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Analysis of 500-ng/l levels of bromate in drinking water by direct-injection suppressed ion chromatography coupled with a single, pneumatically delivered post-column reagent

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Abstract

In July 1997, the US Environmental Protection Agency (EPA) began sampling and analyzing drinking water matrices from US municipalities serving populations greater than 100 000 for low-level bromate (>0.20 μg/l) in support of the Information Collection Rule (ICR) using the selective anion concentration (SAC) method. In September 1997, EPA published Method 300.1 which lowered the Method 300.0 bromate method detection limit (MDL) from 20.0 to 1.4 μg/l. This paper describes the research conducted at the EPA's Technical Support Center laboratory investigating a single post-column reagent, *o*-dianisidine (ODA), which has been successfully coupled to EPA Method 300.1 to extend the MDL for bromate. Initial studies indicate that this method offers a MDL which approaches the EPA's SAC method with the added benefit of increased specificity, shortened analysis time and reduced sample preparation. The method provides excellent ruggedness and acceptable precision and accuracy with a bromate MDL in reagent water of 0.1 μg/l, and a method reporting limit of 0.50 μg/l.

Keywords: Water analysis; Derivatization, LC; Bromate; Inorganic anions; Dianisidine

1. Introduction

In the global environment, human exposure to the three major inorganic oxyhalide disinfection by-products (DBPs) occurs predominantly as a consequence of disinfecting drinking water. Chlorite (ClO_2^-) and chlorate (ClO_3^-) are the DBPs formed when chlorine dioxide (ClO_2) is used to disinfect drinking water [1,2]. The presence of chlorate in hypochlorite treated water has also been reported [3,4]. Conversely, bromate (BrO_3^-) is the DBP formed when source waters containing bromide are ozonated [5,6]. Of lesser significance is the suggestion that iodate (IO_3^-) may result if source waters containing iodide are ozonated [7].

Bromate has been identified as an animal carcinogen [8]. It has also been classified as a group 2B, probable human carcinogen by the International Agency for Research on Cancer [7,9]. Health effects research indicates it to be a suspected human carcinogen which exhibits 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 [10]. Based on its potential toxicity, the US Environmental Protection Agency (EPA) has proposed setting the maximum contaminant level (MCL) for bromate in drinking water at 10 μg/l and requested comments on setting the maximum contaminant level goal

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(MCLG) for bromate to zero [9,10]. The MCL is scheduled for promulgation under Stage 1 of the Disinfectants/Disinfection by-products (D/DBP) Rule at 10 μg/l in November 1998 [11]. Stage 2 of the D/DBP Rule may lower the bromate MCL further. Among a number of considerations, limitations in acceptable compliance monitoring methods at the time played a significant role in establishing the proposed Stage 1 drinking water MCL for bromate at 10 μg/l. Global regulatory agencies are continually striving to monitor bromate levels in drinking and bottled waters in order to establish appropriate regulatory limits. Unquestionably, the analysis of bromate in these matrices will continue to receive tellurian attention, well into the next millennium.

Advances in analytical instrumentation, detection systems and separation techniques have, in many instances, provided analytical chemists the tools required to continually lower method detection limits. Consequently, several methods have been proposed for the low-level analysis of bromate in drinking and bottled waters. The majority of these methods utilize ion chromatography (IC) to separate bromate, which is then quantified using a variety of detection methods. The methods include electrospray IC coupled with mass spectrometric detection [7]; IC coupled with inductively coupled plasma mass spectrometric detection [9]; IC with pre-concentration and conductivity detection [12–14]; IC coupled with a variety of post-column reagents (PCRs) [15–21]; high-performance liquid chromatography (HPLC) coupled with a PCR [22]; and gas chromatography–mass spectrometry (GC–MS) [23]. In general, these methods require sophisticated analytical instruments and techniques, expert analysts and complex sample pre-treatment to eliminate potential interferences.

The sampling and analysis phase of the Information Collection Rule (ICR) was initiated in July 1997 for a period of 18 months. The ICR requires public water systems (PWSs) serving 100 000 or more persons to collect treatment plant operational data as well as monitor source water and finished drinking water for general water quality parameters, DBPs, surrogates for DBPs and DBP precursors. The selective anion concentration (SAC) method [24] was capable of achieving an acceptable method detection limit (MDL) to support the ICR method reporting limit (MRL) criteria of 0.2 μg/l for low-level bromate analysis [25]. The SAC method was developed to meet EPA requirements for additional data on occurrence, as low as possible, below the proposed MCL. The inherent difficulties associated with the method led EPA to decide to support the analysis of ICR samples in its own laboratory. Our experience with the method has shown that the SAC method requires extensive and expensive sample pretreatment to significantly reduce chloride and sulfate. It also requires expert analysts and involves lengthy analysis times. The method is also heavily dependent upon external suppliers quality assurance programs to ensure the quality of their pretreatment cartridges. Accordingly, a more simplistic method was required for the proposed Stage 1 compliance monitoring.

