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Performance evaluation of a method for the determination of bromate in drinking water by ion chromatography (EPA Method 317.0) and validation of EPA Method 324.0

Herbert P. Wagner[a,*], Barry V. Pepich[a], Daniel P. Hautman[b], David J. Munch[b]

[a]*IT Corporation, Technology Applications Group, 26 W. Martin Luther King Drive, Cincinnati, OH 45219, USA*

[b]*US Environmental Protection Agency, Office of Ground Water and Drinking Water, 26 W. Martin Luther King Drive, Cincinnati, OH 45268, USA*

Abstract

The potential carcinogenic nature of bromate has prompted global regulatory agencies, and industrial and academic institutions to publish several methods for the analysis of bromate in both drinking and bottled waters. The United States Environmental Protection Agency (EPA) has reported two methods capable of detecting bromate at or below the promulgated maximum contaminant level of 10.0 μg/l. These methods are EPA Method 300.1 and 317.0. Method 300.1 has been promulgated by EPA for compliance monitoring of bromate under Stage 1 of the Disinfectants/Disinfection By-Products Rule. Due to its sensitivity, selectivity and simplicity, Method 317.0 has been drafted and evaluated for potential use as a future compliance monitoring method. This manuscript describes the performance evaluation work with Method 317.0 and efforts completed at EPA's Technical Support Center that improved the sensitivity of Method 317.0, leading to the development of EPA Method 324.0

Keywords: Water analysis; Validation; Bromate

1. Introduction

In an effort to protect the public from potentially hazardous microorganisms, drinking water supplies are routinely disinfected with a variety of treatment regimes. Consequently, the public is exposed to inorganic oxyhalide disinfection by-products (DBPs) which may also pose potential health risks. Chlorite (ClO_2^-) and chlorate (ClO_3^-) are the dominant DBPs formed when utilities use chlorine dioxide (ClO_2) for disinfection [1,2]. Bromate (BrO_3^-) is predominantly formed when source waters containing bromide are disinfected with ozone [3,4]. The formation of iodate ($IO3^-$) has also been reported to occur when 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]. Health studies have identified bromate as 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]. Accordingly, the United States Environmental Protection Agency (EPA) promulgated a maximum contaminant level (MCL) for bromate in drinking water under Stage 1 of the Disinfectants/Disinfection By-Products (D/DBP) Rule in December 1998; that MCL is currently 10 μg/l [9]. At the same time the maximum

*Corresponding author.

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contaminant level goal (MCLG) for bromate was set at zero [9]. Limitations in acceptable compliance monitoring methods at the time were among a number of considerations that played a significant role in establishing the Stage 1 drinking water MCL for bromate at 10 μg/l. 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 be considered when the bromate MCL is reconsidered for Stage II.

The sampling and analysis phase of the ICR, which spanned a period of 18 months, required public water systems (PWSs) in the USA serving 100 000 or more persons to monitor source water, in-process and finished drinking water for general water quality parameters, DBPs, surrogates for DBPs and DBP precursors. The selective anion concentration (SAC) method [11] was developed by EPA to meet their need for additional data on low-level bromate occurrence. The complexity of the SAC method was responsible for EPA deciding to support the bromate component of the ICR in-house [8] and to seek a less complex method for future compliance monitoring requirements of the D/DBP rule.

EPA Method 300.1 [12], 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, was published in September 1997. Method 300.1 was included in the Stage 1 D/DBP Rule and promulgated by EPA in December 1998 as the compliance monitoring method for bromate [9]. In a continuing effort to simplify the analysis and improve sensitivity for trace levels of bromate in drinking water, in September 1998, EPA presented a postcolumn 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]. EPA published further work in November 1998 including the results of a comparative study of a 3-month segment of ICR samples. These results suggested 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]. During this study a chlorite interference became evident in finished waters from PWSs that employed chlorine dioxide as a disinfectant [15]. This manuscript summarizes the work to eliminate the chlorite interference in samples from PWSs utilizing chlorine dioxide; describes the performance evaluation work of Method 317.0; and summarizes efforts completed at EPA's TSC that improved the sensitivity of Method 317.0, leading to the development of a ''Draft'' EPA Method 324.0. A faster, bromate specific analysis has been developed for analysis of ultra trace concentrations of bromate in drinking water.

