDL) and method reporting limit (MRL) of 0.1 and 0.5 μg/l, respectively, has been developed by the United States Environmental Protection Agency (EPA) for future publication as EPA Method 317.0. The PCR method provides comparable results to the EPA's Selective Anion Concentration (SAC) method used to support the laboratory analysis of Information Collection Rule (ICR) low-level bromate samples and offers a simple, rugged, direct injection method with potential to be utilized as a compliance monitoring technique for all inorganic Disinfectants/Disinfection By-Products (D/DBPs). It has superior sensitivity for bromate compared to EPA Method 300.1, which was promulgated as the compliance monitoring method for bromate under Stage 1 of the D/DBP rule. This paper addresses elimination of the chlorite interference that was previously reported in finished waters from public water systems (PWSs) that employ chlorine dioxide as the disinfectant. An evaluation of Method 317.0 for the analysis of bromate in commercial bottled waters is also reported.

Keywords: Water analysis; Chlorite; Inorganic anions; Inorganic cations; Iron; Bromate

1. Introduction

Inorganic oxyhalide Disinfection By-Products (DBPs) are formed when drinking water supplies are disinfected to minimize the risk from potentially hazardous microorganisms. Chlorite (ClO_2^-) and chlorate (ClO_3^-) are predominantly formed when chlorine dioxide (ClO_2) is used to disinfect drinking water [1,2], and bromate (BrO_3^-) is predominantly formed when source waters containing bromide are ozonated [3,4]. The formation of iodate (IO_3^-) has been postulated to occur if source waters containing iodide are ozonated [5].

Bromate has been listed as an animal carcinogen [6] and has also been classified as a group 2B, probable human carcinogen by the International Agency for Research on Cancer [7]. Based upon health studies, bromate is reported to be a suspected human carcinogen with a potential 10^{-4} risk of cancer after a lifetime exposure in drinking water at 5.0 μg/l and a potential 10^{-5} risk at 0.5 μg/l [8]. Consequently, in December 1998, under Stage 1 of the Disinfectants/Disinfection By-Products (D/DBP) Rule, the United States Environmental Protection Agency (EPA) promulgated a maximum con-

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taminant level (MCL) for bromate in drinking water; the current MCL is 10 μg/l [9]. As well, a maximum contaminant level goal (MCLG) for bromate was also set to zero under Stage 1 of the D/DBP rule [9]. Among a number of considerations at the time, limitations in acceptable compliance monitoring methods played a significant role in establishing the Stage 1 drinking water MCL for bromate at 10 μg/l. It is conceivable that the availability of suitable methods, health risks associated with bromate, occurrence data observed in the Information Collection Rule (ICR) [10], bromate treatability (removal), and other factors will lead to a revised bromate MCL when that MCL is reconsidered for Stage II.

The Selective Anion Concentration (SAC) method [11] was developed to meet the EPA's need for additional data on low-level bromate occurrence. Because of the complexity of the SAC method, a more simplistic method was required for the proposed compliance monitoring requirements for Stage 1 of the D/DBP Rule.

The EPA published Method 300.1 [12] in September 1997, which reduced the Method 300.0 [13] bromate method detection limit (MDL) from 20.0 to 1.4 μg/l using direct injection of the sample. Method 300.1 was promulgated by the EPA in December 1998 as the Stage 1 compliance monitoring method for bromate [9]. In September 1998, the EPA presented a post-column reagent (PCR) method developed at their technical support center (TSC) laboratory that coupled *o*-dianisidine (ODA), as the PCR, directly to EPA Method 300.1 [14]. In November, the EPA published the results of a comparative study of a 3-month segment of ICR samples, which indicated that the PCR addition to Method 300.1 provided similar low-level bromate results to the SAC method which was used to support the ICR [15]. However, this study also identified a potential chlorite interference on the absorbance detector in finished waters from public water systems (PWSs) that employed chlorine dioxide as a disinfectant [15].

The sample collection protocols for the ICR stipulated that the samples from PWSs using chlorine dioxide as the disinfectant must be stabilized at the time of collection by the addition of ethylenediamine (EDA, at a final concentration of 50 mg/l). This stabilization is essential to prevent the oxidation of chlorite during sample collection, shipment and storage prior to analysis [12,16,17]. In contrast, bromate is significantly more stable. Knowing that chlorite is more susceptible to oxidation and/or reduction than bromate, it was postulated that under the appropriate conditions, chlorite could be preferentially removed from a matrix without adversely affecting trace levels of bromate. This paper summarizes the work to eliminate the chlorite interference in samples from PWSs utilizing chlorine dioxide, that was performed during the development of EPA Method 317.0. This paper also reports the results from a limited evaluation of EPA Method 317.0 for the analysis of bromate in commercial bottled waters.

