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New, sensitive and selective method for determining sub- $\mu\text{g}/\text{l}$ levels of bromate in drinking water

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Abstract

Health effects studies suggest that bromate should be regulated at 0.5 $\mu\text{g}/\text{l}$ or less in drinking water. Accordingly, an analytical method is needed to quantify this contaminant with great sensitivity and selectivity. Past efforts to do this have focused on pre-concentration ion chromatographic (IC) separation followed by suppressed conductivity detection. Interfering chloride was removed by passing samples over a silver resin which increased sample analysis time to almost 1 h. In this paper, a new method which uses IC separation with no pre-treatment followed by a post-column reaction to produce tribromide (Br_3^-) from bromate, is applied to the analysis of a variety of aqueous samples. The tribromide ion is detected by UV absorbance at 267 nm. This method is very sensitive for bromate with a limit of quantitation of 0.2 $\mu\text{g}/\text{l}$ and is also very selective. Common anions typically separated by IC exhibit no interference, even at the levels normally found in drinking water. © 1998 Elsevier Science B.V.

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1. Introduction

The oxyhalide disinfection by-product bromate is most commonly associated with the ozonation of drinking water containing bromide and is identified as a potential source of kidney tumors [1]. However, accurate exposure assessment studies at the low concentrations typically found in drinking water have been hindered by the absence of sensitive analytical procedures for detection and quantitation. The Information Collection Rule (ICR) is designed to generate a database of disinfection by-product occurrence throughout the USA drinking water treatment regimen using sensitive analytical methods that have been years in the making [2]. Whereas many of the halogenated organic by-products resulting from

chlorination have been studied for over two decades, the presence of oxyhalides is a relatively new discovery. Bromate, although chiefly associated with ozone treatment of waters containing elevated levels of bromide [3–5], has recently been an indicated contamination in drinking water as a result of chlorination [6–8].

The ICR will collect bromate data from ozonation plants employing US Environmental Protection Agency (EPA) Method 300 [9] with a practical quantitation limit (PQL) of 10 $\mu\text{g}/\text{l}$. This will severely impact the ability to run true bromate exposure assessments to consumers since a preferred 10^{-5} cancer risk maximum contaminant level of 0.5 $\mu\text{g}/\text{l}$ cannot accurately be measured by existing routine analytical procedures. It is of note that several researchers have offered either variants on this method or the use of advanced instrumentation

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in an attempt to achieve this analytical goal [10–14]. So far, however, a simple, more sensitive alternative free from interferences is not in routine use for the analysis of water.

This paper describes the application of a new, simple method for bromate analysis, the chemistry of which was first described by Inoue et al. [15], by employing existing ion chromatographic equipment with additional available accessories. A single injection of an aqueous sample having undergone no special pre-treatment allows detection of iodate, chlorite and bromate through target-specific post-column derivatization. Other common anions found in water such as chloride, sulfate, phosphate and nitrate are invisible to the detector and consequently do not obscure the resulting chromatogram.

2. Experimental

An AS12 analytical column (Dionex, Sunnyvale, CA, USA) is fed a standard carbonate–hydrogencarbonate mobile phase (2.7 mM carbonate–0.3 mM hydrogencarbonate) as described in the column manual and the resulting effluent is mixed with post-column reagent mixture consisting of acidified bromide as described elsewhere [16]. The eluting bromate reacts with the reagent mix generating bromine which, in the presence of an excess of bromide, is converted into the tribromide ion which is detected at 267 nm in a UV spectrophotometer. Tribromide response is directly proportional to the quantity of bromate present in this optimized method which permits complete reaction in a temperature controlled membrane reactor at 60°C and at the pH of the mobile phase.

The reagents used to prepare the mobile phase and bromate standards were reagent grade (Fluka, Ronkonkoma, NY, USA) and the laboratory-grade water (LGW) was generated from a two-stage ion-exchange resin followed by carbon filtration and macroreticular resin filtration (Dracor, Durham, NC, USA).

Bottled “Natural Alpine Spring Water” labeled “collected at source” and containing a chloride level of 2.3 mg/l was purchased from a local grocery store. There was no indication on the label that the

water had undergone any finished treatment nor was any bromide content listed.

