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US Environmental Protection Agency Method 326.0, a new method for monitoring inorganic oxyhalides and optimization of the postcolumn derivatization for the selective determination of trace levels of bromate

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 development of US Environmental Protection Agency (EPA) Method 317.0 provided a more sensitive, acceptable alternative to EPA Method 300.1 to be proposed as one of the recommended compliance monitoring methods for Stage II of the Disinfectants/Disinfection By-Products (DBP) Rule. This work was initiated to evaluate other postcolumn reagents (PCRs) that might be utilized to provide an additional, alternative method in order to augment compliance monitoring flexibility for inorganic oxyhalide DBP anions. Modifications of the method reported by Salhi and von Gunten, which included adjustment and optimization of flow-rates, reaction temperature, and delivery of the PCR, improved the method performance. Method 326.0 incorporates an acidic solution of potassium iodide containing catalytic amounts of molybdenum(VI) as the PCR and provides acceptable precision and accuracy for all analytes and a postcolumn bromate detection limit in reagent water of 0.17 μg/l. Published by Elsevier Science B.V.

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1. Introduction

Globally, potentially hazardous microorganisms in drinking water supplies are controlled using various disinfection processes. A probable consequence of these processes is the potential for formation of inorganic oxyhalide disinfection by-products (DBPs). For example, chlorine dioxide (ClO_2) is the precursor to the formation of chlorite (ClO_2^-) and chlorate (ClO_3^-) [1,2]. Alternatively, chlorate and bromate have been identified in a drinking water disinfected with hypochlorite [3,4]. In addition, ozone is the precursor to the formation of bromate (BrO_3^-) when source waters containing bromide are ozonated [5,6]. Less importantly, ozone has also been reported to be the precursor to iodate (IO_3^-) formation when source waters containing iodide are ozonated [7].

The National Cancer Institute has listed bromate as an animal carcinogen [8]. In addition, the International Agency for Research on Cancer has classified bromate as a group 2B, probable human carcinogen [9]. In 1995, as a result of health effects studies, bromate was 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

*Corresponding author.

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a potential 10^{-5} risk at 0.5 μg/l [10]. Based upon its potential toxicity, in December 1998, under Stage 1 of the Disinfectants/Disinfection By-Products (DBP) Rule, the United States Environmental Protection Agency (EPA) promulgated a maximum contaminant level (MCL) for bromate in drinking water of 10 μg/l, as well as establishing the maximum contaminant level goal (MCLG) at zero [11]. Several factors, including limitations in acceptable compliance monitoring methods, were responsible for establishing the Stage I drinking water MCL for bromate at 10 μg/l.

Method 300.1 [12] is the Stage 1 compliance monitoring method for bromate [11]. It has a detection limit for bromate of 1.4 μg/l in reagent water. Method 317.0 coupled a postcolumn technique to Method 300.1 to reduce the bromate detection limit to 0.12 μg/l [13,14]. Method 317.0 will be proposed as a compliance monitoring method in the Stage II rule.

This work was initiated to find an additional method which could be used to support compliance monitoring for the analysis of the oxyhalide DPBs and bromide, which is the precursor to bromate formation. Various alternative postcolumn methods for the analysis of trace levels of bromate have been reported. These include the use of chlorpromazine as a postcolumn reagent (PCR) [15], postcolumn formation and measurement of the tri-bromide ion [16] and postcolumn formation and measurement of the tri-iodide ion [17]. Evaluation of these methods indicated that the tri-iodide method reported by Salhi and von Gunten had the most potential as an alternative technique. This method incorporates an acidic solution of potassium iodide (KI) containing catalytic amounts of molybdenum(VI) as the PCR. Modifications to this technique, which included adjustment and optimization of flow-rates, reaction temperature, and delivery of the PCR, increased method robustness and performance. Method 326 provides acceptable precision and accuracy for all analytes and a postcolumn bromate detection limit in reagent water of 0.17 μg/l.