2. Experimental

2.1. Reagents

The eluent, standards, stabilization solution, surrogate and all dilutions were prepared using 18 MΩ water (Barnstead, PN 163437, Debuque, IA, USA). American Chemical Society (ACS) reagent grade Na_2CO_3 was used to prepare 9.0 m*M* carbonate eluent (Aldrich, catalog No. 22,348-4, Milwaukee, WI, USA) which was membrane filtered (0.45 μm) and degassed with helium prior to use. The post-column reagent was prepared by adding 40 ml of 70% redistilled nitric acid (Aldrich, catalog No. 22,571-1) to approximately 300 ml reagent water in a 500-ml volumetric flask and adding 2.5 g of ACS reagent grade KBr (Sigma, catalog No. P-5912, St. Louis, MO, USA). A 250-mg amount of purified grade ODA (Sigma, catalog No. D-3252) was dissolved, with stirring, in 100 ml of spectrophotometric grade methanol (Sigma, catalog No. M-3641). After dissolution, the ODA solution was added to the nitric acid/KBr solution and diluted to volume with 18 MΩ water. The reagent was shown to be stable for 1 month [14,18]. EDA preservation solution (100 mg/ml) was prepared from 99.5+% EDA (Aldrich, catalog No. 39,108-5). Dichloroacetate (DCA) surrogate solution was prepared from dichloroacetic acid, potassium salt (Aldrich, catalog No. 34,808-2; 0.065 g/100 ml reagent water). An aqueous 1000 mg/l hydrogensulfite solution was prepared from sodium

hydrogensulfite (Fisher Scientific, catalog No. S654-500, Fair Lawn, NJ, USA). An aqueous 1000 mg/l ferrous iron [Fe(II)] solution was prepared using ferrous sulfate heptahydrate (Sigma, catalog No. F-7002; 0.124 g/25 ml reagent water containing 6 μl of concentrated nitric acid). Sulfuric acid (Fisher Scientific Certified ACS Plus, A 300-500, (0.25 *M*)) was used to acidify samples for experiments evaluating the preferential removal of chlorite.

2.2. Standard and sample preparation

The calibration standards, continuing calibration check standards and spiking solutions were prepared using an EPA ICR 1.0 mg/ml National Exposure Research Laboratory (NERL) bromate stock solution. The PCR calibration and method accuracy was verified using a second source quality control standard made with ACS reagent grade potassium bromate (Alfa, catalog No. 300487, Danvers, MA, USA) and EPA Performance Evaluation (PE) standards. All bromate calibration and continuing calibration check standards were stabilized with the addition of EDA stabilization solution (50 μl/100 ml of sample). All samples were stabilized at collection with EDA according to the procedures outlined ICR Sampling Manual [16]. DCA was used as the surrogate in EPA Method 300.1 and therefore was added to all standards and samples just prior to analysis (10 μl/5.0 ml of sample). Dionex autosampler vials were used to filter all standards and samples prior to analysis.

2.2.1. Removal of chlorite by oxygenation

The reagent water samples involved in the evaluation of oxygenation as the means of preferentially removing chlorite were acidified to a pH of approximately 2 with the addition of 100 μl of 0.25 *M* sulfuric acid per 10 ml of sample prior to oxygenation. An aluminum block heater (Barnstead, Thermolyne Model DB16525) was used to heat the samples during the oxygenation studies.

2.2.2. Removal of chlorite using hydrogensulfite

The samples involved in the evaluation of hydrogensulfite as the means of preferentially removing chlorite were acidified to a pH of approximately 2 with the addition of 100 μl of 0.25 *M* sulfuric acid per 10 ml of sample prior to addition of the hydrogensulfite reagent.

2.2.3. Removal of chlorite using ferrous ion

The EDA stabilized samples involved in the evaluation of iron as the means of preferentially removing chlorite were acidified to a pH of approximately 6 with the addition of 33 μl of 0.25 *M* sulfuric acid per 10 ml of sample prior to addition of the ferrous iron reagent.

2.3. Instrumentation

A Dionex autosampler and load inject valve with a 220-μl sample loop were connected to the Dionex DX-500 microbore pump, which delivered the eluent (1.3 ml/min), to a Dionex 4 mm AG9-HC guard and AS9-HC analytical column for separation. Following electrolytic suppression, (100 mA; external water source mode) the suppressed eluent entered a Dionex CDM-2 conductivity detector. The effluent from the CDM-2 was connected to one port of a mixing T. The PCR was delivered (0.7 ml/min) to the mixing T using a Dionex PC-10 pneumatic controller pressurized with helium. A Dionex, 500-μl knitted reaction coil enclosed in a Dionex PCH-2 column heater at 60°C was connected to the third port of the mixing T. The effluent from the reaction coil entered a Dionex AD20 absorbance detector with a 10 mm cell path length, set at 450 nm and 0.05 absorbance units (AU) full-scale. The effluent from the absorbance detector was directed to waste. A Dionex Advanced Computer Interface (ACI) was incorporated to facilitate unattended operation and automatic shutdown of the PCR and column heater. A personal computer (PC) with Peak Net software (version 4.3) was utilized to control the instrument and for data processing.