In September 1997, EPA Method 300.1 was published as an update to Method 300.0. Method 300.1 reduced the bromate MDL from 20.0 to 1.4 μg/l using direct injection of the sample [26]. This manuscript presents a unique method developed at the EPA Technical Support Center (TSC) laboratory that couples a post-column reagent, *o*-dianisidine (ODA), directly to EPA Method 300.1. This configuration adds low-level bromate capability to Method 300.1 and provides a rugged, direct injection analysis for all DBPs in drinking water. The PCR addition to Method 300.1 approaches the MDL and MRL achieved with the SAC method while offering the additional advantage of providing bromate formation potential by quantifying bromide concentrations for municipalities, which disinfect with ozone. ODA [22] was chosen as the post-column reagent for reasons of simplicity. It was speculated that pneumatic delivery of a single post-column reagent would contribute minimal noise to the system thereby providing a superior MDL and MRL.

2. Experimental

2.1. Reagents

The eluent, standards, stabilization solution, surrogate and all dilutions were prepared using 18 MΩ

water (Barnstead, PN 163437, Debque, IA, USA. American Chemical Society (ACS) primary standard 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 stable for one month when stored at room temperature and normal illumination [22]. Ethylenediamine (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).

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 was verified against a second source quality control standard using ACS reagent grade potassium bromate (Alfa, catalog No. 300 487, 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). According to the ICR sampling manual, all samples were stabilized at collection with EDA. 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 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 AG9HC guard and AS9HC analytical column for separation. Following electrolytic suppression, (300 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 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. Preliminary studies

Prior to initiating actual IC method development work, preliminary studies were conducted to determine the feasibility of using ODA as a post-column reagent on Method 300.1. Since Method 300.1 is a suppressed IC method, any bromate exiting the suppressor would be in a suppressed, carbonic acid media rather than in a pH 6.4 tetrabutylammonium hydroxide–acetic acid mobile phase used in the HPLC method [22]. It was confirmed visually that the ODA reagent [22] would react with an aqueous bromate standard by simply combining 1 ml of a 2.5 mg/l bromate solution and 0.5 ml of the ODA reagent [22] and heating the mixture for 60 seconds at 60°C in a block heater. The next step was to determine if similar results could be obtained

using pumps, without incorporating any columns, to deliver the reagent water and the ODA reagent to a mixing T. A 48-in. glass bead reaction coil immersed in a 60°C water bath was connected to the third port of the mixing T (1 in.=2.54 cm). The effluent from the reaction coil entered an absorbance detector connected to a strip chart recorder. Following injection of 250 μl of the 2.5 mg/l aqueous bromate standard, a large peak was evident on the strip chart recorder. After ensuring that the back pressure generated by connecting the mixing T, reaction coil and absorbance detector to an Anion Micro Membrane Suppressor (AMMS) would not damage the suppressor (i.e., <130 p.s.i.; 1 p.s.i.=6894.76 Pa), it was a simple task to determine that a similar peak from the absorbance detector could be obtained following separation of the bromate on an AS9HC column and chemical suppression of the eluent. A considerable amount of baseline noise, contributed by the pumps used to deliver the eluent and PCR, was observed with this configuration. However, this was significantly reduced when a pneumatic delivery system was used to deliver the ODA. The initial studies indicated that a MDL and MRL approaching the SAC method could be attainable with the PCR addition to Method 300.1. Consequently, state-of-the-art post-column equipment was acquired to proceed with further method development work. Once the optimal conditions were established for the post-column reaction, the instrument stability, method precision and MDL/MRL studies were evaluated on both a DX-300 with external controlled electrolytic suppression and a DX-500 with normal electrolytic suppression (300 mA; external water source mode). Both the DX-300 and DX-500 utilized microbore pumps.

3.2. Optimization of post-column reaction conditions

The oxidation reactions, products and kinetics of 3,3′-dimethoxybenzidene (ODA, *o*-dianisidine) with various oxidizing agents, including potassium bromate in acidic solutions have been documented [27]. Since this application involved ODA as a PCR addition to a suppressed IC method and no literature references were available regarding optimization of these parameters, our initial studies involved examination of the post-column reaction conditions.

