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Use of ion chromatography with post-column reaction for the measurement of tribromide to evaluate bromate levels in drinking water

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Abstract

A user-friendly ion chromatography method in conjunction with a post-column reaction (PCR) achieves practical quantitation limits for the oxyhalides bromate and chlorite of 0.05 μg/l and 0.10 μg/l, respectively. This level of measurement allows for the accurate assessment of bromate contributed to finished drinking waters that have been chlorinated using sodium hypochlorite. The target sensitivity of oxyhalides in the presence of other major ion species typically found in drinking water is achieved by PCR using excess bromide under acidic conditions to form a tribromide species that is detected by ultraviolet spectrometry. The method setup involves non-hazardous materials, as opposed to other recently developed methods that employ somewhat hazardous chemicals for generating the reaction necessary for the detection of bromate at sub-μg/l levels. No pretreatment of the samples is required, other than filtration and quenching of oxidant residual.

Keywords: Water analysis; Tribromide; Bromate; Chlorite; Oxyhalides; Bromide; Chlorate; Iodate; Inorganic anions

1. Introduction

Bromate is known to be a byproduct of bromide-containing source waters that undergo ozonation, and has been shown as a contaminant in sodium hypochlorite feedstock solutions used for disinfection [1,2]. Bromate is classified as a probable carcinogen by the US Environmental Protection Agency (EPA) and is currently regulated in treated drinking water at a maximum contaminant level (MCL) of 10 μg/l based on a cancer risk of 10^{-4} at 5 μg/l [3]. Chlorite is also classified as a health concern [4] and is found in drinking water as a chlorine dioxide by-product [5,6], and a hypochlorite decomposition product [7,8]. The lack of sensitive analytical techniques for the detection and quantitation of these oxyhalides affect the regulatory-making process in establishing lower limits for these compounds based on the correlation with toxicological exposure assessment studies. The method developed in this study achieves a reliable quantitation of bromate corresponding to an extrapolated 10^{-6} cancer risk from the current regulated limit.

Several methods have been developed in an attempt to obtain the analytical sensitivity needed for low-level detection of bromate. Most procedures use a pre- or post-column chemical reaction in conjunction with a separation technique such as IC [9,10], high-performance liquid chromatography (HPLC) [11,12], or GC [13], to convert the target compound to another easily detectable species. However, these

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methods appear non-ideal in that there is a need for several timely reaction steps involving multiple chemicals, or that the reagents themselves are toxic, therefore presenting a hazard to the user and the environment. For example, toxic chlorpromazine has been used as a reagent in an ion chromatography (IC) method with post-column reaction (PCR) for achieving the detection of bromate at 5.0 μg/l [10]. The recently drafted EPA Method 317.0 (a revision to Method 302.0) achieves a better limit of detection for bromate by an IC-PCR method, but utilizes *o*-dianisidine, a potential human carcinogen, as a major post-column reagent [14]. The statistically based method detection limit (MDL) is reported as 0.12 μg/l, although in practice, the practical quantitation limit (PQL) would be expected to be around five times this value for the method. IC has also been used in conjunction with inductively coupled plasma mass spectrometry (ICP-MS) by using large injection volumes to achieve a sub-μg/l detection of bromate [15–17]. However, this type of instrumentation is expensive to acquire as well as maintain.

Our method utilizes a high capacity anion-exchange column, enabling large injection volumes of samples to be loaded. The resolved target species first pass through a conductivity detector and then undergo the post-column reaction with sodium bromide in the presence of nitrous acid. The acidic conditions are generated from sodium nitrite via a chemical suppressor unit, and it may be possible to enhance sensitivity by manually mixing acid and bromide for the PCR [18], however, further studies would have to be conducted to evaluate the reaction kinetics. A stable tribromide species is formed and detected by UV at 267 nm. The commonly occurring anions in typical drinking water samples (i.e., chloride, sulfate, phosphate, and nitrate) are invisible to the detector and therefore do not interfere with the UV-PCR chromatography. The method is built on an IC-PCR technique previously developed in our laboratory, which achieved a 0.2 μg/l quantitation limit for bromate utilizing a different anion-exchange column and requiring two chemical suppressor units to generate the acidic conditions for the post-column reaction mixture [19,20].