3. Results and discussion

The PCR addition to Method 300.1 provided excellent results for the analysis of trace bromate levels in source, in-process and finished water samples from PWSs which utilized ozone as the disinfectant [14,15]. One of the most stringent requirements for an EPA compliance monitoring method is that it

must be applicable to all types of sample matrices in which the target analytes require analysis. The masking interference of high concentrations of chlorite with the PCR method prevented application of the method to chlorine dioxide disinfected waters (see Fig. 1). This deficiency needed to be resolved before the PCR method could be used to effectively monitor trace bromate in samples from all types of PWSs.

3.1. Preferential removal of chlorite

In order for Method 317.0 to be applicable to chlorine dioxide disinfected PWSs, a means for preferentially removing chlorite was required. Various techniques such as exposure to ultraviolet radiation; filtration through activated granular charcoal; treatment with peroxide; purging with oxygen; and treatment with reducing agents such as hydrogen-sulfite and ferrous iron were examined for their ability to remove high levels (1000 μg/l) of chlorite without affecting trace (1.0 μg/l) levels of bromate.

3.1.1. Preliminary investigations for chlorite removal

Exposure of solutions containing 500 μg/l chlorite and 2 μg/l bromate in quartz cells to a broad spectrum UV light source resulted in depletion of both the chlorite and bromate species. A scan of individual 40 mg/l chlorite and bromate solutions indicated that chlorite weakly absorbed at 260 nm whereas bromate showed no absorption whatsoever at this wavelength. Although promising, this alternative was abandoned when no narrow band light source with sufficient intensity to illuminate the samples at 260 nm could be obtained.

A second option involved filtration of similar solutions listed above through activated carbon. However, again this avenue was unsuccessful and resulted in loss of both chlorite and bromate.

Finally, hydrogen peroxide was evaluated as a potential oxidant to preferentially oxidize chlorite. Although excess peroxide is theoretically readily destroyed by heating, this avenue was abandoned when resolution problems (introduction of an interference), which were speculated to result from

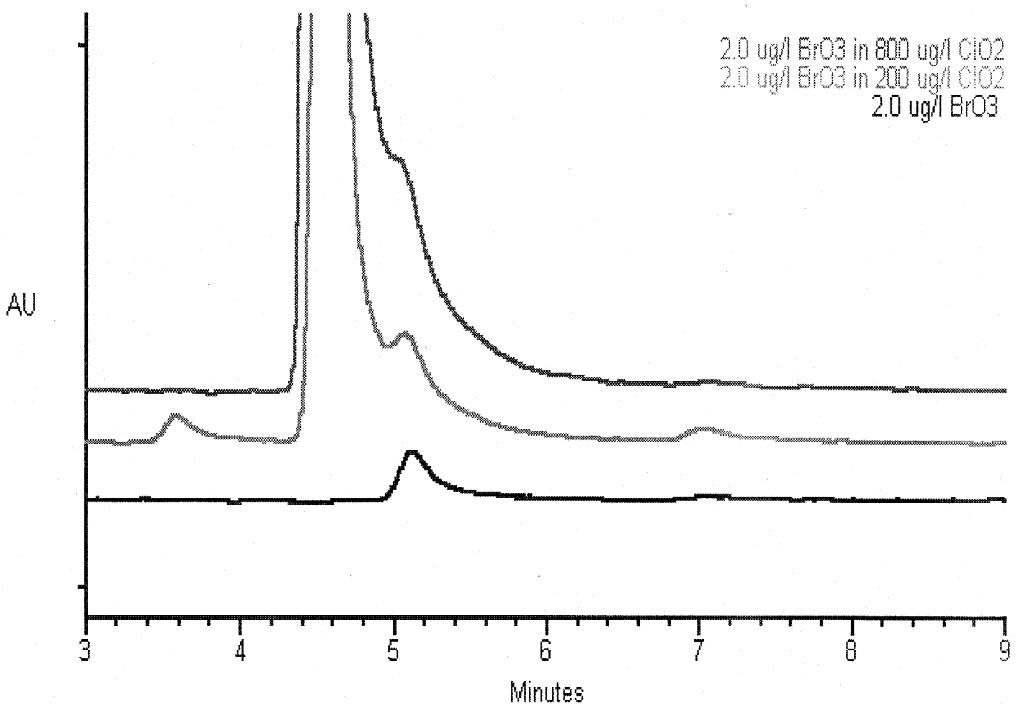

Fig. 1. Chlorite interference on the absorbance detector in chlorine dioxide treated waters.