3.2.1. Optimization of wavelength for the reaction product

The first step involved a UV–visible scan of the reaction products formed by reacting 1.0 ml of 200 and 2500 μg/l aqueous bromate standards with 0.5 ml of the ODA reagent at 60°C for 60 seconds. The solutions were scanned from 350 to 650 nm to determine the wavelength of maximum absorption (λ_{max}). In this application, the λ_{max} was 450 nm, which agreed well with the literature value of 447 nm [27].

3.2.2. Optimization of reaction temperature

The effect of temperature on the reaction of acidic bromate with ODA was evaluated by examining the peak obtained from the absorbance detector when a 5.0 μg/l bromate aqueous standard was injected and the reaction coil was heated to 40, 60 and 80°C (settings available on the PCH-2 column heater). In this work, the optimal reaction temperature was determined to be 60°C (peak area at 60°C was 3–5 times the area at 40 and 80°C).

3.2.3. Optimization of PCR addition Method 300.1

The reaction of acidic bromate with ODA has been suggested to be first order in terms of ODA and bromate and second order in terms of H^+ concentration [27]. An eluent flow-rate of 1.3 ml/min was chosen to closely parallel that of Method 300.1. Using a 2.0 μg/l bromate spike in reagent water, the flow-rate of the PCR was varied from 0.4 to 1.0 ml/min with 0.7 ml/min providing optimal results. After establishing the optimal reaction temperature and wavelength, the reaction conditions for the post-column addition of the ODA reagent to Method 300.1 were further optimized by altering the concentration of one of the post-column constituents while the other two remained constant.

3.2.4. Potassium bromide concentration

Bromide (Br^-) has been reported to play a significant role in the mechanism of oxidation reactions involving bromate in acidic solutions [27,28]. As well, the addition of bromide has reportedly been found to increase the reaction velocity [29]. To

optimize the bromide concentration in this application, the bromide concentration (as KBr) was varied from 0.5 to 7.5 g of KBr per 500 ml of reagent while the ODA and HNO_3 concentrations were held constant at 250 mg and 32 ml, respectively. The optimal bromide concentration was determined to be 2.5 g/500 ml (see Fig. 1).

3.2.5. Nitric acid concentration

Since the H^+ concentration has been reported to be second order in the reaction between ODA and bromate in acidic medium [27], the nitric acid concentration was varied from 8.0 to 50.0 ml/500 ml of reagent, while the ODA and KBr concentrations were held constant at 250 mg and 2.5 g, respectively. The optimal nitric acid concentration was determined to be 40.0 ml/500 ml (see Fig. 2).

3.2.6. ODA concentration

The ODA concentration has been suggested to follow first-order kinetics [27] and consequently was varied from 80 to 750 mg/500 ml of reagent while the HNO_3 and KBr concentrations were held constant at 32 ml and 2.5 g, respectively. The optimal ODA concentration was determined to be 250 mg/500 ml (see Fig. 3).

3.2.7. Software-based signal filtering (smoothing)

The final stage of method optimization included incorporating software filtering of the absorbance signal to improve the precision of peak measurements, minimize non-random noise and improve peak appearance [30,31]. Calibration data were evaluated with Olympic and Savitzky–Golay smoothing routines, using the Peaknet software, in both peak height and peak area modes. Since peak area is not significantly affected by the choice of smoothing parameters [30], Olympic smoothing (25 points, 5 s with 1 iteration) was chosen using peak area for quantitation.