2. Experimental

2.1. Reagents

The eluent, standards, stabilization solution, surrogate and all dilutions were prepared using 18 MΩ water. 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. A 2000 μ*M* solution of ammonium molybdate tetrahydrate [$(NH_4)6Mo_7O_{24}{\cdot}4H_2O$, Fluka, catalog No. 09878, Milwaukee, WI, USA] was prepared by dissolving 0.247 g in 100 ml of reagent water. This reagent was stored in an opaque plastic storage bottle and prepared fresh monthly. The postcolumn reagent was prepared by adding 43.1 g of potassium iodide (Fluka, catalog No. 60400) to a 1000 ml volumetric flask containing about 500 ml of reagent water. A 215 μl volume of the molybdate catalyst solution was added to the volumetric flask and diluted to volume with reagent water. The PCR was sparged with helium for 20 min to remove all traces of dissolved oxygen and immediately placed in the PC-10 delivery vessel (see Section 3.5.1) and pressurized with helium. The reagent was stable for 24 h. Ethylenediamine (EDA) preservation solution (100 mg/ml) was prepared from 99.5+% EDA (Aldrich, catalog No. 39,108-5). Dichloroacetate 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 ferrous iron [Fe(II)] solution was prepared using ferrous sulfate heptahydrate (Sigma, catalog No. F-7002, St. Louis, MO, USA; 0.124 g/25 ml reagent water containing 6 μl of concentrated nitric acid). Sulfuric acid (Fisher Scientific Certified ACS Plus, A 300–500) was used to prepare the 150 m*M* regenerant solution as well as 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 information collection rule (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). Dichloroacetic acid (DCA) was used as the surrogate in EPA Method 317.0 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 225 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 from the Dionex PC-10 pneumatic controller pressurized with helium was delivered (0.4 ml/min) to the ''eluent in'' port of an ASRS II suppressor, operated using 150 m*M* sulfuric acid (2.5 ml/min) as the regenerant. The ''eluent out'' port was connected to the mixing T. A Dionex, 500 μl knitted reaction coil enclosed in a Dionex PCH-2 column heater at 80 °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 352 nm and 0.05 absorbance units (AU) full-scale. The effluent from the absorbance detector and the regenerant out from the second suppressor were 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 with Peak Net software (version 4.3) was utilized to control the instrument and for data processing (see Fig. 1).

3. Results and discussion

3.1. Development of EPA Method 317.0 and publication of Revision 2.0

Supply difficulties (variability in the reactivity in different lots) with the major supplier of the o-dianisidine (ODA) PCR encountered in the Fall of 2000 led to Revision 2.0 to EPA Method 317.0 [18]. These difficulties, combined with the desire to have a second method for compliance monitoring for all

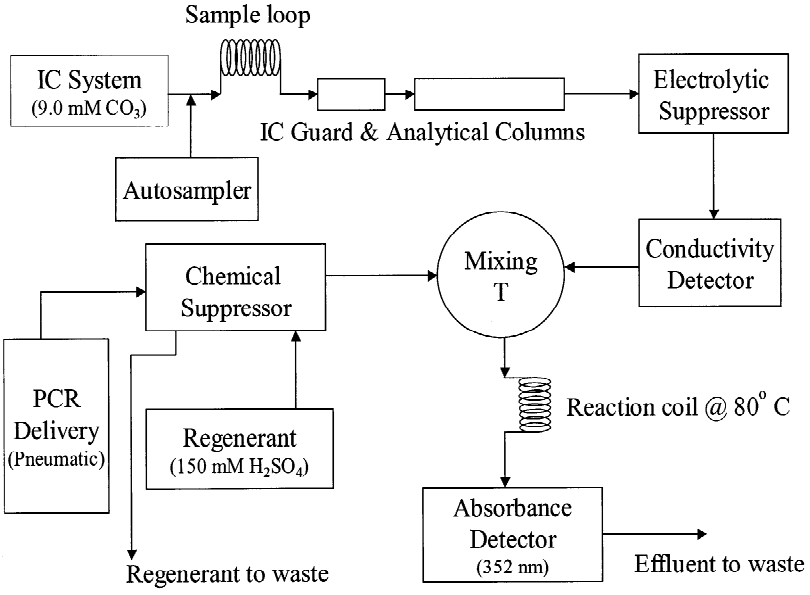

Fig. 1. Schematic of ion chromatography (IC) system used for EPA Method 326.0.

inorganic DBPs with similar sensitivity for bromate, prompted investigation of other postcolumn methods published in recent years for the analysis of trace levels of bromate.