Table 1
Bromate stability in reagent water during oxygenation

Time (h)	Chlorite (μg/l)	Bromate (μg/l)
0	208	3.7
0.5	122	3.9
1.0	60	3.8
1.5	46	3.9
2.0	6	3.6

peroxide reaction by-products and/or residual peroxide, were encountered.

3.1.2. Chlorite removal by purging with oxygen

Preliminary studies involving purging reagent water containing high levels of chlorite and trace levels of bromate with oxygen at 40°C for several hours were unsuccessful in removing chlorite. However, promising results were obtained when the sample was acidified to a pH of approximately 2 prior to purging with oxygen. After several hours the chlorite level was reduced to zero while the bromate concentration remained relatively unchanged.

The next stage involved quantitative assessment of bromate under similar conditions. Acidified reagent water containing 200 μg/l chlorite and 4 μg/l bromate was purged with oxygen at 40°C and the chlorite and bromate concentrations measured every 30 min. No loss of bromate was evident after 2 h during which time the chlorite level diminished to almost zero (see Table 1). Further investigation indicated that this oxidation of chlorite was dependent upon numerous variables such as oxygen flow-rate, acid concentration and temperature. In addition, the presence of metal ions, residual chlorine and/or other components capable of catalyzing the oxidation of chlorite are likely supplementary variables [12]. It was also observed that similar results, in terms of chlorite removal, could be obtained if the acidified samples, without oxygenation, were allowed to sit at room temperature for approximately 120 h.

According to ICR sample collection protocols [17], samples for the analysis of oxyhalide anions required stabilization with EDA to prevent oxidation of chlorite during shipment and storage of the samples prior to analysis. When an ICR sample containing approximately 600 μg/l chlorite was spiked with 7 or 12 μg/l bromate, acidified and either purged with oxygen for 2 h or allowed to sit at room temperature for 120 h, similar results, in terms of chlorite removal and bromate stability, were obtained. In this matrix, the chlorite was completely removed after 1 h purging with oxygen at 40°C or after 24 h at room temperature. No loss of bromate was evident even after 120 h at room temperature (see Fig. 2). Conversely, when other ICR samples with native chlorite levels ranging from <10 to 1600 μg/l were spiked with trace levels of bromate, acidified and purged with oxygen, it became evident that oxygenation, as a means of removing chlorite in samples from PWSs, was very matrix dependent. One sample with 1600 μg/l native chlorite still contained approximately 500 μg/l chlorite even after 2 h of oxygenation at 40°C which masked the trace bromate concentration. However, other ICR samples with high chlorite levels exhibited no problem with chlorite removal. These results suggested that each sample from chlorine dioxide treatment facilities

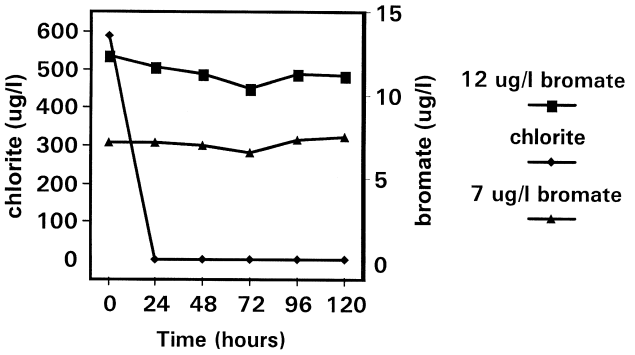

Fig. 2. Preferential removal of chlorite and bromate stability in a PWS sample after acidification and oxygenation.

would require slightly different treatment (depending, in part, upon the native chlorite concentration) prior to analysis for trace bromate. Consequently, work continued to find a more robust alternative, which would provide one treatment for all matrices.

3.1.3. Chlorite removal by treatment with hydrogensulfite

The removal of chlorine dioxide residuals and chlorite from drinking water disinfected with chlorine dioxide has received wide spread attention in recent years. Various sulfur-based reducing agents such sulfur dioxide, metahydrogensulfite and thiosulfate as well as other reducing agents such as ferrous iron have been successfully used to remove undesirable residuals and by-products from drinking water [19–23]. In general, these methods have not met with great success due to the formation of other undesirable constituents. However, these alternatives held potential for preferentially removing the chlorite interference with the post-column ion chromatographic (IC) analysis of trace levels of bromate.