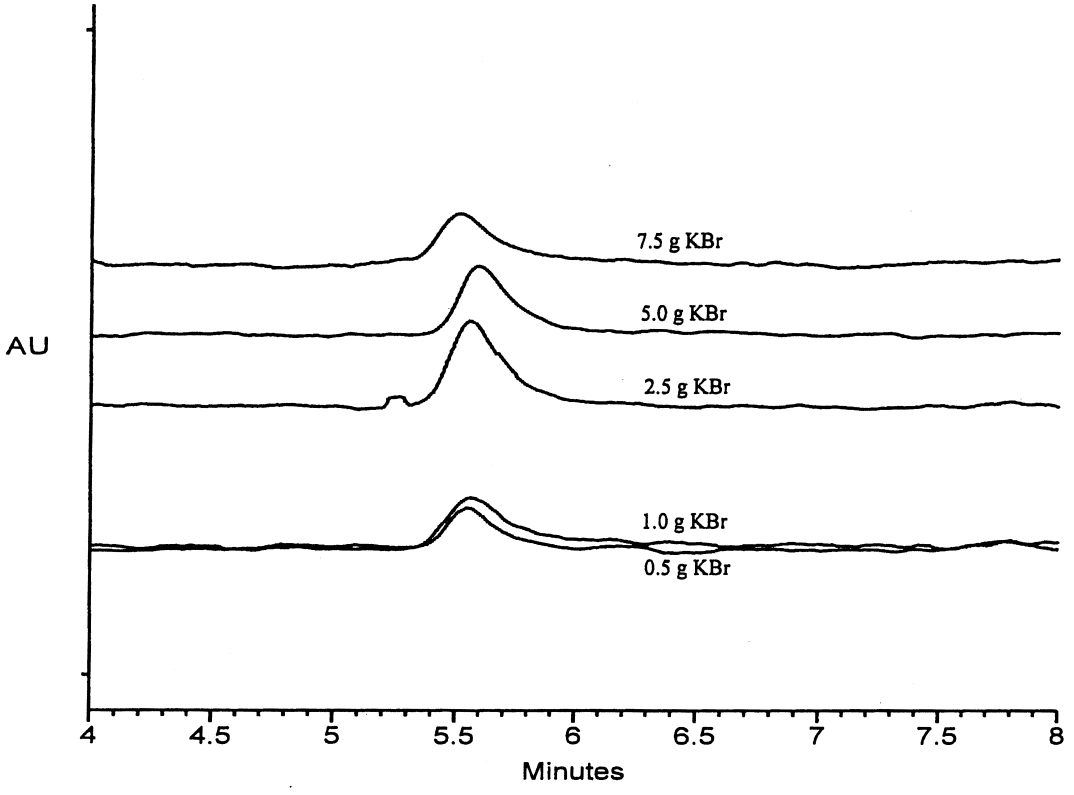

Fig. 1. Optimization of potassium bromide concentration.

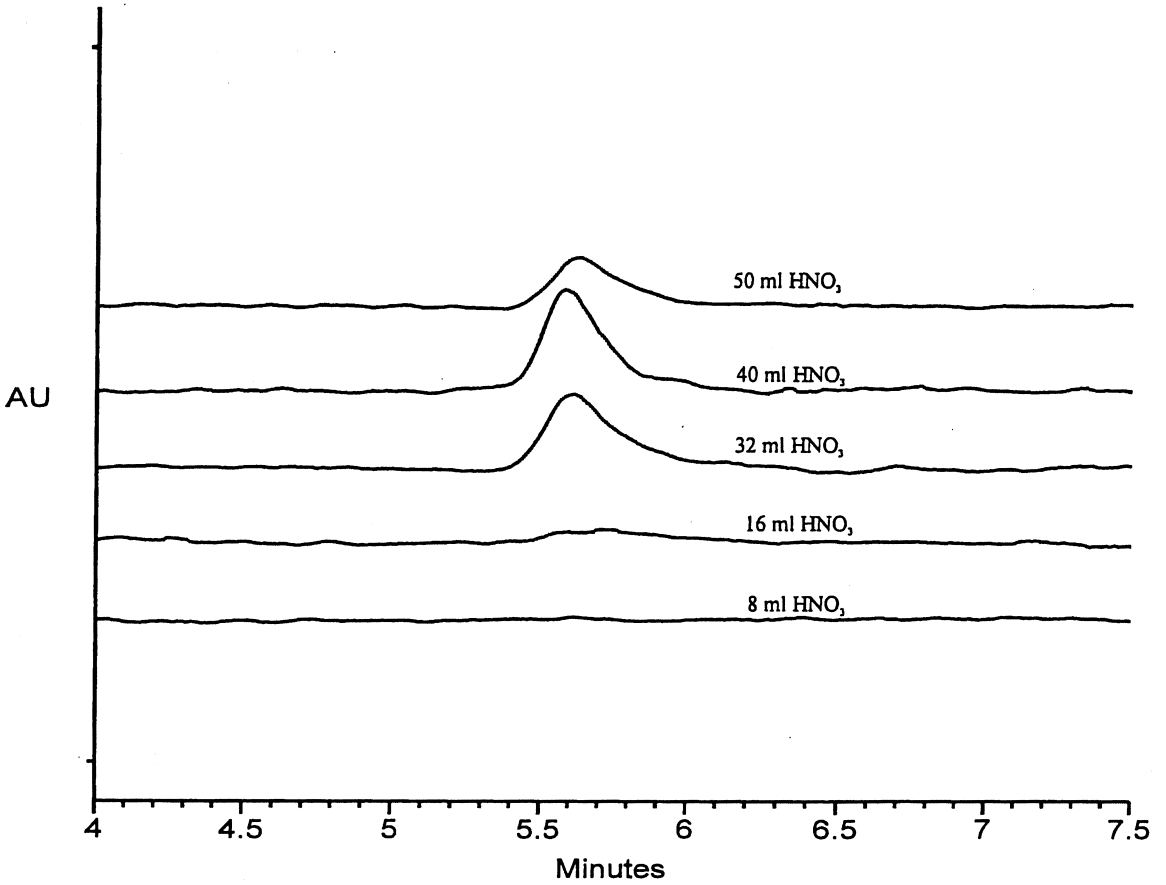

Fig. 2. Optimization of nitric acid concentration.