3.2. Reports of other postcolumn techniques

In recent years, several postcolumn methods have been reported for the analysis of trace levels of bromate in drinking water. Our recent efforts were directed at evaluating only those postcolumn methods which we felt would allow simultaneous analysis of the inorganic oxyhalide DBPs and trace bromate. The alternative postcolumn reagents evaluated were chlorpromazine [15], formation and measurement of the tri-bromide ion [16] and formation and measurement of the tri-iodide ion [17].

3.3. Evaluation of chlorpromazine

One of the original postcolumn methods for the analysis of trace levels of bromate involved reaction with chlorpromazine [15]. This technique involved the use of two postcolumn reagents and was originally designed as a bromate-specific method. The major drawback of the method was the use of large volumes of fairly concentrated hydrochloric acid (2.0 ml/min of 2 *M* HCl), required to acidify the bromate/chlorpromazine mixture prior to measurement of the colored complex at 530 nm.

Problems were encountered when attempts were made to incorporate suppressed conductivity detection for the other anions prior to the postcolumn reaction with chlorpromazine. The main difficulty experienced was the high backpressure exerted on the suppressor as a result of the high flow-rates of the two postcolumn reagents (combined 2.5 ml/min). Efforts to replace these high flows, especially for HCl, with a lower flow using a more concentrated solution were not successful and consequently efforts to adapt chlorpromazine to parallel EPA Method 317.0 protocols were unsuccessful. The method, as published, has the potential to be a viable bromate-specific method.

3.4. Evaluation of a direct mixing tri-iodide and tri-bromide technique

Two other postcolumn methods for the analysis of trace concentrations of bromate published in recent years involve formation and measurement of the tri-bromide ion [16] and the tri-iodide ion [17]. Both of these original methods incorporated the use of a second suppressor in the formation of the tri-bromide and/or tri-iodide ion prior to UV detection. Subsequent work, published by Echigo et al. [19], involved the use of a direct mixing technique in order to simplify the method and eliminate the need for the second suppressor. Because of the anticipated ease of operation, and the higher wavelength used to monitor the tri-iodide species, the direct mixing tri-iodide technique was the first choice to be evaluated. However, difficulties were again experienced when attempts were made to adapt the direct mixing technique to parallel EPA Method 317.0 protocols. Stability issues with the potassium iodide/ammonium molybdate (KI/Mo) solution, and the fact that this solution could not be delivered using a piston pump, required that the two postcolumn reagents be delivered pneumatically using two Dionex PC-10 delivery modules. Consequently, the flow-rates of the two postcolumn reagents could not be measured independently, and it was assumed that both reagents were being delivered equally. Accordingly, although the direct mixing technique could not be successfully incorporated as a suppressed conductivity method to provide simultaneous data for all inorganic oxyhalide DBP anions, the technique, as published, has the potential to be a bromate-specific method.

Efforts were also directed at evaluation of the tri-bromide ion in the direct mixing mode. Although stability of the potassium iodide/sodium nitrite solution was not a critical issue, the lower wavelength used to monitor the tri-bromide ion posed potential interference problems and the difficulties experienced above in delivering two postcolumn reagents pneumatically negated further investigation of either of these two direct mixing techniques.

3.5. Modifications to the tri-iodide method incorporating a second suppressor

Several potential difficulties required resolution before the tri-iodide method [17] could be adapted to parallel EPA Method 317.0 protocols, (especially unattended overnight operation). These included eluent flow-rate, stability and delivery of the KI/Mo solution, the very high 10 ml/min flow-rate of the

H_2SO_4 regenerant used in the second suppressor as well as optimization of the reaction temperature and the potassium iodide and ammonium molybdate concentrations.

3.5.1. Eluent flow-rate and KI/Mo stability/delivery

In order to simulate EPA Method 317.0 protocols, the eluent flow-rate was increased to 1.3 ml/min without adversely affecting the backpressure (<120 p.s.i.; 1 p.s.i.=6894.76 PA) placed on the conductivity suppressor and without restricting delivery of the KI/Mo PCR.

