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Pre-concentration techniques for bromate analysis in ozonated waters

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Abstract

Ozonation of surface waters that contain bromide result in the formation of bromate which has been identified as a potential carcinogen. Regulation of bromate at the preferred concentration of less than 5 μg/l is being delayed due to lack of a validated analytical method for quantification at this level. This paper describes the integrated use of a silver cation resin to reduce closely eluting chloride from aqueous samples followed by a chelation column to remove leached silver prior to pre-concentration of 4-ml samples on an anion-exchange column. A borate eluent used under gradient conditions allows for bromate determination at 0.5 μg/l in treatment plant waters that, hitherto, were reported to be devoid of bromate.

1. Introduction

Although bromate has been used in the beverage and bread-making industry for some time, there are now new risk assessment data that indicate bromate as a potential carcinogen [1]. The drinking water industry, in its efforts to reduce the amount of halogenated by-products in finished water, is poised to encourage more use of ozone technology to achieve this goal. However, recent studies have revealed the formation of bromate at levels in excess of 10 μg/l in bromide-rich waters which have been ozonated [2]. The World Health Organization, taking a conservative view, recently recommended a limit of 25 μg/l bromate in drinking water [3], in part due to the inability to effectively quantify lower levels. The United States Environmental Protection Agency (U.S. EPA), on the other hand, has suggested restrictions on bromate in drinking water based on extrapolations of toxicological studies which use high bromate doses on animals to the levels associated with average drinking habits in humans [4]. With this standpoint and following negotiation with various interest groups from both the general public and industry, a regulatory level of 10 μg/l bromate has been settled for in the United States in the short term [5]. In fact, the life-time risks associated with bromate ingestion from drinking water require much more stringent regulations. In order to comply with lower level restrictions it is necessary to have available an analytical technique which can simply and rapidly analyze bromate at the low μg/l levels. Currently, the practical quantitation level (PQL) for bromate in drinking water is 10 μg/l [6] based on the ion chromatographic (IC) techniques commonly applied by the U.S. EPA in the determination of inorganic anions in water [7] and the modifications to this approach taken specifically for bromate analysis [8,9]. This technique involves the direct injection of up to 100 μl of aqueous sample onto an anion-exchange column with

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subsequent elution using suppressed conductivity detection. Anion elution order is such that employing the commonly used carbonate eluent, levels of bromate at or near the detection limit were often swamped by the peak due to chloride which is always present in natural waters at a level of 3 orders of magnitude higher. In order to alleviate this problem, researchers have employed a cation resin in the Ag^+ form as a pre-treatment step to precipitate out a large proportion of the chloride in the aqueous sample prior to injection into the IC system [10,11].

In a gallant attempt to extend this methodology to the analysis of bromate at sub ppb levels, Hautman [12] devised a selective anion concentration technique in which 12 replicate "heart-cut" analyses of 1 ml samples were successively injected and the bromate selectively diverted to a concentration column. Although this method achieved a PQL of 0.25 μg/l in natural water samples, the analysis time for each individual sample was 4 hours and only the bromate constituent was quantified.

There are no reports in the literature on the use of direct pre-concentration for increased sensitivity in bromate detection in aquatic matrices. The major fear associated with this approach has been the non-selectivity of concentration of all the anions present in the aqueous sample and the consequent possibility of overloading the concentrator column. However, coupled with the use of pre-treatment to selectively reduce the quantity of certain anions in excess with respect to the trace quantities of bromate, the technique of pre-concentration is a viable solution to the challenge of lowering the detection limits for bromate in aquatic matrices.

2. Experimental

2.1. Aqueous samples

The development of an analytical approach was undertaken initially on synthetic aqueous samples with a controlled ionic strength which paralleled that expected in typical samples obtained in water treatment. Once developed, the analytical method was applied and validated on samples obtained from natural water sources which were subjected to controlled laboratory ozonation. The characteristics of these two groups of samples are summarized in Table 1. Once validated, the method was then used to determine the bromate levels in the effluent of various water treatment plants utilizing ozone and where ambient bromide levels were different.

2.2. Sample preparation

As the goal of this work was to quantify low μg/l levels of bromate in the presence of high mg/l levels of chloride, sample pre-treatment for chloride reduction was undertaken by syringe filtering all aqueous samples through an On-Guard Ag cation resin (Dionex, Sunnyvale, CA, USA) at a rate of about 2 ml/min. The resin functions by selectively removing the silver salts with low solubilities. While this value is low for silver chloride and bromide (0.89 and 3.7 mg/l, respectively), bromate is unaffected by the resin as its silver salt has a much higher solubility (13.3 g/l).

In order to prevent the leached silver from these resins reaching the concentrator or analytical columns, a chelator column (MetPac CC-1, Dionex) was introduced between the sample loop and the concentrator column.