Preliminary results were very encouraging using hydrogensulfite (mixture of sodium hydrogensulfite and sodium metahydrogensulfite) to remove chlorite. No chlorite interference was evident and acceptable precision [7.1% relative standard deviation (RSD); $n=7$] was obtained when 10 ml of a reagent water (EDA stabilized) containing 1000 μg/l chlorite and 5 μg/l bromate was acidified and treated with 30 μl of a 1000 mg/l hydrogensulfite solution prior to analysis. As well, acceptable precision was obtained over a 23-h period with a 5 μg/l (9.9% RSD; $n=25$) and a 1 μg/l (16.9% RSD; $n=25$) bromate spike in reagent water. When treated in a similar manner, spike recoveries of 97.2% and 99.2% were observed in two ICR samples that contained 1000 and 825 μg/l native chlorite. However, when low level bromate solutions were exposed to the same concentrations of hydrogensulfite in the absence of chlorite, the bromate levels were diminished. It became evident that chlorite was preferentially reduced by hydrogensulfite but in the absence of chlorite, bromate was also reduced. Consequently, if hydrogensulfite were used to remove chlorite, the native chlorite concentration would have to be determined and the stoichiometric concentration of hydrogensulfite calculated prior to treating each sample with hydrogensulfite. Although either purging with oxygen and/or treatment with hydrogensulfite provided a workable, albeit cumbersome method for chlorite removal, a more universal, simplistic procedure was sought.

3.1.4. Chlorite removal by treatment with ferrous iron [Fe(II)]

The removal of residual chlorite from drinking water incorporating ferrous iron under slightly acidic (pH 5–6.5) conditions has been extensively studied [19,21–23]. The molar stoichiometry, based on Eq. (1) predicts that 3.3 mg of Fe(II) would be required to completely reduce 1.0 mg ClO_2^- [21].

$$4Fe^{2+} + ClO_2^- + 10H_2O \rightarrow 4Fe(OH)_3(s) + Cl^- + 8H^+ \quad (1)$$

Because elevated levels of iron were projected to pose potential fouling problems with the AS9HC column and the suppressor membrane, efforts were directed towards finding an acceptable means of removing iron from slightly acidic solutions. Solid-phase extraction (SPE) cartridges containing a cation-exchange resin in the hydrogen form have been used to reduce sample pH and to remove cationic species such as Fe(III) in some sample matrices [24]. It was necessary to determine if Fe(II) could be removed in a similar manner.

When Fe(II) is added to drinking water samples containing chlorite, a portion of the Fe(II) is oxidized to $Fe(OH)_3$, while the excess remains as Fe(II). In order to assess the completeness of the removal of both forms of the iron from acidic solutions treated with Fe(II), inductively coupled argon-plasma atomic emission spectroscopy (ICP-AES) was utilized to measure the total iron concentrations before and after its addition. To test the removal of iron from water samples, 7 mg/l Fe(II) was added to EDA stabilized reagent water samples containing up to 2.1 mg/l ClO_2^-. After treatment the samples were analyzed by ICP-AES. As indicated in Table 2, both the particulate filter and SPE cartridge were necessary to reduce the iron to acceptable levels and thereby prevent fouling of the IC system.

After ensuring that essentially no iron would contaminate the IC columns or suppressor membrane, the next stage was to determine the fate of

Table 2
ICP determination of total iron levels in chlorite treated reagent water

Sample No.	Sample description	Iron (μg/l)
1	Reagent water fortified with Fe(II)	3900
2	Sample 1 treated with H^+ SPE cartridge	49
3	Reagent water with EDA, fortified with Fe(II), acidified	3200
4	Sample 3 treated with H^+ SPE cartridge	57
5	Reagent water fortified with Fe(II), acidified	3900
6	Sample 5 treated with 1000 μg/l ClO_2^- and particulate filter only	1400
7	Reagent water with EDA, fortified with Fe(II), acidified	3200
8	Sample 7 treated with 1000 μg/l ClO_2^- and particulate filter only	480
9	Reagent water 1 fortified with Fe(II), acidified	3000
10	Sample 9 with EDA, acidified and treated with 1000 μg/l ClO_2^- and particulate filter and H^+ SPE cartridge	1.4
11	Reagent water 2 fortified with Fe(II), acidified	5100
12	Sample 11 with EDA, acidified and treated with 1500 μg/l ClO_2^- and particulate filter and H^+ SPE cartridge	3.0
13	Reagent water 3 fortified with Fe(II), acidified	7100
14	Sample 13 with EDA, acidified and treated with 2100 μg/l ClO_2^- and particulate filter and H^+ SPE cartridge	3.7

trace levels of bromate in treated reagent water. When an EDA stabilized reagent water containing 1000 μg/l chlorite and 3.0 μg/l bromate was similarly treated with 2500, 3750 and 5000 μg/l Fe(II), no masking of the bromate peak by chlorite (as in the untreated sample) was evident on the absorbance detector and no loss of bromate recorded (see Fig. 3).