Application of the method is demonstrated on a variety of waters from treatment plants in which hypochlorination was used as the mode of disinfection. The sensitivity achieved in the method enables an accurate assessment for sub-μg/l levels of bromate contributed to drinking waters treated with sodium hypochlorite. Commercially produced hypochlorite feedstocks, also evaluated by the method, demonstrate the presence of bromate as a contaminant. Using accurate and reliable dosing information provided from each water treatment facility, the observed and predicted amounts of bromate in finished waters treated with sodium hypochlorite are compared and reported as a mass balance. Iodate and chlorate, which are not currently classified by the EPA as a health concern, are also evaluated by the method.

2. Experimental

2.1. Chromatographic instrumentation

The IC modules (Dionex, Sunnyvale, CA, USA) consist of an ASM-3 automated sampler, an eluent degas unit in conjunction with a GPM-2 gradient pump, a LCM-3 conductivity detector, and a VDM-2 variable-wavelength detector. A RS232 advanced computer interface used with AI-450 v. 3.32 and PeakNet v. 4.30 computer software enables processing of data. A Dionex Ionpac AG9-HC guard column (25×4 mm) followed by an IonPac AS9-HC (250×4 mm) high-capacity anion-exchange analytical column provides chromatographic resolution of the target anions from a 1000 μl sample injection volume. An isocratic program is utilized with a mobile phase flow-rate of 1.2 ml/min. A Dionex ASRS-II chemical suppressor functions to lower the background conductivity of the mobile phase while enhancing the detection of the target analytes. Equipment utilized for the PCR setup includes a DQP-1 post-column pneumatic controller for delivery of the reaction mixture at a flow-rate of 0.6 ml/min. A Dionex ASRS-ULTRA suppressor facilitates the generation of the acidic conditions from sodium nitrite. The resulting solution meets with eluting oxyhalides, and passes through a Dionex CH-1 column heater at 60°C equipped with a 2.5 mm I.D.×0.5 mm I.D. reaction coil before entering the UV detector. The detector is equipped with a 9 μl

cell volume with a 6 mm path, and a wavelength set at 267 nm.

2.2. Chemicals and solutions

All reagent solutions, standards, and calibrators were prepared in deionized (DI) water generated from a system (Virginia Water Systems, Richmond, VA, USA) equipped with mixed bed ion-exchange and organic scavenger tanks, delivering finished water at a measured resistance of 18 MΩ. All chemicals were purchased as analytical or certified A.C.S. grade, unless specified otherwise, from Fisher Scientific (Fair Lawn, NJ, USA).

The IC mobile phase of 9.0 m*M* sodium carbonate is prepared by passing through a 0.45 μm nylon 66 membrane filter (Alltech Associates, Deerfield, IL, USA) under vacuum, then sparged with ultra high purity (UHP) helium (Holox, Norcross, GA, USA) for 20 min prior to use. Concentrated sulfuric acid is used for the preparation of the regenerant solutions, 25 m*M* for chromatographic separation and 0.75 *M* for PCR. The post-column reaction mixture consists of 0.145 m*M* sodium nitrite and 2 *M* sodium bromide. The mobile phase, regenerant solutions, and PCR mixture are stored and operated under pressure with UHP helium. Potassium iodate, potassium bromate (analytical grade, Mallinckrodt, Paris, KY, USA), sodium chlorite (80%, Fluka, Buchs, Switzerland), and sodium chlorate (>99%, Fluka, Buchs) are prepared as 1 g/l anion stock standards.