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 sodium carbonate (Na_2CO_3 Aldrich, Catalogue No. 22,348-4, Milwaukee, WI, USA) was used to prepare 9.0 m*M* carbonate eluent used for Method 317.0. The Na_2CO_3 and ACS certified-grade sodium hydrogencarbonate ($NaHCO_3$ Fisher, Catalogue No. S233-500, Fair Lawn, NJ, USA) were used to prepare 12.0 m*M* carbonate/5.0 m*M* bicarbonate eluent for Method 324.0. All eluents were membrane filtered (0.45 μm) and degassed with helium prior to use. The postcolumn reagent was prepared by adding 40 ml of 70% redistilled nitric acid (Aldrich, Catalogue 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, Catalogue No. P-5912, St. Louis, MO, USA). Two hundred and fifty milligrams of purified grade *o*-dianisidine (Sigma, Catalogue No. D-3252) were dissolved, with stirring, in 100 ml of spectrophotometric grade methanol (Sigma, Catalogue No. M-3641). After dissolution, the o-dianisidine 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 [14,16]. Ethylenediamine (EDA) preservation solution (100 mg/ml) was prepared from 99.5+% EDA (Aldrich, Catalogue No. 39,108-5). Dichloroacetate surrogate solution was prepared from dichloroacetic acid, potassium salt (Aldrich, Catalogue No. 34,808-2; 0.065 g/100 ml reagent water). An aqueous 1000 mg/l ferrous iron [Fe(II)]

solution was prepared using ferrous sulfate heptahydrate (Sigma, Catalogue 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 were verified using a second source quality control standard made with ACS reagent grade potassium bromate (Alfa, Catalogue No. 300487, Danvers, MA, USA) and also using 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 procedures outlined in the ICR Sampling Manual [17]. Dichloroacetic acid (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.

2.3. Instrumentation

A Dionex autosampler and load inject valve with a sample loop (225 μl for Method 317.0 and 750 μl for Method 324.0) 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 set at 0.5 (μS) full-scale. 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, potted 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

3.1. Initial development of Method 317.0

Any analytical method developed for drinking water should be applicable to all types of anticipated sample matrices, regardless of water source (surface or ground) or treatment process employed. The PCR addition to Method 300.1 was shown to provide 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]. This work also discussed the potential interference of chlorite on the absorbance detection of trace levels of bromate [15]. The presence of trace concentrations of bromate in non-ozonated water, (such as chlorine dioxide and/or chloramine disinfected water) was previously reported using conductivity detection, but not extensively studied [18]. Consequently, it became evident that the masking interference of chlorite prevented application of the method to chlorine dioxide disinfected waters. In order for Method 317.0 to be considered as a future compliance monitoring method, the method had to be applicable to all matrices and consequently, this deficiency had to be resolved [19].

3.1.1. Preferential removal of chlorite

The preliminary development of EPA Method 317.0 identified a potential problem associated with high levels of chlorite in finished waters from chlorine dioxide PWSs [15]. Since chlorite is more sensitive to oxidation and/or reduction than bromate,

it was speculated that chlorite could be preferentially removed from a matrix without adversely affecting trace levels of bromate. Various treatments, which included exposure to UV radiation, treatment with activated carbon, treatment with peroxide, purging with oxygen and the use of reducing agents such as metabisulfite or Fe(II) were assessed to determine their ability to preferentially remove chlorite. Treatment with ferrous iron was the only viable option [19].

3.1.2. Preferential removal of chlorite using ferrous iron [Fe(II)]

The use of ferrous iron under slightly acidic conditions to remove residual chlorite in drinking water is well documented [20–23]. Based on Eq. (1), the molar stoichiometry predicts that 3.3 mg of Fe(II) would be required to completely reduce 1.0 mg of ClO_2^- [20].

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

Elevated levels of iron in the IC flow-path are known to pose fouling problems with the AS9-HC column and the suppressor membrane [24]. It was established that the iron hydroxide formed during the reaction of ferrous iron with chlorite could be removed from solution using a 0.45μm particulate filter and any unreacted or excess ferrous iron is removed from solution by utilizing a solid-phase extraction (SPE) cartridge containing an anion-exchange resin in the hydrogen form, thereby preventing fouling of the IC system [19].