Since KI is photosensitive, the KI/Mo PCR solution was observed to develop a light yellow color with time, even when stored under helium in the opaque plastic PC-10 delivery container inside the PC-10 pressurization vessel. Purging the KI/Mo solution with helium immediately after preparation to remove all oxygen, as recommended by Echigo et al. [19], did not completely eliminate the problem. Consequently, in order to facilitate overnight (24 h) operation, the external wall of the PC-10 plastic pressurization vessel was wrapped with ''duct tape'' to prevent any light exposure to the KI/Mo PCR [care must be exercised to leave about 1/16th of an inch (1 in.=2.54 cm) at both the top and bottom of the vessel free of tape to allow for proper sealing of the top and bottom]. To facilitate complete elimination of all exposure of the KI/Mo PCR to external light, the delivery line from the PC-10 to the mixing tee was wrapped with aluminum foil. In this manner, no coloration of the KI/Mo PCR was observed after continuous, unattended operation over 24 h.

3.5.2. Optimization of regenerant flow-rate

With the aim of improving method sensitivity, Salhi and von Gunten's method [17] incorporated the use of a peristaltic pump to deliver the 150 m*M* sulfuric acid regenerant to the second suppressor at a flow-rate of 10 ml/min to acidify the KI/Mo PCR just prior to entering the mixing tee. In addition to the increased expense for a peristaltic pump, a regenerant flow-rate of 10 ml/min would require a very large regenerant reservoir for overnight, unattended operation (approx. 15 l for 24 h). Attempts were made to alleviate this limitation by altering the regenerant concentration and reducing the regenerant flow-rate. Once it was established that a lower flow-rate did not adversely affect the results, the peristaltic pump was replaced with pneumatic delivery of the regenerant using helium. These changes did not significantly impact the results for a 1.0 μg/l aqueous bromate standard and consequently 150 m*M* H_2SO_4 regenerant at a flow-rate of 2.5 ml/min was incorporated into the method.

3.5.3. Optimization of postcolumn reaction temperature

The original tri-iodide method [17] utilized a reaction coil at room temperature. When the Dionex knitted, potted reaction coil was operated at room temperature, no signal was observed on the absorbance detector. It was assumed that with the increased flow-rate, the length of this reaction coil was too short to allow complete formation of the tri-iodide ion. Consequently, the reaction coil was operated at 40, 60 and 80 °C. As shown in Fig. 2, under these conditions, the optimum reaction temperature was 80 °C.

3.5.4. Optimization of KI concentration

To investigate the effect of potassium iodide concentration on the formation of the tri-iodide ion, the KI concentration was varied between 0.065 and 0.52 *M* while the molybdate(VI) concentration was held constant. A 5.0 μg/l aqueous bromate standard was analyzed incorporating the various KI concentrations and, as indicated in Fig. 3, the optimum KI concentration was 0.26 *M*. This is in agreement with the concentration reported by Salhi and von Gunten [17].

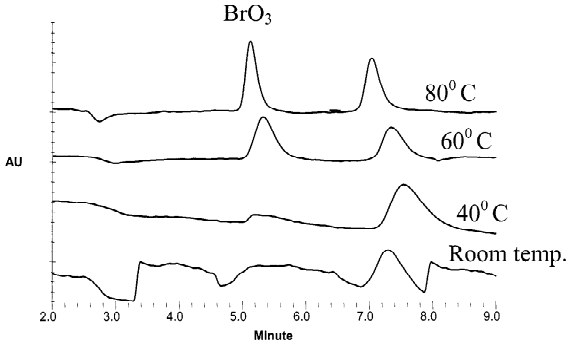

Fig. 2. Optimization of reaction temperature (the *y* scales are equal but the baselines have been offset for clarity).

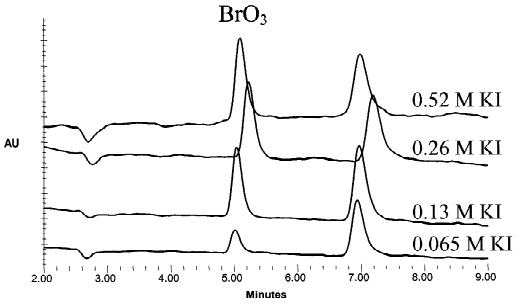

Fig. 3. Optimization of KI concentration (the *y* scales are equal but the baselines have been offset for clarity).