2.3. Sample collection and preparation

Based on an agreement made with the USA drinking water utilities participating in our study, the identity of the treatment plants and sample results provided in this presentation are coded. The ''Alpha'' Facility is located in the mid-west of the country and utilizes ozone and hypochlorination as modes of treatment. The ''Beta'' Facility located on the west coast, uses only combined chlorine for disinfection facilitated by separate dosing of hypochlorite and ammonia. Acid washed 40 ml volatile organic analysis (VOA) vials (Laboratory Supply Distributors, Mt. Laurel, NJ, USA) with caps containing PTFE-lined septa were sent to each corresponding facility for aqueous sample collection. A hypochlorite feedstock sample, as well as dosing information, was also requested from each treatment plant. Samples were shipped and returned in a refrigerated ice-chest. Upon receipt back to the University of North Carolina laboratory, samples were stored at 4°C until time of analysis. Multiple low-level calibration solutions were prepared from respective 1 g/l anion stock standards. A 1:10 000 dilution was made of each sodium hypochlorite feedstock sample for IC-PCR analysis. This dilution factor was required to ensure that the analytical column capacity for total ionic species would not be exceeded. Oxidant residual in treated drinking water samples and dilute hypochlorite feedstocks were sufficiently quenched using a stock solution of 100 mg/ml ethylenediamine (EDA) (99.5%, Fluka). Due to the limited amount of sample volume available, matrix spikes for water samples were prepared in 10 ml volumetric flasks. Spikes for dilute hypochlorite feedstock solutions were prepared in larger 100 ml volumes. All blanks, calibrators, samples, and spikes were filtered prior to analysis using 0.45 μm nylon syringe filters (Nalgene, Rochester, NY, USA).

3. Results and discussion

3.1. Quantitation limits

PQLs were established at the lowest level that could be reliably reproduced by the method during routine laboratory operating conditions. To establish the PQL of each analyte, six or seven replicate injections of the corresponding anion standard prepared in DI water were analyzed. The PQLs and MDLs determined for each target species by the method are provided in Table 1. The MDL is a statistical value, inclusive of the precision based on the DI water blank, and defined as the minimum concentration of a substance that can be measured and reported with 99% confidence and that the analyte concentration is greater than zero. The blank response measured for each analyte was below detection. The relative standard deviation (RSD) was between 7.8 and 18% for the target analytes. Greater variability is generally expected for values close to the detection limit, so RSDs below 20% are acceptable. Peak height responses provided reliable for

Table 1
Practical quantitation limits and method detection limits established for the target analytes

Detection	Analyte	PQL (μg/l)	*n*	SD (μg/l)	RSD (%)	$t^{c}_{(n-1,\ 1-\alpha=0.99)}$	MDL (μg/l)
UV-PCR[a]	Iodate	0.06	7	0.01	12	3.707	0.04
	Chlorite	0.10	6	0.02	18	4.032	0.08
	Bromate	0.05	7	0.004	7.8	3.707	0.01
	Chlorate	70.0	7	8.5	12.2	3.707	31.5
Conductivity[b]	Bromide	10.0	7	1.5	15.4	3.707	5.6
	Chlorate	10.0	7	1.0	10.1	3.707	3.7

[a] Based on peak height responses.
[b] Based on peak area responses.
[c] Obtained from a "*t*" Variate Table [22]; *n* is the number of replicate injections; RSD, (standard deviation/average)×100; MDL, ("*t*" value×standard deviation).

integration for the target species by UV-PCR chromatography, whereas peak areas were used for calculating concentrations by conductivity detection. Chlorate detection by UV-PCR is not as sensitive as by conductivity, most likely as a result of slow chemical conversion of the analyte with the post-column reaction mixture. Fig. 1 shows UV-PCR chromatograms of iodate, chlorite, and bromate at sub-μg/l concentrations. Peaks were identified based on a match to retention times established from a 1.0 μg/l mixed oxyhalide standard.

3.2. Application

As a preliminary screening of the method, synthetic water was prepared to mimic the ionic strength of anion species present in tap water. The standard mixture was used to establish analyte retention times by conductivity, and served as a one-point calibrator for estimating concentrations of the target species present in a tap water sample (Orange County Water and Sewer Authority, NC, USA). The total number of equivalents contributed from each anionic species in tap water was then calculated to ensure that a column capacity well below 190 μequiv. (maximum capacity for the AS9-HC column) would be achieved for routine analyses with a 1000 μl sample injection volume.