3.3. Calibration of the PCR addition to Method 300.1

The precision and accuracy data for the conductivity detection of the Method 300.1 analytes (chlorite, bromate, bromide and chlorate) have been published previously [26]. Consequently, during this work, only the surrogate (DCA) was monitored on the conductivity detector along with monitoring the PCR absorbance values for bromate. In any event, only the last three standards used to calibrate the PCR addition to Method 300.1 (0.5, 1.0, 2.0, 5.0, 10.0, 15.0 μg/l) were above the Method 300.1 MRL for bromate by conductivity detection. Regression analysis of the peak area calibration data using a quadratic fit ($y=ax^2+bx+c$) provided correlation coefficients (r^2) of 0.998 or better. Peak area precision for the surrogate by conductivity detection of less than 5% relative standard deviation (RSD) was observed in all instances

3.4. Instrument stability

The instrument stability for the PCR addition to Method 300.1 was evaluated over a 24-h period by successively analyzing eight replicates, from five individual vials which contained 0.5, 1.0, 2.0, 5.0 and 10.0 μg/l bromate spikes in Cincinnati tap water (a chlorinated surface water). Excellent instrument stability over 24 h, expressed as % RSD, was observed for all bromate levels on both the DX-300 and DX-500 (Table 1). With the DX-300 the bromate

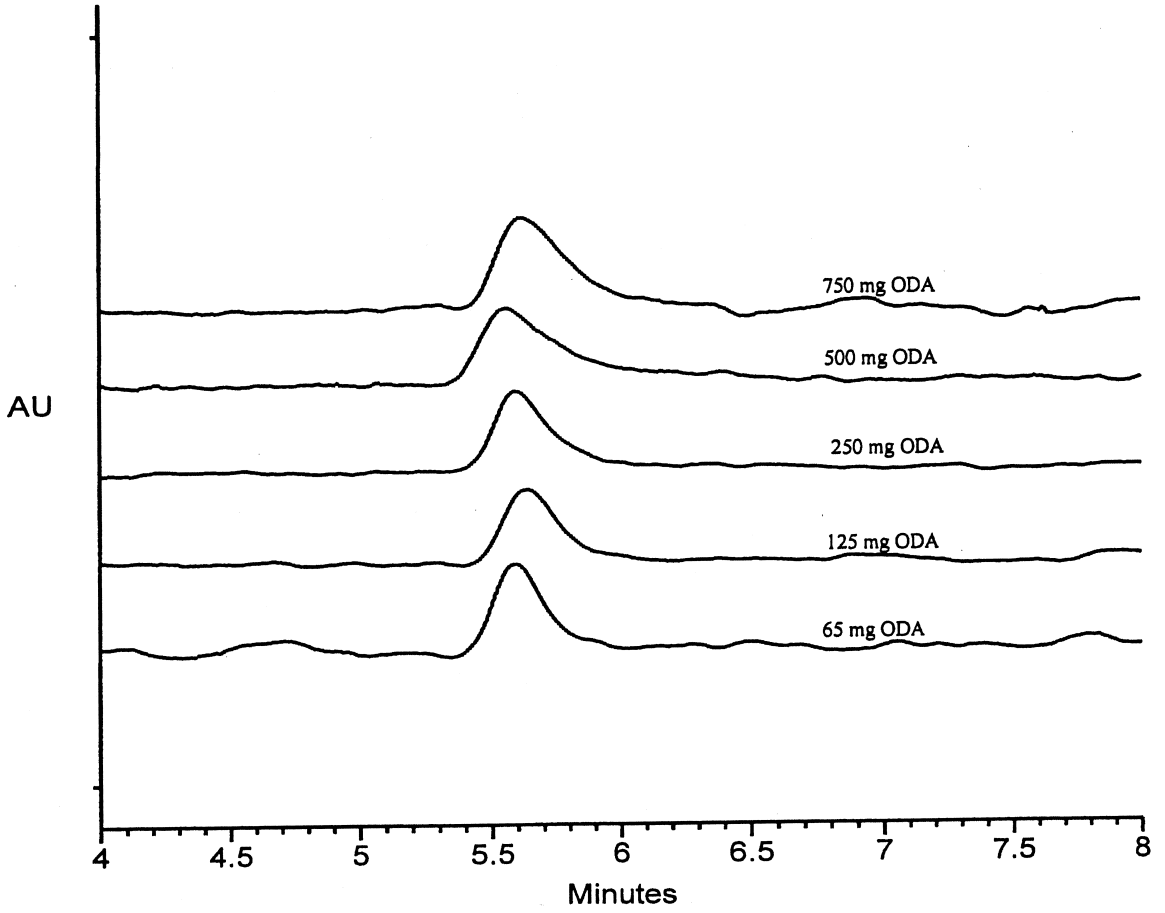

Fig. 3. Optimization of ODA concentration.