Table 1
Characteristics of aqueous matrices analyzed

Characteristic	Synthetic water [a] (mg/l)	Natural water [b] (mg/l)
TOC [c]	<1 (C)	7.56 (C)
Chloride	50	7.0
Nitrate	44	0.25
Sulfate	60	24
Bromide	0.2	0.05

[a] Synthetic water made by dilution of concentrates of each anion in deionized, distilled water with minimum resistance of 18.2 MΩ · cm.
[b] Natural water source was University Lake, Carrboro, NC, USA.
[c] TOC = Total organic carbon.

2.3. Instrumentation

The ion chromatographic system used in this work was the Dionex Model 4500i which was employed with the following modifications in operation. A 4-ml pre-treated aqueous sample was loaded into a loop designed from 7 m of 0.1 cm internal diameter polypropylene tubing and placed in the loading position (port numbers 3 and 6) across a 6-port rotary injection valve (Rheodyne, Cotati, CA, USA). While in this position, deionized, distilled water held in a 4-l Nalgene bottle was pumped at 0.75 ml/min, using a pulse-dampened single-piston pump, across the chelator column and through a 4-way slider valve (at port number 4) and out to waste (at port number 8). Simultaneously, the eluent for the ion chromatography was flowing at 2 ml/min through the AG10-SC concentrator column placed across the loop position on the opposite side of the slider valve (port numbers 1 and 5). The borate eluent then flowed through the AS9SC analytical column, anion membrane suppressor (AMMSII) and conductivity detector (module CDM-2). The plumbing for the chromatographic system is shown in Fig. 1 and illustrates the positions of the two valves for sample loading and sample analysis. In the pre-concentration step (valve positions shown in the insert), the deionized distilled water is used to flush the 4-ml aqueous sample at 0.75 ml/min through the MetPac CC-1 chelator column and on to the concentrator column in the same direction as eluent flow. After loading, the valves are switched back to their original positions and the concentrated sample is swept on to the analytical column. During this time, the next sample can be loaded into the loop. The analysis of bromate was performed using a 5 m*M* sodium tetraborate–boric acid eluent. Immediately after elution of the bromate peak, the eluent strength was raised to 50 m*M* to purge the remaining anions from the column. Conductivity suppression was achieved with 25 m*M* sulfuric acid regenerant at a flow rate of 10 ml/min. With a clean, equilibrated chromatographic system, a typical background conductivity at the start of the analytical run was 4 μS.

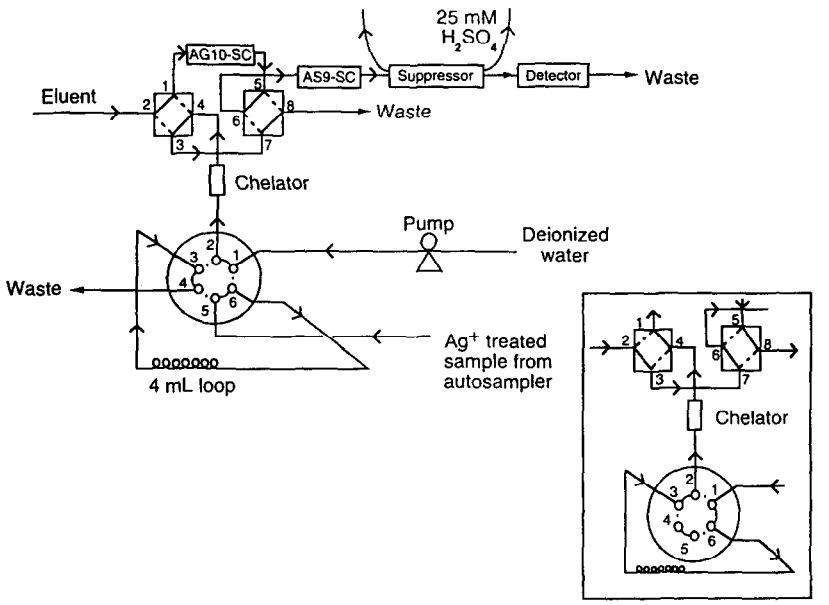

Fig. 1. Schematic of IC plumbing for loop loading or sample analysis (valve positions for sample pre-concentration shown in the insert).

2.4. Reagents

The reagent water used in the preparation of standards, eluents, and synthetic water matrix was prepared in the laboratory by a Corning 3-l mega-pure all-glass distillation system (Model LD-2a, Corning, NY, USA). The source water for the still was purified tap water which had passed through a cartridge-type deionizer (Corning Ultra High Purity) filtering and demineralizing the water. The cartridge is replaced once a month or when the conductivity of the effluent water rises above a pre-determined value.

Boric acid and sodium tetraborate decahydrate used in the preparation of a 100 m*M* concentrate for eluent use were both ACS grade materials assayed at >99.5% purity (Fisher Scientific, Pittsburgh, PA, USA). Dilutions of this stock to both 5 m*M* and 50 m*M* were made as required from the reagent water and were filtered through Whatman glass fiber filters (Whatman, Clifton, NJ, USA) in an all-glass Buchner filtration system prior to use. Sulfuric acid used as the suppressor regenerant was Ultrex purity grade (J.T. Baker, Phillipsburg, NJ, USA). Sodium bromate, chloride, nitrate, sulfate and bromide used in the preparation of the synthetic aqueous solutions were all assayed at 99% purity or higher (Aldrich, Milwaukee, WI, USA). Ethylene diamine in liquid form used in the residual disinfectant quenching experiments was also obtained from Aldrich and assayed at >99% purity.