The MCL for chlorite was established at 1000 μg/l under Stage 1 of the D/DBP Rule. In samples from PWSs disinfected with chlorine dioxide, the chlorite level should rarely exceed 1000 μg/l since above this level the PWS would be out of compliance. It was decided that the final Method 317.0 protocols for removing chlorite would incorporate a slight excess of Fe(II) to ensure complete removal of up to 1200 μg/l chlorite [19].

The optimal conditions for chlorite removal involved treating a 10 ml aliquot of sample with 33 μl of sulfuric 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 the sample analyzed using Method 317.0 [19].

The final phase of this work was to ensure that treatment of the samples with Fe(II) could be incorporated into the analysis of large analysis batches utilizing Method 317.0. It was confirmed that the bromate in samples treated with Fe(II) was sufficiently stable to allow processing of the entire analysis batch and that the bromate concentrations in the processed samples were stable over a sufficient period of time to allow automated analysis of the entire analysis batch [19].

3.1.3. Analysis of PWS samples using Method 317.0

A total of 351 ICR samples (source, in-process and finished waters) covering a 3-month segment of the ICR were analyzed for inorganic DBPs and trace bromate concentrations utilizing Method 317.0. A total of 202 samples were from ozonation facilities that utilized ozone in combination with chloramine and/or chlorine dioxide, and a total of 149 samples were from non-ozonation facilities that used chlorine dioxide in combination with chloramine. Samples from the non-ozonation PWSs were fortified with chlorite, bromate, chlorate and bromide and the samples from ozonation PWSs were fortified with trace levels of bromate. All samples from the non-ozonation plants were analyzed a second time after treatment with Fe(II) to determine if trace concentrations of bromate were native in these matrices. The presence of chlorite in these matrices would have masked the trace concentrations of bromate during the original analysis. To complete this assessment, a Laboratory Fortified Matrix (LFM) was then prepared from each of these sample matrices, treated with Fe(II) and analyzed. These LFMs were prepared to establish the accuracy of bromate recovery following the chlorite removal process. The performance evaluation of Method 317.0 as an automated, potential future compliance monitoring method was conducted by analyzing the samples, in sequential analysis batches, with the IC system

Table 1
EPA Method 317.0 average LFM recoveries in ozonation plants

Fortification level (μg/l), number of replicates	Bromate (% recovery)
LFM at 0.5 μg/l ($n=4$)	115
LFM at 2.0 μg/l ($n=6$)	111
LFM at 5.0 μg/l ($n=8$)	110
Laboratory duplicates ($n=10$)	6.4% RPD

running continuously for 5 days at a time until the study was completed.

3.1.4. Ozonation PWSs

According to the quality control protocols relevant to duplicates and fortified matrices for Method 317.0, one laboratory duplicate (LD) and one LFM were included for every 10 field samples in each analysis batch. For the analysis of trace bromate levels by absorbance detection, the LFMs were fortified with 0.5, 2.0 and 5.0 μg/l bromate. The presence of bromate was detected in 114 of the 202 samples from the ozone PWSs and ranged from the MRL of 0.5–15.4 μg/l. The average recovery for the laboratory fortified matrices (see Table 1) were 115% (0.5 μg/l; $n=4$), 111% (2.0 μg/l; $n=6$) and 110% (5.0 μg/l; $n=8$). The relative percent differences (RPDs) for the laboratory duplicates were calculated using EPA protocols [12] and averaged 6.4% [(see Table 1) (0.6–24.8; $n=10$)]. Several other laboratory fortified matrix samples were influent samples that did not contain bromate. Acceptable method performance, in terms of precision and accuracy, was obtained for the sequential analysis of batches for trace bromate levels in samples from ozonation PWSs using Method 317.0 (operating continuously for 5 days).