Table 1
PCR addition to Method 300.1 instrument stability

	Bromate spikes in Cincinnati tap water (μg/l)				
	0.5	1.0	2.0	5.0	10.0
DX-300 Bromate RSD (%, n=8)	10.8	10.2	8.4	4.0	2.7[a]
DX-300 Surrogate RSD (%, n=8)	2.4	1.9	1.7	1.2	1.4
DX-500 Bromate RSD (%, n=8)	5.0	5.1	4.3	3.4	3.5
DX-500 Surrogate RSD (%, n=8)	1.1	0.9	0.9	0.9	0.9

[a] n was actually 7 since one outlier was rejected using Dixon's Outlier test [32].

precision ranged from 2.7–10.8% RSD and the surrogate, determined via the conductivity detector, ranged from 1.4–2.4% RSD while on the DX-500 the bromate precision ranged from 3.4–5.1% RSD and the surrogate from 0.9–1.1% RSD.

3.5. Method precision

The method precision for the PCR addition to Method 300.1 was evaluated over a 22-h period by successively analyzing seven replicates containing 0.5, 1.0, 2.0, 5.0, 10.0 and 15.0 μg/l bromate spikes in reagent water with the DX-500 and seven replicates containing 0.5, 2.0 and 10.0 μg/l with the DX-300. Acceptable precision (Table 2), expressed as % RSD, was obtained for all bromate levels. On the DX-300, the bromate precision ranged from 5.2–7.3% RSD and the surrogate ranged from 1.7–2.4% RSD, while on the DX-500, the bromate precision ranged from 1.6–10.8% RSD and the surrogate from 2.0–4.9% RSD.

3.6. Reagent water method detection and method reporting limit (MDL and MRL)

The MDL and MRL for the PCR addition to method 300.1 were determined according to EPA protocols [33]. The calculated MDL for bromate in reagent water using the PCR addition to Method 300.1 was determined by analyzing a total of eight replicates of a 0.5 μg/l bromate spike in reagent water on three successive days. Due to time constraints, the DX-300 MDL was determined using seven replicates on a single day. The MRL is defined as either 3-times the MDL or a signal-to-noise ratio of 5:1; which ever is greater. The MDL was calculated to be 0.12 μg/l for the DX-500 ($n=8$) and 0.13 μg/l for the DX-300 ($n=7$). The MRL, estimated at a signal-to-noise ratio of 5:1; for both the DX-300 and DX-500 was established at 0.5 μg/l.

3.7. Comparison of Method 300.1 MDLs without and with PCR addition

The PCR addition to Method 300.1 provided acceptable instrument stability (for overnight operation), method precision and a bromate MRL of 0.5 μg/l which was similar to the SAC method and would closely parallel the ICR criteria for low-level bromate analysis. It was then necessary to confirm that the PCR addition to Method 300.1 did not alter the conductivity detection of the Method 300.1 analytes (chlorite, bromate, bromide and chlorate). The DX-500 was calibrated in the normal manner, without the PCR addition, using mixed chlorite, bromate, bromide and chlorate standards. The MDLs for the four Method 300.1 analytes were then determined by analyzing eight replicates of an aqueous mixed standard containing 2.0 μg/l chlorite, bromate, bromide and chlorate. Eight replicates were then analyzed with the PCR on-line. The addition of the PCR to Method 300.1 did not alter Method 300.1 MDLs (Table 3), and they were similar to those originally reported using 2 mm columns [26].