3.5.5. Optimization of Mo(VI) concentration

The catalytic effect of molybdate(VI) on the postcolumn formation of the tri-iodide ion was evaluated by varying the $(NH_4)6Mo_7O_{24}{\cdot}4H_2O$ concentration between 22, 43 and 86 μ*M* while the KI concentration was held constant. As shown in Fig. 4, analysis of a 5.0 μg/l aqueous bromate standard indicated that, at these concentrations, the Mo(VI) did not significantly alter the method sensitivity for bromate. Consequently, a Mo(VI) concentration of 43 μ*M*, as reported by Salhi and von Gunten [17], was included.

3.5.6. Software-based signal filtering (smoothing)

The final step to adapt the tri-iodide method to parallel EPA Method 317.0 protocols involved incorporating the same software-based signal filtering smoothing routine (Olympic smoothing, 25 points, 5 s with one iteration, with peak area quantitation) incorporated in Method 317.0 [14].

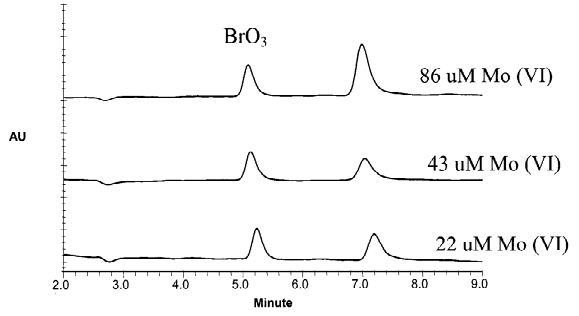

Fig. 4. Optimization of Mo concentration (the *y* scales are equal but the baselines have been offset for clarity).

3.6. Method ruggedness

Previous work in our laboratory [20] indicated that sample injections greater than 300 μl were problematic if both conductivity and absorbance data were required. Consequently, a sample loop of 225 μl was incorporated into this method. The method ruggedness was evaluated incorporating the aforementioned parameters.

3.6.1. Instrument stability

The instrument stability for the PCR portion of the new method was evaluated over a 24-h period by analyzing 16 replicate vials containing reagent water fortified with 1.0, 5.0 and 15 μg/l bromate. The precisions, expressed as relative standard deviation (RSD), for the three bromate concentrations were determined to be acceptable at 10.7, 3.32 and 2.09% RSD, respectively (Table 1).

3.6.2. Chlorite removal evaluation

The final test of the method ruggedness was to ensure the new postcolumn reagent and conditions would not interfere with EPA Method 317.0 chlorite removal protocols. Eighteen samples from Public Water Systems (PWSs), which utilize chlorine dioxide disinfection, were analyzed using EPA Method 317.0 protocols for removing chlorite. The native samples were analyzed, treated with ferrous iron and analyzed and then fortified with either 1.0 or 5.0 μg/l bromate and then treated with ferrous iron and analyzed. The native chlorite levels ranged from less than the minimum reporting level (MRL) to 1300 μg/l, and the native bromate levels ranged from 0.33 to 0.37 μg/l. Acceptable bromate spike recoveries of 98.0 to 109% (4.1% RSD, $n=9$) for the 1.0 μg/l spike, and 99.6 to 111% (3.3% RSD, $n=9$) for the 5.0 μg/l fortification level were reported in all

Table 1
Instrument stability in reagent water over 24 h

	BrO_3		
	1.0 μg/l	5.0 μg/l	15 μg/l
Mean ($n=16$)	1.05	5.45	15.4
SD	0.1125	0.1810	0.3327
RSD (%)	10.7	3.32	2.09

Table 2
Bromate spike recoveries in PWS samples disinfected with chlorine dioxide

Sample description	BrO_3^- spike (μg/l)	ClO_2^- (μg/l)	BrO_3^- (μg/l)	Recovery		
				Average (%)	Range (%)	RSD (%)
Sample (n=9)	1.0	<MRL to 1300	Masked			
Sample treated	1.0	<MRL	<MRL to 0.33			
Sample treated +spike	1.0	<MRL	<MRL to 1.36	104	98.0 to 109	4.1
Sample (n=9)	5.0	<MRL to 770	Masked			
Sample treated	5.0	<MRL	<MRL to 0.37			
Sample treated +spike	5.0	<MRL	5.2 to 5.56	104	99.6 to 111	3.3

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 following treatment to remove the chlorite interference (Table 2).