3.1.5. Non-ozonation PWSs; initial analysis

Again, one LD and one LFM were included for every 10 field samples in each analysis batch. For the analysis of the inorganic DBPs by conductivity detection, the LFMs were prepared at either 25, 200 and 500 μg/l for each of the anions chlorite, bromate, bromide and chlorate. Chlorite was present in 74 of the 149 samples from the non-ozone PWSs with an average concentration of 370 μg/l (8–1600 μg/l). Although bromide is only of significance in influent waters, the values were reported for all sample matrices. Bromide was found in 125 of the 149 samples with an average concentration of 136 μg/l (7–1200 μg/l). The presence of chlorate was confirmed in 91 of the 149 samples with an average concentration of 114 μg/l (5–1100 μg/l). The average laboratory fortified matrix recoveries for the 25, 200 and 500 μg/l fortification levels for the three conductivity target analytes ranged from 83.1 to 97.9% (see Table 2). The RPDs for the laboratory duplicates for chlorite averaged 2.3% (0.1–5.4; $n=11$), for bromide averaged 7.3% (0.1–24.7; $n=14$) and for chlorate averaged 4.0% [(0.1–7.4; $n=11$) (see Table 2)]. Several other laboratory fortified matrix samples were influent samples that did not contain some of the target analytes. Acceptable method performance, in terms of precision and accuracy, was obtained for chlorite and chlorate levels in samples from non-ozonation PWSs using Method 317.0 when analyzing sequential analysis batches with the system operating continuously for 5 days.

3.1.6. Non-ozonation PWSs; second and third analysis

In this instance, since every sample was to be

Table 2
EPA Method 317.0 average LFM recoveries in non-ozonation plants

Fortification level (μg/l), number of replicates	Recovery%			
	Chlorite	Bromate	Bromide	Chlorate
25.0 μg/l ($n=5$)	84.1	97.4	97.9	97.4
200 μg/l ($n=5$)	85.4	95.9	94.0	96.3
500 μg/l ($n=4$)	83.1	91.0	85.3	93.3
Laboratory duplicates	2.3% RPD ($n=11$)		7.3% RPD ($n=14$)	4.0% RPD ($n=11$)

Table 3
EPA Method 317.0 average LFM recoveries in non-ozonation plants

Fortification level (μg/l), number of replicates	Bromate (% recovery)
LFM at 0.5 μg/l ($n=26$)	105
LFM at 2.0 μg/l ($n=24$)	101
LFM at 5.0 μg/l ($n=24$)	101

fortified, no duplicates were included in the analysis batch. Only the 74 finished drinking water samples that contained chlorite were examined. The unfortified and bromate fortified matrix samples (0.5, 2.0 and 5.0 μg/l bromate) were treated with Fe(II) and analyzed. The presence of native bromate that was masked by chlorite in the original analysis of the sample was detected in 5 of the 74 samples and ranged from 1.02 to 2.68 μg/l. One of the positive hits was from a PWS that listed chloramine, chlorine dioxide and ozone as potential disinfectants, four listed chloramine and chlorine dioxide as being used, and one listed chlorine dioxide as the only disinfectant. The spike recoveries for the 0.5 μg/l level averaged 105% (82.0–120; $n=26$); for the 2.0 μg/l level averaged 101% (89.0–108%; $n=24$) and for the 5.0 μg/l level averaged 101% [(78.6–108%; $n=24$) (see Table 3)]. Acceptable method performance, in terms of precision and accuracy, was obtained for trace bromate fortification levels in samples from non-ozonation PWSs using Method 317.0 when analyzing sequential analysis batches with the system operating continuously for 5 days.

3.2. Efforts to increase Method 317.0 sensitivity

In an effort to further increase the sensitivity of the PCR procedure, thus reducing the minimum reporting level (MRL), efforts were directed at establishing a faster, bromate specific method with the lowest possible MRL.