Hypochlorite solutions supplied by the Alpha and Beta facilities were quenched of free chlorine immediately at the time of preparation of the 1:10 000 dilution. IC-PCR analysis of each facility's dilute feedstock indicated bromate present as a contami-

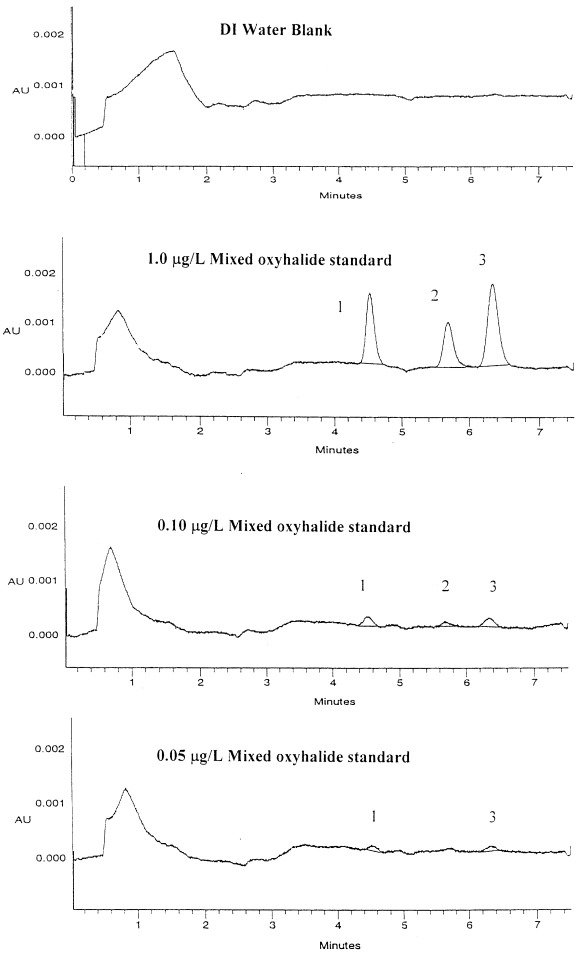

Fig. 1. UV-PCR chromatograms of target oxyhalide species in DI water at different sub-μg/l levels. 1, Iodate (4.5 min); 2, chlorite (5.7 min); 3, bromate (6.3 min).

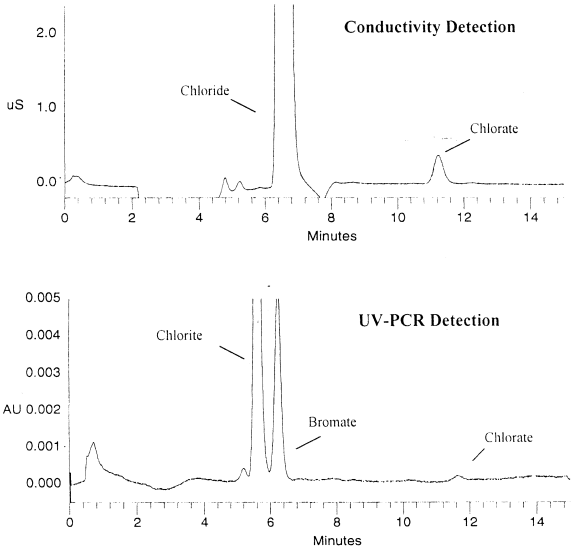

Fig. 2. Chromatograms for a 1:10 000 sodium hypochlorite feedstock dilution received from the Beta Facility. Peaks by conductivity: chloride, not quantified (6.6 min); chlorate, 78.2 μg/l (11.23 min). Peaks by UV-PCR detection: chlorite, 18.08 μg/l (5.6 min); bromate, 3.59 μg/l (6.2 min); chlorate, 78.2 μg/l (11.6 min).

nant. Reported values reflected a 1% relative percent difference (RPD) from replicate analyses of each feedstock sample. Fig. 2 shows the conductivity and UV-PCR chromatograms of the 1:10 000 dilute hypochlorite feedstock from the Beta facility. Significant levels of chloride mask the measurement of bromate by conductivity at 6.6 min. However, the PCR method is ideal in that chloride is not detected by UV, and allows for good chromatographic resolution of bromate from the other oxyhalides. Bromate concentration was determined as 36 mg/l from the original 15.4% solution obtained from the Beta facility, and a good spike recovery for the analyte was demonstrated at 92%. The hypochlorite feedstock supplied by the Alpha facility indicated a level of 20.6 mg/l of bromate in the 13.2% solution, with a spike recovery obtained at 107%.