Natural organic matter (NOM), used as a source of total organic carbon (TOC) in the synthetic solutions, was reconstituted from a concentrate obtained from the Kralingen Plant of the Water Supply Company Europoort, Rotterdam, Netherlands. Ozonation of this water was undertaken by a procedure described elsewhere [17].

The local tap water analyzed in this work, collected at the University of North Carolina, was chlorinated at the Orange Water and Sewage Authority drinking water treatment plant (Carrboro, NC, USA) and had a residual of about 1.2 mg/l free chlorine. Bromide in this water is below 50 µg/l. Samples were quenched of chlorine, prior to analysis, by the addition of 50 mg/l ethylene diamine.

The samples from a pilot ozonation plant study were provided by the Jefferson Parish Water Treatment Plant, Jefferson, LA, USA.

3. Results

3.1. Quantitation limits

The limits of sensitivity of this method were assessed by determining quantitation limits both statistically by the method detection limit (0.1 µg/l) and practically by the practical quantitation limit (0.2 µg/l). These results indicate sub-ppb bromate detection in laboratory-grade water with no other components present and using a 150-µl sample loop volume. For the determination of these limits, a concentration of bromate was selected (0.5 µg/l) that provided a discernible response above baseline noise. The analyte was injected seven times and the average height (31 counts) and area (358 counts) recorded together with relative standard deviation (6.8 and 13%, respectively). Both height and area could be used for calibration when baseline stability was not compromised by sample integrity. The method detection limit (MDL) was calculated as defined in the Code of Federal Regulations [18] and the PQL was selected as the lowest level of analyte that produced a distinct peak with signal to baseline noise ratio of at least three. It is possible that in the future, these limits may be further lowered by use of

newly available high capacity anion columns which will permit a higher sample loading volume. The resolution of three oxyhalide chromatographic peaks at their PQL is indicated in Fig. 1 and is compared with the analysis of laboratory-grade water containing no added species. It is clear that this method permits rapid separation of these oxyhalides and produces peaks clearly discernible from baseline noise at these levels. Using peak area for quantitation, bromate calibration in the range from PQL to 10 $\mu\text{g}/\text{l}$ produced a regression coefficient (r^2) of 0.9989. In practice, the linear range extends beyond 200 $\mu\text{g}/\text{l}$.

3.2. Application

3.2.1. Drinking water

Local tap water was analyzed as collected and after boiling a sample in a pre-cleaned vessel on a hot plate, the latter to determine if consumed boiled water offered an enhanced exposure route. Replicate samples of each were spiked with 0.5 $\mu\text{g}/\text{l}$ (the boiling water before heating). The results of these analyses indicate the absence of bromate in this particular chlorinated tap water both cold and hot. Spike recoveries were 94% in cold and 103% in boiled water.

The bottled water analysis suggests that the source water contained bromide and had undergone some

form of oxidation (possibly ozonation) prior to bottling in order to achieve such a high bromate level (13.1 $\mu\text{g}/\text{l}$) assuming that indeed the water was collected from a natural spring as suggested on the bottle's label. Bromide at levels as high as 0.7 mg/l in mineral waters is a natural phenomenon resulting from geochemical weathering [19] but it is apparent that the bottled water industry is possibly unaware of the impact of using in-laboratory oxidation for improved taste and odor on the resulting by-products. A 0.5 $\mu\text{g}/\text{l}$ bromate spike in the bottled water matrix produced a 103% recovery.

3.2.2. Synthetic waters

The prime goal for the development of this low level analytical method is the applicability to a wide range of drinking waters varying in TOC, natural bromide, and treatment. With this in mind, controlled experiments were performed employing a synthetic aquatic matrix. The first set of experiments was designed to determine the impact of a high ionic strength medium on bromate recovery and the result is illustrated for 0.4 $\mu\text{g}/\text{l}$ bromate in Fig. 2. The concentrations of anions employed were chosen to reflect a reasonably high ion-containing natural water and only those ions present at the highest levels were selected for this matrix namely, chloride (50 mg/l), sulfate (60 mg/l), alkalinity (100 mg/l as hydrogencarbonate) and nitrate (20 mg/l). The second synthetic matrix comprised reconstituted natural organic matter as a source of organic carbon, alkalinity as a source of inorganic carbon, a buffer capacity and bromide. Bromate calibration in this water provided the same linear relationship to detector response as that in LGW and a comparison of the chromatographic peaks in both matrices is shown in Fig. 3. Ozonation of this water at varying ozone to TOC doses and different levels of alkalinity and bromide provided an opportunity to investigate correlations between bromate (at sub-ppb levels) and transferred ozone dose in these waters [17]. A chromatogram indicating the result of employing an ozone to TOC dose of 0.85 in a synthetic water containing 50 $\mu\text{g}/\text{l}$ bromide and 1 mM carbonate buffered at pH 7 is illustrated in Fig. 4 together with the result of a 5 $\mu\text{g}/\text{l}$ bromate spike in this sample (95% recovery). The shape of the chromatogram is somewhat different to those previously presented.