3.7. Method performance

The method performance was evaluated by determining the detection limit, precision, and accuracy of the method using the new postcolumn reagent.

3.7.1. Reagent water detection limit and MRL

The reagent water detection limit for the new postcolumn reagent and conditions were determined according to Glaser et al. [21]. The calculated detection limit for bromate in reagent water (RW) was determined by analyzing eight replicates of a 0.5 μg/l bromate spike in reagent water on three successive days. The MRL was defined as either three times the detection limit or a signal-to-noise ratio of 5:1, whichever is greater. The detection limit was calculated to be 0.17 μg/l (2.998 times the standard deviation for n=8) and the MRL calculated at three times the detection limit to be 0.5 μg/l.

3.7.2. Method precision and accuracy (spike recovery)

The precision for the new PCR method was determined by analyzing eight replicates, from the same solution, of a 1.0 μg/l bromate spike in reagent water. Acceptable precision of 4.1% RSD was obtained for the eight replicates. Also, the method precision expressed as RSD and accuracy expressed as recovery were also determined by analyzing eight replicates of 1.0 and 5.0 μg/l bromate spikes in RW, a simulated high inorganic water (HIW) and a simulated high organic water (HOW). Acceptable precision (2.03 to 4.44% RSD) and accuracy (spike recoveries ranging from 98.0 to 119%) were observed in all matrices (Table 3).

Table 3
Method precision and accuracy (RSD and recovery)

Sample	BrO_3	
	1.0 μg/l	5.0 μg/l
Reagent water (RW)		
Mean (n=8)	1.06	5.18
RSD (%)	4.44	2.05
Recovery (%)	99.0 to 111	101 to 107
High inorganic water (HIW)		
Mean (n=8)	1.06	5.21
RSD (%)	4.22	2.03
Recovery (%)	98.0 to 112	101 to 107
High organic water (HOW)		
Mean (n=8)	1.13	5.23
RSD (%)	3.40	3.18
Recovery (%)	108 to 119	101 to 111

Table 4
Method accuracy (1.0, 3.0 and 7.0 μg/l spike recoveries in ozone disinfected PWS samples; $n=10$)

	Method 326.0			Method 317.0		
	Native (μg/l)	BrO_3 spike (μg/l)	Recovery (%)	Native (μg/l)	BrO_3 spike (μg/l)	Recovery (%)
Mean		1.0	97.9		1.0	106
RSD (%)		1.0	13.5		1.0	9.4
Range	0.79–1.69	1.0	78.0–113	0.76–1.66	1.0	90.0–129
Mean		3.0	97.3		3.0	108
RSD (%)		3.0	9.3		3.0	9.3
Range	0.61–3.00	3.0	82.3–109	0.42–3.10	3.0	91.3–122
Mean		7.0	94.0		7.0	105[a]
RSD (%)		7.0	7.5		7.0	3.7
Range	0/48–3.94	7.0	86.7–107	0.47–3.99	7.0	100–113

[a] $n=9$, one value excluded due to instrument difficulties.

3.7.3. Method accuracy (comparison to EPA Method 317.0 data)

The accuracy of Method 326 was also evaluated by comparing the PCR bromate data obtained from 30 PWS, finished water samples from municipalities, which incorporate ozone disinfection. The samples were analyzed for the native bromate level and then fortified with either 1.0, 3.0 or 7.0 μg/l bromate and reanalyzed using both EPA Method 317.0 and the new PCR method designated as EPA Method 326.0. The native bromate levels ranged from <MRL to 3.00 μg/l. Acceptable precision, expressed as percent RSD for the spike recoveries, ranged from 3.7 to 13.5% RSD, and acceptable accuracy, expressed as spike recovery, ranged from 78.0 to 129% recovery were obtained for all 30 samples with both methods (Table 4).

4. Conclusions

The KI/Mo postcolumn reagent, combined with the modified experimental protocols, has provided a suitable alternative to EPA Method 317.0 for the analysis of inorganic oxyhalide disinfection by-products and trace levels of bromate. Acceptable precision and accuracy were obtained with the new method, which will be designated as EPA Method 326.0. EPA Method 326.0 is scheduled to undergo an external laboratory validation during the Summer of 2002 and will be published by EPA in the Summer of 2002.

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