3.8. Method accuracy (spike recovery)

The accuracy of the PCR addition to Method 300.1 was assessed by determining the bromate spike recoveries in 20 ICR samples. Influent, in process and finished waters from a variety of treatment facilities were analyzed on the DX-300. The disinfection treatments included municipalities using

Table 2
PCR addition to Method 300.1 method precision

	Bromate spiking level in reagent water (μg/l)					
	0.5	1.0	2.0	5.0	10.0	15.0
DX-300 Bromate RSD (%, $n=7$)	5.2		6.1		7.3	
DX-300 Surrogate RSD (%, $n=7$)	1.8		2.4		1.7	
DX-500 Bromate RSD (%, $n=7$)	10.8	6.1	2.0	1.8	2.9	1.6
DX-500 Surrogate RSD (%, $n=7$)	4.9	2.1	2.9	2.0	3.3	3.0

Table 3
Method 300.1 MDLs without and with PCR addition

Method/spike level (No. of replicates)	ClO_2^- (μg/l)	BrO_3^- (μg/l)	Br^- (μg/l)	ClO_3^- (μg/l)
300.1 MDL fortified at 2.0 μg/l (n=8)	0.45	0.98	0.54	0.92
300.1+PCR MDL fortified at 2.0 μg/l (n=8)	0.89	0.71	0.69	0.62
300.1 reported MDL [26]	0.89	1.44	1.44	1.31

chlorine dioxide, ozone and combinations of the two (including the use of chloramine). The native bromate levels ranged from <0.5 to 12.6 μg/l. The samples were spiked with bromate at 0.5, 2.0 and 5.0 μg/l and the spike recoveries ranged from 76 to 113%.

3.8.1. Method accuracy (comparison to SAC results)

The accuracy of the PCR addition to Method 300.1 was also evaluated by comparing the bromate concentration in ICR samples which had already been analyzed using the SAC method. Prior to initiating this final comparative study, the SAC calibration standards and quality control second source (QCSS) standard were analyzed using the PCR method to assess the presence of any bias in instrument calibration. The same calibration standards were not used to calibrate both instruments (SAC and PCR addition to Method 300.1) and consequently the cross comparison of instrument calibration revealed approximately a 12% difference in the SAC and PCR addition to Method 300.1 calibrations. Accordingly, a 12% bias (the SAC being consistently lower than the PCR) in comparative results was anticipated resulting from the variation in calibration standards between the two methods.

Influent, in process and finished waters from a variety treatment facilities (for 20 different ICR samples) were analyzed using the DX-500. The disinfection treatments included municipalities using chlorine dioxide, ozone and combinations of the two (including the use of chloramine). The bromate concentrations by SAC averaged 4.9 μg/l and ranged from <0.2 to 11.10 μg/l while the PCR average was 5.1 μg/l and ranged from <0.5 to 11.29 μg/l. Excellent agreement between the two methods was obtained for the 20 samples (see Table 4).

3.9. Identification of potential chlorite interference

Chlorite (ClO_2^-) has also been reported to react with ODA [22]. The bromate spike recovery data for chlorine dioxide treated municipal waters identified the potential for a chlorite interference with the PCR method. Although acceptable recoveries of 86% and 91% were obtained for 0.5 and 5.0 μg/l bromate spikes in influent water samples from municipalities using chlorine dioxide, a 2.0 μg/l bromate spike level in finished municipal water treated with chlorine dioxide appeared as a shoulder on the chlorite peak which elutes prior to the bromate peak (see Fig. 4). In these samples, resolution of the bromate peak on the absorbance detector appeared to be dependent upon the chlorite concentration. For instance, chlorite levels >200 μg/l were found to affect the quantita-

Table 4
PCR addition to Method 300.1 method accuracy (DX-500)

Sample No.	Municipality	Treatment[a]	Bromate (μg/l)	
			SAC	PCR
1	A	O, CA	<0.2	<0.5
2	A	O, CA	0.43	0.31
3	A	O, CA	1.35	1.14
4	B	CA, CD	<0.2	<0.5
5	B	CA, CD	<0.2	<0.5
6	C	O, CA	4.05	4.53
7	C	O, CA	4.24	4.12
8	C	O, CA	4.14	4.39
9	D	O	3.17	3.55
10	D	O	11.10	11.29
11	D	O	7.98	8.29
12	E	O	<0.2	<0.5
13	E	O	<0.2	<0.5
14	F	O	<0.2	<0.5
15	F	O	5.09	5.11
16	F	O	9.78	10.04
17	G	O, CA	<0.2	<0.5
18	G	O, CA	2.55	2.82
19	H	CD	<0.2	<0.5
20	H	CD	<0.2	<0.5

[a] CA=Chloramine; CD=chlorine dioxide; O=ozone.