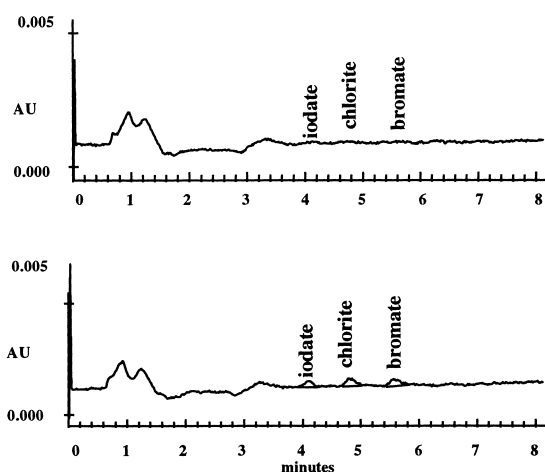


Fig. 1. Ion chromatogram illustrating background (upper) and oxyhalide response at PQL (lower): iodate (0.1 $\mu\text{g}/\text{l}$), chlorite (0.4 $\mu\text{g}/\text{l}$), bromate (0.2 $\mu\text{g}/\text{l}$).

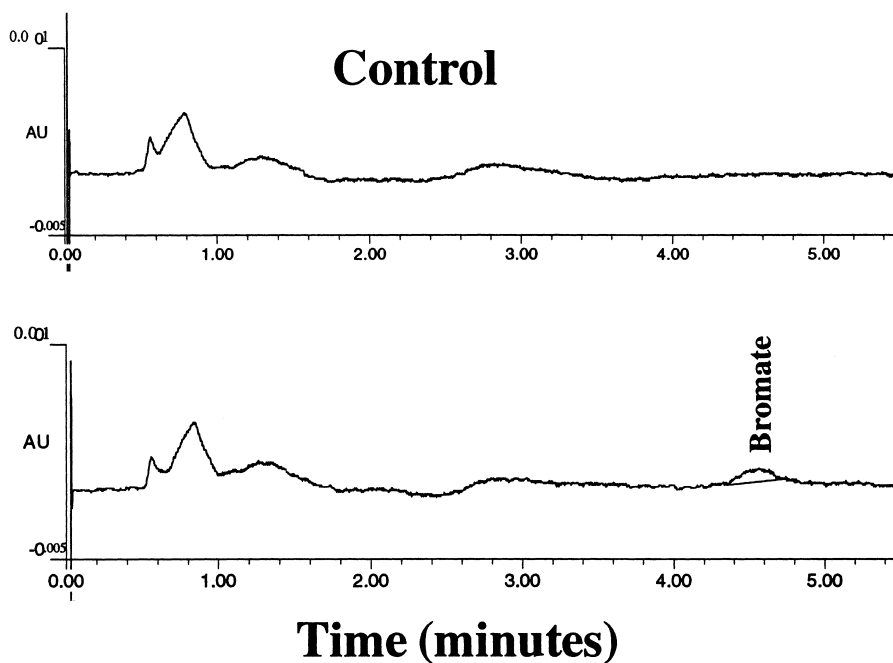


Fig. 2. Analysis of 0.4 $\mu\text{g}/\text{l}$ bromate in synthetic water (lower chromatogram) compared to laboratory-grade water (upper chromatogram).