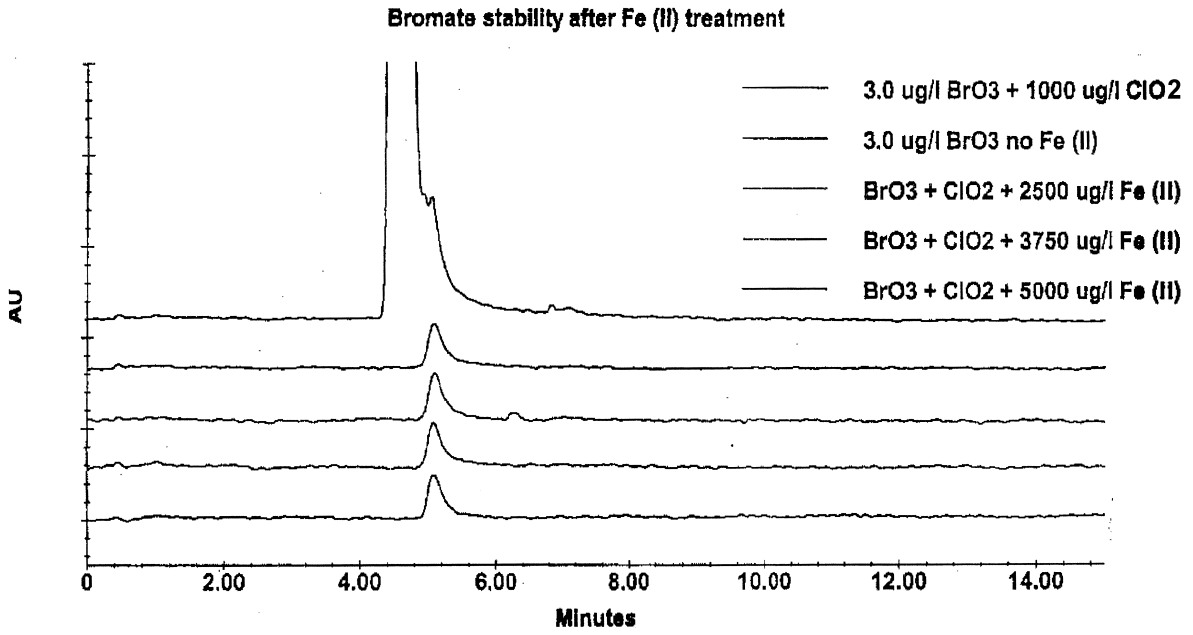

Fig. 3. Removal of chlorite interference in reagent water using Fe(II).

3.1.4.1. Bromate stability in reagent water and a PWS sample treated with Fe(II)

The next step was to establish that the Fe(II) treatment would be compatible with the analysis of large analysis batches (up to 20 field samples can be analyzed in a single analysis batch with Method 317.0). The goals were to confirm that the bromate in samples treated with Fe(II) was sufficiently stable to allow processing of the entire batch and to establish that the bromate concentrations in the processed samples were stable over a sufficient period of time to allow automated analysis of the complete analysis batch.

The affect of treatment time on bromate stability was assessed by acidifying an EDA stabilized reagent water containing 1000 μg/l chlorite and 2.2 μg/l bromate and an ICR sample spiked with 1.1 μg/l bromate and treating the samples with 3300 μg/l Fe(II). The solutions were allowed to sit for 10, 20, 40, 60, 90 and 120 min before passing through a particulate filter and SPE cartridge in the hydrogen form. No loss of bromate was detected in either sample during the 2 h treatment time (see Fig. 4).

Bromate stability in the autosampler vials after Fe(II) treatment and subsequent removal was investigated next. An EDA stabilized reagent water containing 1000 μg/l chlorite and 2.0 μg/l bromate was acidified, treated with 3300 μg/l Fe(II) for 10 min and then passed through a particulate filter and SPE cartridge in the hydrogen form. Eighty-five autosampler vials containing the surrogate were filled with the treated sample and analyzed over 36 h. Essentially no loss of bromate was evident after 36 h suggesting the treated samples to be stable for automated analysis (see Fig. 5).

3.1.4.2. Optimized conditions for chlorite removal with Fe(II)

Under Stage 1 of the D/DBP Rule, the MCL for chlorite was established at 1000 μg/l. Chlorite levels above 1000 μg/l should very seldom be encountered in a PWS disinfected with chlorine dioxide since the municipality would be out of compliance. Since the preceding work established that an excess of Fe(II) had no deleterious effect on either chlorite or bromate, the final protocols for chlorite removal incorporated a slight excess of Fe(II) to ensure complete removal of up to 1200 μg/l chlorite.