3.2.1. Incorporation of 1.0 ml sample loop

The initial efforts to increase the method sensitivity involved simply increasing the sample loop size from 225 to 1000 μl. Promising results in terms of instrument calibration and method detection limit (MDL) were obtained with the 1 ml loop. However, difficulties were encountered when some ICR samples were analyzed in this way. Overloading of the column (which was attributed to exceptionally high levels of other anionic species such chloride and sulfate) resulted in splitting of the bromate peak in these matrices (see Fig. 1). In some instances, the surrogate was also adversely affected by the presence of high levels of chloride and sulfate. Treating these samples with SPE cartridges (in the barium form to remove sulfate; in the silver form to remove chloride; and in the hydrogen form to remove silver) eliminated the overloading problems. However, the

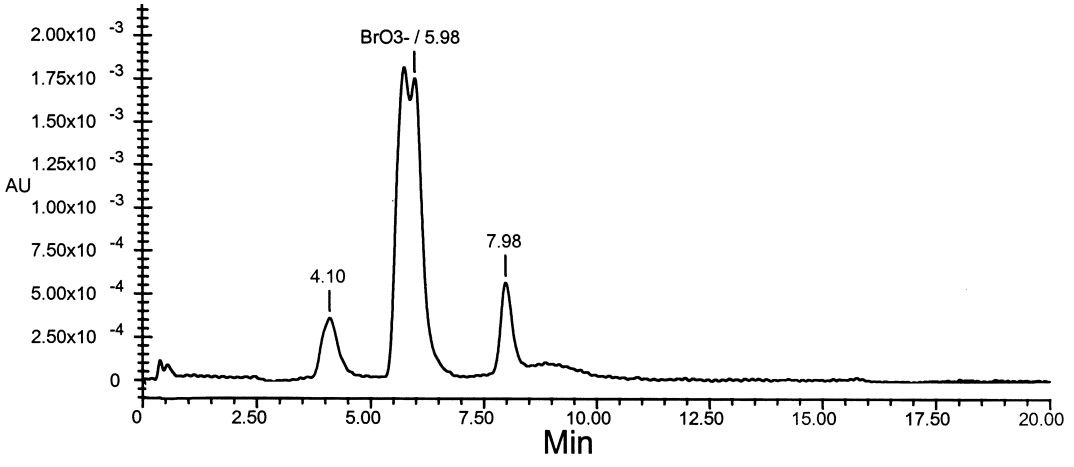

Fig. 1. Splitting of the bromate peak on absorbance detector due to column overloading.

use of sample clean-up cartridges contributes significant expense and time requirements to the analysis. Consequently, other alternatives were investigated to eliminate the need for sample pre-treatment.

3.2.2. Incorporation of alternative eluent and 750 μl sample loop

Increasing the eluent strength (12 m*M* carbonate; 5 m*M* hydrogencarbonate) resulted in sulfate eluting from the column in 15 min without drastically affecting resolution of the early eluting peaks and resulted in a 25% reduction in analysis time. As well, decreasing the sample loop size to 750 μl overcame the splitting of the bromate peak, which was attributed to column overloading.

Although this method was designed to be an ultra trace method specific for bromate using the PCR portion of Method 317.0, the conductivity detector was also incorporated to monitor the surrogate (DCA) in order to assess column performance on the conductivity detector for each analysis. The MDL was established using EPA protocols [25] and was determined by analyzing 8 replicates of 0.15 μg/l bromate spike in EDA stabilized reagent water. The calculated MDL was 0.042 μg/l (10.3% RSD). The MRL (defined as three times the MDL) was calculated to be 0.13 μg/l.

3.2.3. Analysis of PWS samples with proposed Method 324.0

A total of 234 ICR samples (first 2 months) that were previously analyzed using Method 317.0 (source, in-process and finished water) were analyzed for ultra trace bromate concentrations utilizing draft Method 324.0. A total of 133 samples were from ozonation PWSs that utilized ozone, alone or in combination with chloramine and/or chlorine dioxide and a total of 101 samples were from non-ozonation facilities that used chlorine dioxide alone or in combination with chloramine. The samples from the ozonation PWSs and the influent samples that did not contain chlorite from the non-ozonation plants were fortified with bromate (0.2, 2.0 and 5.0 μg/l) according to Method 317.0 quality control protocols. All finished water samples from the non-ozonation plants were analyzed a second time after treatment with Fe(II) to establish if trace concentrations of bromate were native in these matrices which would have been masked by the presence of chlorite during the original analysis. To complete this assessment, these samples were analyzed a third time after being fortified with low-levels of bromate (0.2, 2.0 and 5.0 μg/l) and treated with Fe(II) to establish the accuracy of the chlorite removal process. The performance evaluation of draft Method 324.0, in the automated mode, was assessed by analyzing the samples, in sequential analysis batches, with the system operating continuously for 5 days until the study was completed.