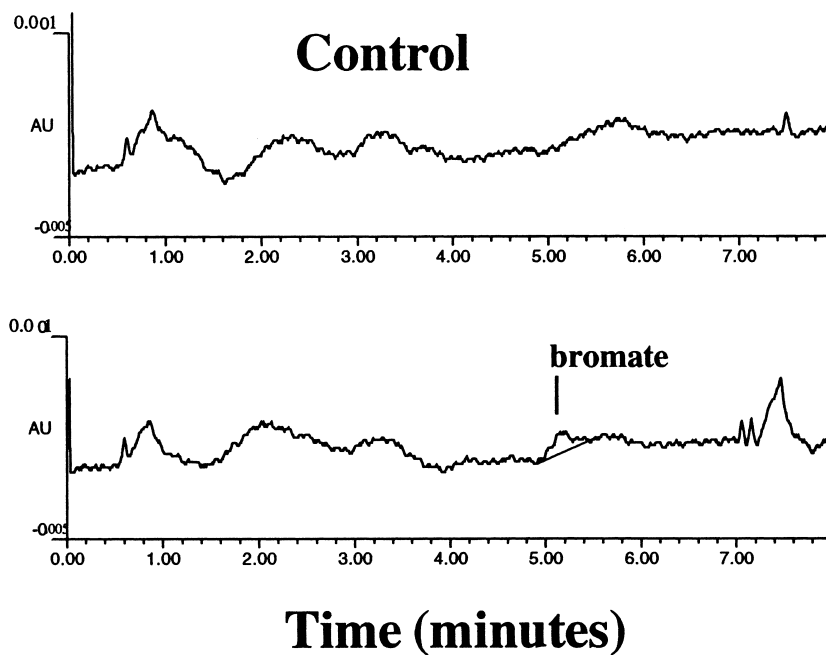


Fig. 3. Analysis of 0.8 $\mu\text{g}/\text{l}$ bromate in NOM matrix (2.5 ppm C, 2 mequiv./l alkalinity, 1 mequiv./l phosphate buffer).

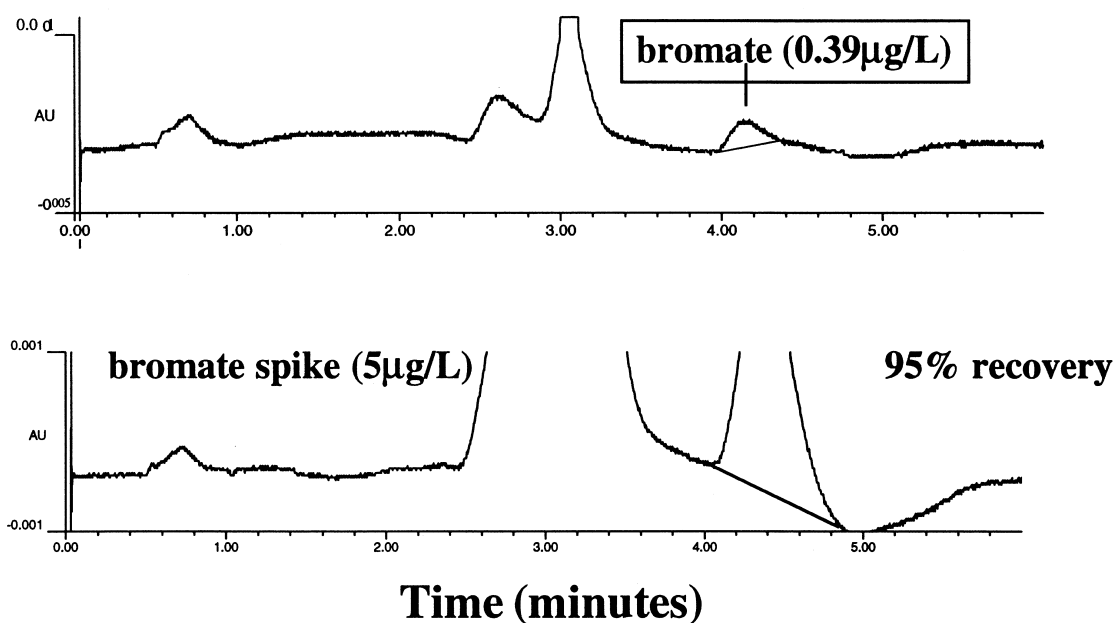


Fig. 4. Ozonated synthetic water (O_3 ; TOC=0.85, $50 \mu\text{g/l Br}^-$, 1 mM CO_3^{2-} , pH 7).