The optimized conditions for chlorite removal involved treating a 10 ml aliquot of sample with 33 μl of acid, swirling to ensure complete mixing followed by addition of 40 μl of Fe(II) solution. The mixture was allowed to stand for 10 min before filtering through a particulate filter followed by treatment with a SPE cartridge in the hydrogen form. A sufficient quantity of the treated sample was collected (depending upon the autosampler vial capacity), the surrogate added and then analyzed using Method 317.0.

3.1.5. IC analysis of ICR samples from chlorine dioxide plants treated with Fe(II)

Twenty-one ICR samples, from 21 PWSs that used chlorine dioxide as the disinfectant were ana-

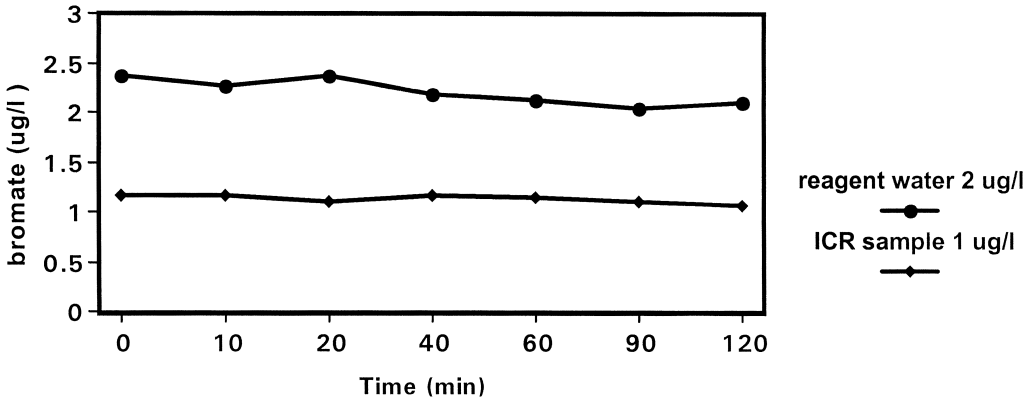

Fig. 4. The effect of Fe(II) reaction time on bromate stability in reagent water and an ICR sample treated with excess Fe(II).

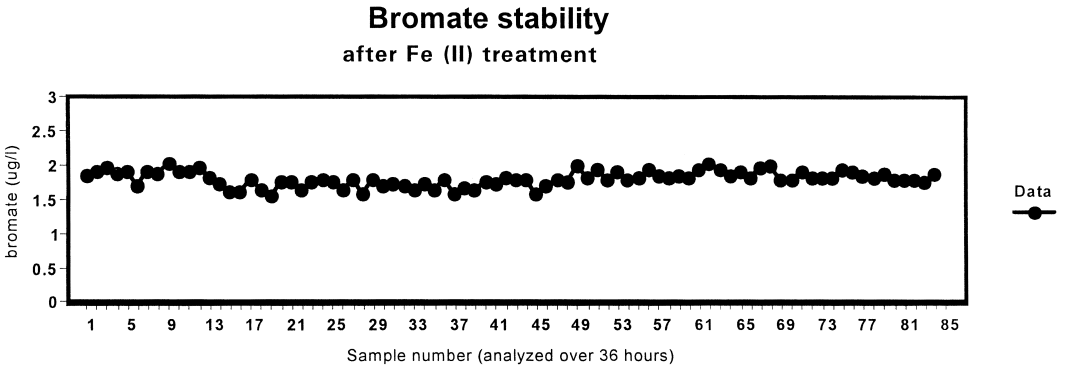

Fig. 5. Bromate stability in reagent water after treatment with Fe(II).

lyzed for bromate content using Method 317.0. Nine of the 21 PWSs also listed chloramine being used in conjunction with chlorine dioxide and one plant listed chlorine dioxide, chloramine and ozone as potential disinfectants. All samples were analyzed three times. In the first instance, the sample was analyzed as received to determine levels of chlorite, chlorate and bromide. The second analysis involved treating the sample with Fe(II) to determine if bromate was native in the sample but masked by the elevated levels of chlorite. The third analysis involved fortifying the sample with bromate levels of 0.5, 2.0 or 5.0 μg/l prior to the addition of Fe(II) to determine the precision and accuracy of the spike recoveries (chlorite removal process). In all instances, the samples were treated using the optimized chlorite removal protocols and with the surrogate being added after the chlorite removal step, just prior to analysis.