Water quality characteristics of samples collected and supplied by the Beta Facility included an average total organic carbon (TOC) content of 1.8 mg/l, alkalinity of 16–22 mg/l as $CaCO_3$, and pH of 8.6–9.0. Entering raw water received at this treatment plant is hypochlorinated upstream 80 miles away at a dose of 0.5 mg/l, however the chlorine residual in the water once reaching the Beta facility is essentially zero (1 mile=1609 m). The raw water undergoes coagulation, flocculation, and sedimentation, and the clarified water is then treated with a 15.4% hypochlorite solution at a dose of 2.5–3.0 mg/l prior to filtration. (Ammonia is added post-filtration at this facility). Fig. 3 shows chromatograms by conductivity and UV-PCR for the raw water sample. Again, even with a significant presence of chloride, chlorite and bromate are well resolved as indicated by UV-PCR detection. The 0.14 (±0.01) μg/l concentration of bromate observed in the raw water is likely attributed to contamination present in the hypochlorite solution used 80 miles upstream. Using the dose information provided and the amount of bromate per gram of free chlorine determined by IC-PCR analysis of the hypochlorite feedstock, a mass balance of 117% is achieved based on the actual to predicted level of bromate (0.12 μg/l) present in the raw water. Fig. 4 shows chromatograms for the clarified water treated with hypochlorite on-site at the facility. As would be expected, the chlorite, bromate, and chlorate levels

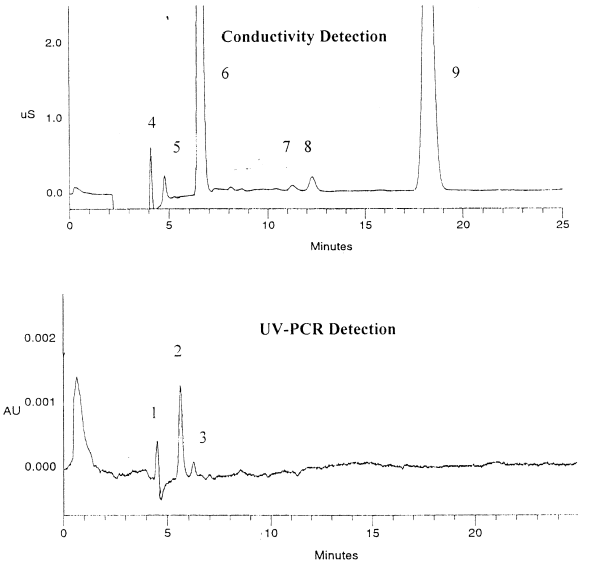

Fig. 3. Chromatograms by conductivity and UV-PCR detection for the analysis of a raw water sample collected from the Beta Facility. 1, Iodate (0.52 μg/l); 2, chlorite (1.51 μg/l); 3, bromate (0.14 μg/l); 4, fluoride (not quantified); 5, unidentified; 6, chloride (not quantified); 7, chlorate (13.0 μg/l); 8, nitrate (not quantified); 9, sulfate (not quantified).