3.2.4. Ozonation municipalities and influent samples from non-ozonation municipalities

Following the quality control protocols specific to the LDs and LFMs for Method 317.0, one LD and one LFM were included for every 10 field samples in each analysis batch. The LFMs were fortified with 0.2, 2.0 and 5.0 μg/l bromate. The presence of bromate was detected in the same 79 PWS samples that gave positive results for bromate previously using Method 317.0. In this instance the bromate concentrations ranged from the MRL of 0.13 to 16.6 μg/l. A total of 12 positive hits for bromate, (>0.13 μg/l but <0.5 μg/l) were reported with draft Method 324.0 which were not reported using Method 317.0. Nine of the positive results were from PWSs listed as using ozone only, two were from PWSs listed as using chloramine and ozone and one from a PWS using chlorine dioxide disinfection. The average bromate concentration for the 79 samples reported using Method 317.0 was 3.30 μg/l and 3.35 μg/l using draft Method 324.0. Since the samples were analyzed using both methods, a Student's *t*-test was incorporated to determine the similarity of the methods. A *t*-value of 0.925 indicated that the two methods provided similar results [(critical *t*-value is 1.99 at a 95% confidence level for $n=79$) (see Fig. 2)]. The average laboratory fortified matrix recoveries were 103% (0.2 μg/l; $n=3$), 115% (2.0 μg/l; $n=8$) and 112% [(5.0 μg/l; $n=6$) (see Table 4)]. The RPDs for the laboratory duplicates averaged 4.3% [(0–22.3; $n=17$) (see Table 4)]. The precision of both methods, defined in terms of relative standard deviation (RSD) of the bromate fortified samples ranged from 4.9 to 12.3% RSD (see Table 5). Acceptable method performance, in terms of precision and accuracy, was obtained for the analysis of

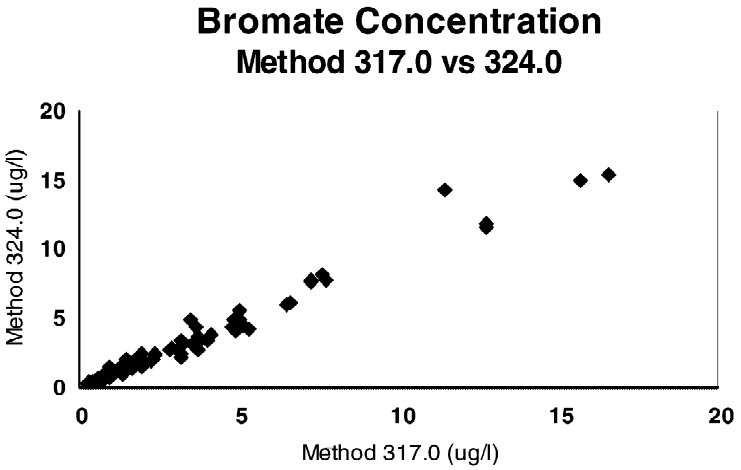

Fig. 2. Bromate concentrations with Method 324.0 vs. 317.0.

Table 4
EPA Method 324.0 average LFM recoveries in ozonation plants

Fortification level (μg/l), number of replicates	Bromate (% recovery)
LFM at 0.2 μg/l ($n=3$)	103
LFM at 2.0 μg/l ($n=8$)	115
LFM at 5.0 μg/l ($n=6$)	112
Laboratory duplicates ($n=17$)	4.3% RPD

Table 5
Precision of Method 317.0 and 324.0 (bromate LFM recoveries)

Fortification level (μg/l) number of replicates	RSD (%)	
	Method 317.0	Method 324.0
LFM at 0.5 μg/l ($n=26$)	9.3	
LFM at 0.2 μg/l ($n=18$)		12.3
LFM at 2.0 μg/l ($n=24$)	4.9	
LFM at 2.0 μg/l ($n=17$)		11.9
LFM at 5.0 μg/l ($n=24$)	7.1	
LFM at 5.0 μg/l ($n=16$)		10.6