The native chlorite levels ranged from <MRL to 1600 μg/l. The 0.5 μg/l bromate spike recovery averaged 98.6% ($n=7$) and ranged from 92.0 to 110% with a 6.3% RSD. The 2.0 μg/l bromate spike recovery averaged 102% ($n=7$) and ranged from 99.0 to 106% with a 2.1% RSD. The 5.0 μg/l bromate spike recovery averaged 110% ($n=7$) and ranged from 103 to 122% with a 6.2% RSD (see Table 3).

The presence of bromate, which appeared as a shoulder and/or which was completely masked by the chlorite peak when the original untreated samples were analyzed, was identified in three of the 21

Table 3
Bromate spike recoveries in ICR samples from PWSs using chlorine dioxide

Sample description	BrO_3^- spike (μg/l)	ClO_2^- (μg/l)	BrO_3^- (μg/l)	Recovery (%)		
				Average	Range	RSD (%)
Sample	0.5	<MRL to 720	Masked[a]			
Sample treated	0.5	<MRL	<MRL			
Sample+spike treated	0.5	<MRL	0.43 to 0.55	98.6	92.0–110	6.3
Sample	2.0	<MRL to 1600	Masked			
Sample treated	2.0	<MRL	<MRL			
Sample+spike treated	2.0	<MRL	2.0 to 2.1	102	99.0–106	2.1
Sample	5.0	<MRL to 780	Masked			
Sample treated	5.0	<MRL	<MRL and 0.9, 1.2, 2.2			
Sample+spike treated	5.0	<MRL	5.2 to 8.1	110	103–118	7.0

[a] The term ''Masked'' in the original analysis of the sample does not indicate the presence of bromate but indicates that the presence of bromate could not be detected because of the masking interference of chlorite.

samples. In the one sample that listed ozone as a potential disinfectant, the presence of bromate in the unfortified sample would be expected if ozone was part of the disinfection process. However, the presence of bromate in two of the nine samples from plants listed as using chloramine along with chlorine dioxide in the unfortified Fe(II) treated samples was interesting. In these samples the native bromate levels were observed to be 2.18 and 1.24 μg/l, and the recoveries of a 5.0 μg/l bromate spike were 118 and 105%, respectively. No bromate was detected above the MRL in any of the 11 chlorine dioxide plants or the other seven chlorine dioxide/chloramine plants. These results confirmed a previously published report in the Federal Register ''that more sensitive methods for measuring bromate may indicate that other disinfectant/oxidants produce bromate, and that/or bromate may be a contaminant in some source waters'' [25]. The presence of bromate in a non-ozonated source water, before the contact point of disinfection/oxidation, was also previously reported [25].

3.2. Determination of bromate levels in commercially bottled waters using Method 317.0

The final stage of this work was to evaluate an alternative source of chlorite free, ozonated water using Method 317.0. Two sets of commercially bottled waters, consisting of 17 spring waters and three mineral waters were purchased approximately 6 months apart. The samples were degassed, if required, and analyzed for native bromate concentration using Method 317.0. All samples were then spiked with either 0.5, 2.0 or 5.0 μg/l bromate and reanalyzed.

The native bromate levels ranged from less than the MRL of 0.5 to 59 μg/l and were comparable to the highest levels of 42 μg/l reported by the US Food and Drug Administration [18] in locally purchased bottled waters in the USA and 37 μg/l reported in Canadian bottled waters by Health Canada [26]. The average spike recovery was 103% and ranged from 84.4 to 122%.

4. Conclusions

Previous application of the post-column reagent addition to EPA Method 300.1 for monitoring trace bromate from public water systems that use chlorine dioxide at some point in their treatment, was hindered by a chlorite response on the UV–Vis detector. A number of procedures were investigated as a means to preferentially remove chlorite without adversely affecting bromate levels. Of these, the procedure that employs Fe(II) in acidic solution was found to be most effective. The elimination of this interference problem was the final step toward the development of EPA Method 317.0.

EPA Method 317.0 provides a rugged, simple, direct injection analysis for analysis of the inorganic D/DBPs, chlorite, chlorate and trace bromate, as well as bromide which is the precursor to bromate formation. The method provides low-level bromate results comparable to the SAC method and with the appropriate removal of chlorite prior to analysis, can be utilized to analyze samples from all PWSs. Method 317.0 exhibits superior bromate sensitivity to Method 300.1 that was promulgated as the compliance monitoring method for bromate under Stage 1 of the D/DBP Rule.

Confirmation of the presence of bromate in non-ozonated PWSs, disinfected with chlorine dioxide/chloramine, adds reassurance to the statement in the Federal Register [25] that the analysis of bromate in non-ozonated source waters may become a future requirement. Method 317.0 would seem well suited for this application as well.

Bromate formation potential, expressed as bromide concentration, is also available when untreated source waters are analyzed using Method 317.0.

Acceptable spike recoveries for bromate added to commercially bottled waters were also obtained when these samples were analyzed using Method 317.0.

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