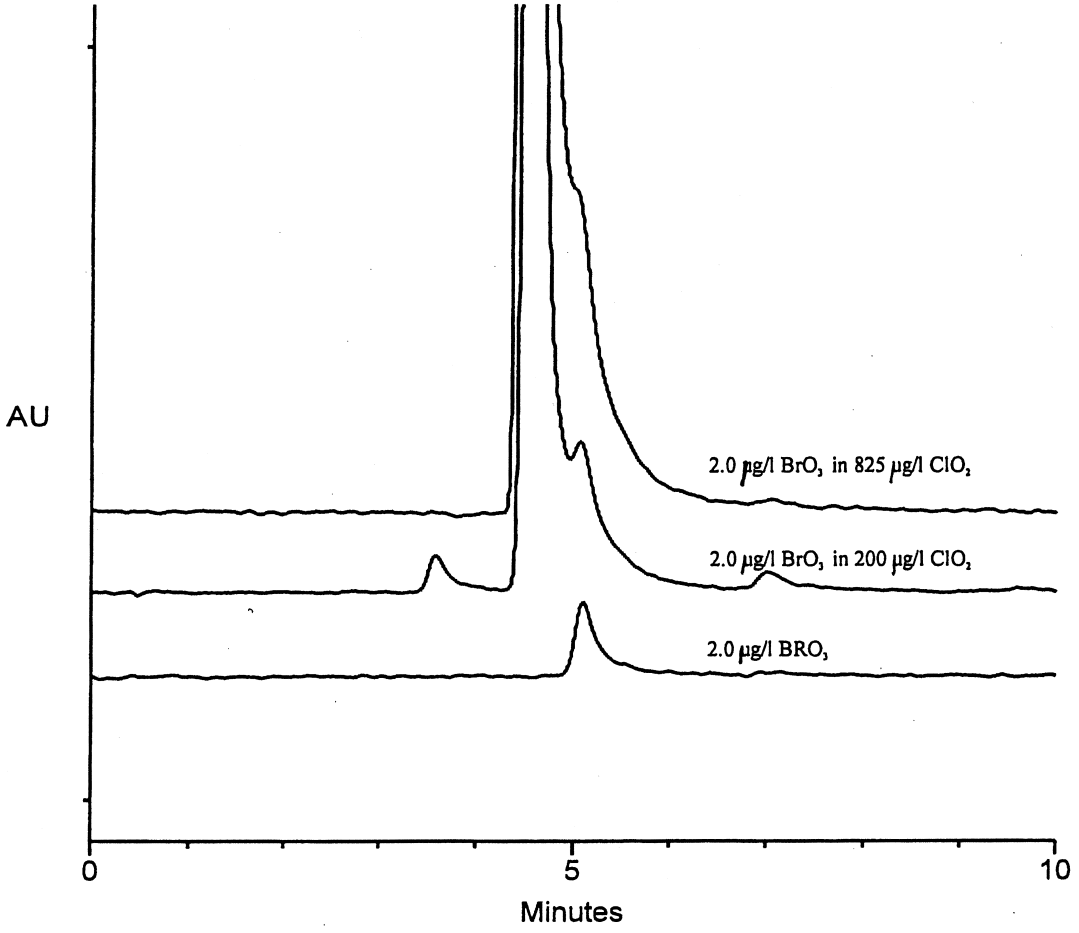

Fig. 4. Potential chlorite interference with the PCR addition to Method 300.1.

tion of bromate at the 2 μg/l concentration. The importance of the chlorite interference with the PCR method is currently being investigated. It appears that only when chlorine dioxide is used in conjunction with ozone will the interference be of significance. Studies to remove this chlorite interference without adversely affecting low-level bromate are currently in progress.

4. Conclusions

The PCR addition to EPA Method 300.1 offers a relatively simple, very rugged, direct injection analysis capable of measuring low-level bromate (>0.5 μg/l). The PCR method is an attractive alternative to the more complex SAC method, has a MDL of 0.1 μg/l, a MRL of 0.5 μg/l and gives acceptable precision and accuracy. It provides low-level bromate results (>0.5 μg/l) comparable to the SAC method for all ICR samples analyzed from municipalities using ozone as the disinfectant. As well, bromate formation potential (bromide levels) for these plants would also be available if untreated source waters were analyzed. In addition, the other DBP levels (chlorite and chlorate) could be obtained simultaneously using the PCR addition to Method 300.1.

With the PCR addition to Method 300.1, high levels of chlorite, such as those observed in municipal water supplies treated with chlorine dioxide, can interfere with the analysis of bromate at low-levels.

An in-depth, three-month comparative study of PCR addition to Method 300.1 and the SAC method using actual ICR samples has been initiated. The suitability of this method to serve a role in future EPA compliance monitoring for low-level bromate is also currently being evaluated. Additionally, alternative means of lowering the MDL for the PCR addition to Method 300.1 and the applicability of the method for the analysis of bottled waters and are also being evaluated.

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