Table 6
EPA Method 324.0 average LFM recoveries in non-ozonation plants

Fortification level (μg/l), number of replicates	Bromate (% recovery)
LFM at 0.2 μg/l ($n=17$)	110
LFM at 2.0 μg/l ($n=16$)	97.2
LFM at 5.0 μg/l ($n=16$)	98.2

trace bromate levels in samples from ozonation plants using Method 324.0. Sequential analysis batches of samples from the ozonation PWSs and the influent samples from the non-ozonation PWSs were analyzed with the IC system operating continuously for 5 days.

3.2.5. Non-ozonation PWSs; second and third analysis

In this instance, since every sample was to be fortified, no duplicates were included in the analysis batch. Only the finished water samples that were shown to contain chlorite when previously analyzed using Method 317.0 were utilized. The unfortified and bromate fortified matrix samples (0.2, 2.0 and 5.0 μg/l bromate) were treated with Fe(II) and analyzed in a similar manner. The presence of native bromate that was masked by chlorite in the original analysis of the sample was detected in 5 of the 49 samples and ranged form 0.16 to 0.24 μg/l. Three of the positive hits were from PWSs that listed chloramine, chlorine dioxide and ozone as potential disinfectants, one listed chloramine and chlorine dioxide as being used, and the other listed chlorine dioxide exclusively. The LFM recoveries for the 0.2 μg/l level averaged 110% (85–130; $n=17$); for the 2.0 μg/l level averaged 97.2% (75.5–116%; $n=16$), and for the 5.0 μg/l level averaged 98.2% [(73–114%; ($n=16$) (see Table 6)]. Acceptable method performance, in terms of precision and accuracy, was

obtained for the analysis of trace bromate levels in non-ozonation PWSs using Method 324.0. Sequential analysis batches of samples from the non-ozonation PWSs were analyzed with the IC system operating continuously for 5 days.

4. Conclusions

EPA Method 317.0 provides a rugged, simple, direct injection method for the analysis of the inorganic DBPs, chlorite, chlorate and trace bromate, as well as bromide which is the precursor to bromate formation. If the appropriate chlorite removal protocols are utilized, Method 317.0 can be successfully employed to analyze trace bromate in PWS samples disinfected with any combination of disinfectant. The method exhibits improved bromate sensitivity to Method 300.1 that was promulgated as the compliance monitoring method for bromate under Stage 1 of the D/DBP Rule.

The simplicity and sensitivity of EPA Method 317.0 offers an excellent potential future compliance monitoring method with ease of operation. As well, the method has no difficulty meeting the quality assurance/quality control criteria while operating in an automated manner for several days.

Confirmation of the presence of bromate in non-ozonated PWSs, disinfected with chlorine dioxide/chloramine, adds credibility to the statement in the Federal Register [8] 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.

A faster, bromate specific method (324.0) has been developed for the analysis of ultra trace bromate concentrations in drinking waters. Method 324.0 provides comparable results to Method 317.0 with increased sensitivity for bromate concentrations in PWSs, which utilized all combination of disinfectants. Method 324.0 continually met all of the quality assurance/quality control criteria while operating in a fully automated manner for several days.

5. Nomenclature

ACI	Advanced Computer Interface
ACS	American Chemical Society
D/DBP Rule	Disinfectants/Disinfection By-Products Rule
DBPs	Disinfection by-products
DCA	Dichloroacetate
EDA	Ethylenediamine
EPA	Environmental Protection Agency
ICR	Information Collection Rule
LD	Laboratory Duplicate
LFM	Laboratory Fortified Matrix
MCL	Maximum contaminant level
MCLG	Maximum contaminant level goal
MDL	Method detection limit
MRL	Minimum reporting level
NERL	National Exposure Research Laboratory
ODA	Orthodianisidine
PC	Personal computer
PCR	Postcolumn reagent
PE	Performance Evaluation
PWS/s	Public water system/s
RPD/s	Relative Percent Difference/s
RSD	Relative Standard Deviation
SAC	Selective Anion Concentration
TSC	EPA's Technical Support Center

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