The doublet appearing at around 3 min is at a position that would normally represent the elution of bicarbonate for this column. However, subsequent work with bicarbonate at this concentration in a TOC-free water did not exhibit this trend. Hence, we can probably attribute the doublet to some aspect of the TOC (its concentration onto and/or retrieval from an XAD column). This type of water represents an extreme natural aquatic matrix and is for illustrative purposes only. The presence of this doublet does not interfere with the analysis of bromate nor the PQL established earlier for LGW. Consequently, we can reasonably extrapolate the effectiveness of this method towards sensitive bromate analysis in all drinking waters.

The analytical method was then applied in practice to the determination of bromate in a pilot ozonation plant treating a surface water with low-level bromide ($<50 \mu\text{g/l}$) at a variety of ozone to TOC doses. The results of one of these tests is illustrated in Fig. 5 and compares the background raw water to the levels of bromate found at two ozone doses (0.625 and 1.25 mg/l). These samples indicate the applicability of this analytical method to the determination of sub-ppb levels of bromate that are indeed likely to be

found in ozonated waters that contain low bromide. The availability of this relatively simple methodology will provide the tools for assessing exposure to bromate in drinking water that has hitherto been impeded by the lack of sensitivity of existing methodologies. This analytical methodology will provide the EPA and the water quality monitoring community with the ability, using existing analytical equipment with simple add-on accessories, to fulfil the goals of the ICR and criteria for future drinking water regulations by achieving the required sensitivity very easily in oxyhalide analysis.

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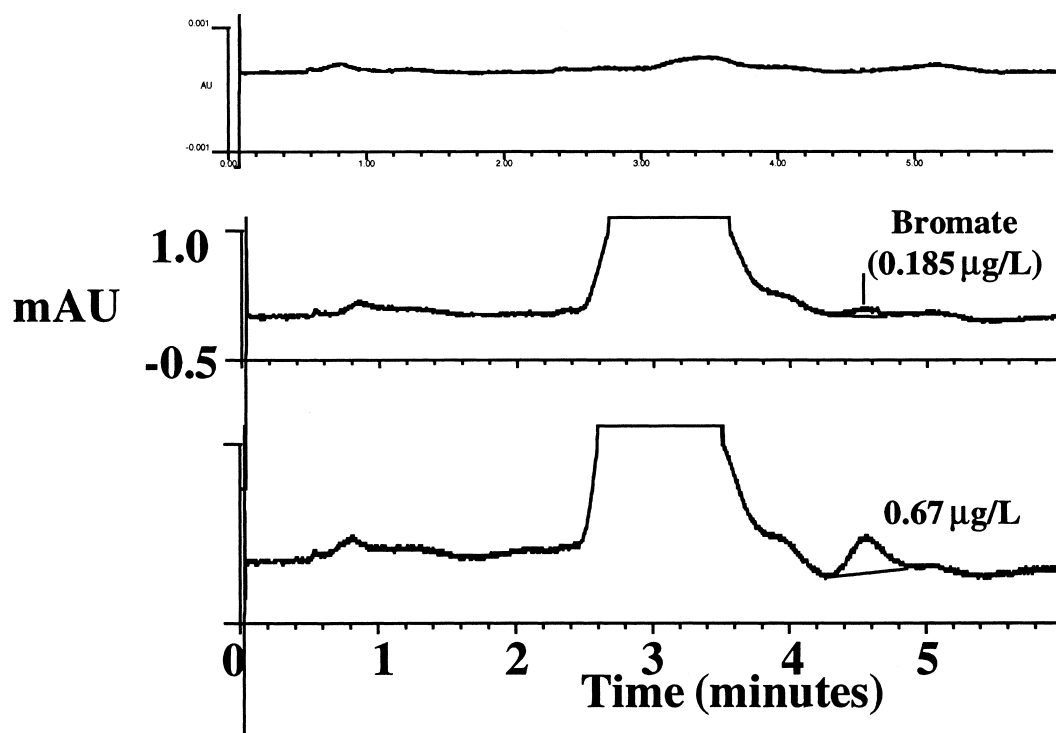


Fig. 5. Measurement of bromate in ozonated surface water at various ozone to TOC doses (mg/mg). TOC=2.5 mg/l; 0 (upper), 0.25 (middle) and 0.5 (bottom).

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