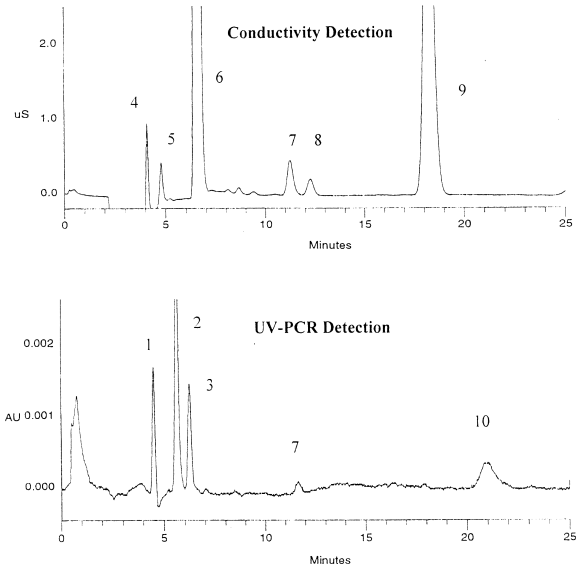

Fig. 4. Chromatograms by conductivity and UV-PCR detection for the analysis of a clarified water sample collected from the Beta Facility. Water was chlorinated at a dose of 2.5–3.0 mg/l from a 15.4% sodium hypochlorite feedstock solution. 1, Iodate (1.36 μg/l); 2, chlorite (3.43 μg/l); 3, bromate (0.85 μg/l); 4, fluoride (not quantified); 5, unidentified; 6, chloride (not quantified); 7, chlorate (100.3 μg/l); 8, nitrate (not quantified); 9, sulfate (not quantified); 10, unknown contaminant.

increased after the addition of hypochlorite. A mass balance of 101–122% was calculated between measured and predicted bromate concentrations for this particular sample due to hypochlorite addition. An increase in iodate concentration is suspected due to the presence of iodide in the water being rapidly oxidized by the treatment process through a hypoiodous acid intermediate [21]. Multiple low-level calibration curves (up to 10.0 μg/l) prepared of iodate, chlorite, and bromate in DI water by UV-PCR showed good linear regression coefficients (r^2) of 0.9999, 0.9953, and 0.9999. A higher-level chlorate calibration (up to 150.0 μg/l) measured by conductivity detection, produced a regression coefficient of 0.9973. Spike recoveries obtained for all the target analytes from the real water matrices ranged between 86% and 113%.

Chromatographic results of the hypochlorite dilute feedstock and water samples from the Alpha Facility were consistent for the method. The entering raw water to the Alpha Facility is comprised lake source water combined with wash water from a nearby wastewater treatment facility. Water quality characteristics include a pH of 8.27 for raw water, TOC of 1.8–2.0 mg/l, alkalinity of 102 mg/l as $CaCO_3$, and finished water pH of 7.76. Entering water to the facility contains an average bromide concentration of 28 μg/l (reported by the facility) and is treated at an ozone dose of 1.3 mg/l. A sodium hypochlorite dose of 1.3 mg/l is applied after clarification and filtration. IC-PCR analysis results from the raw water sample indicated a bromate level of 0.06 (±0.01) μg/l, which may be attributed to contamination via a hypochlorite application utilized at the nearby wastewater treatment plant. As expected from the reaction of bromide with ozone, the amount of bromate measured in the ozonated water samples was elevated to a level of 2.9 μg/l. The final chlorinated water sample indicated 3.0 μg/l of bromate, resulting in only a calculated 50% mass balance against a predicted level of 0.2 μg/l that would be contributed from the hypochlorite solution used for treatment. (Both reported bromate values had a 1% RPD between each of their replicate analyses). Deviation from a unified mass balance from hypochlorinated drinking water samples may be attributed to the degradation of the hypochlorite feedstocks in transit, affecting accurate concentrations of free chlorine used in calculations. In addition, the dose information provided by each facility may have been slightly inaccurate, and represented an average daily dose value instead of the exact dose at the time the water sample was collected. Low-level calibration regression coefficients of the target analytes for this facility ranged from 0.9997 to 0.9968. Spike recoveries ranged from 75 to 87% for iodate, bromate, and iodate. A fair recovery of 66% was obtained for chlorite, and may be attributed to the age of the stock standard solution used or error from the small volume measurements used for preparation.

4. Conclusion

This user-friendly IC-PCR method successfully demonstrates the capability of detecting down to a 0.05 μg/l level of bromate in chlorinated drinking waters. The good chromatographic separation and detection of target oxyhalides by UV-PCR is

achieved with the simultaneous analysis of routine anions by conductivity. Non-hazardous materials are utilized, and the PCR setup can be easily adapted to existing IC instrumentation typically found on-site at drinking water facilities. In its current configuration, this method demonstrates another level of diversity for IC in that it offers an additional path for monitoring environmental contaminants that are otherwise insensitive by direct analysis.

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