2.5. Method

Synthetic aqueous solutions at an ionic strength of 2.74 mequiv./l were made up according to the description in Table 1. Repeated injections of 4 ml of these solutions, containing 5 μg/l bromate after passing through the silver resin and the chromatographic system described in Fig. 1, without the chelation column caused a gradual but very distinct deterioration in the resolution between bromate and the remaining chloride. This manifested itself in two ways; gradual reduction in retention time of the bromate peak and eventual coalescence of the bromate and chloride peaks. This is demonstrated in Fig. 2. The inclusion of the chelation column as shown in Fig. 1 allowed in excess of 100 injections of samples containing 10 μeq of anions before any significant deterioration in column performance could be discerned. At this time, the concentrator and analytical columns were restored to their full capacity by washing with acetonitrile for 20 min at 1 ml/min. Additional problems were identified if an anion trap placed in the eluent stream ahead of the slider valve was allowed to become overloaded or was removed. Anion impurities in the eluent will accumulate on the concentrator column and decrease its available capacity for sample anions if the anion trap does not function very effectively. Organic impurities can also affect the performance of the chromatography and may leach into aqueous samples which are stored for long periods in polymer-based autosampler vials. Preparation of these vials requires that after washing, they are filled with reagent water, capped and left to stand overnight. After this step, the vials are rinsed again several times with reagent water before being rinsed and then filled with aqueous sample to be analyzed.

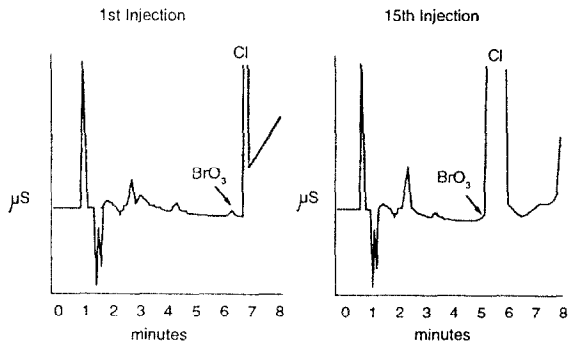

Fig. 2. Loss of bromate resolution from chloride. (Note: plumbing of Fig. 1 used without chelation column).

3. Results

3.1. Calibration

In view of the aim to optimize pre-concentration for the greatest sensitivity of bromate detection, no attempt was made in this method to quantify other anions. The chromatographic

conditions were determined from repeated injections of bromate in synthetic water and then the conditions were applied to water treatment samples for validation. Quality assurance of bromate calibration was undertaken by statistical analysis of the chromatographic response obtained from 7 injections at the 0.5 μg/l level. This concentration was selected as the lowest practical level at which a discernable response was obtained relative to the detector noise. The method detection limit (MDL) was determined according to the Code of Federal Regulations [13]:

$$MDL = tS + b$$

where $t = 3.143$ (Student's t value for 6 degrees of freedom and 99% confidence level), S = standard deviation of seven replicate analyses, and b = mean value of blank.

The blanks in these experiments were the reagent water in the synthetic matrix and raw University Lake water in the natural water matrix. In both cases, the background level of bromate was at the noise level. Applying the above definition for detection limits, a value below that selected for the determination was indicated in both matrices. An alternative approach was to study the signal-to-noise ratio and select the signal which is at 3 times the noise signal as a practical reporting level (PRL). Table 2 summarizes the statistics of both approaches and indicates that all detection limits are below the selected 0.5 μg/l level, although the actual values are slightly different for both matrices. Since quantification in field samples will normally be required in natural water matrices, it is more practical to apply the higher detection limit in sample analyses.

Calibration curves in both matrices were established from triplicate injections of bromate-spiked aqueous matrix in the range 0–5 μg/l. The regression coefficient (r^2) for both synthetic and natural water matrices was very acceptable (0.996–0.997). A typical chromatogram of one of the calibration points (1.28 μg/l) is shown for the synthetic water matrix in Fig. 3a.

Recovery studies of bromate spiked into both matrices at the 5 μg/l level indicated a slight loss of analyte in natural water compared to synthetic water and this was reflected in the slightly lower gradient of the natural water calibration curve. This is quite a common occurrence among environmental samples and has often been the source of controversy in deciding absolute concentrations in one matrix when calibration is undertaken in another. In this case, the difference is statistically insignificant although the analyst will have to assure a similar comparison when analyzing natural waters with different physical characteristics.

3.2. Laboratory controlled ozonation of surface water

The natural water characterized in Table 1 was collected at the entrance to the Orange County Water and Sewage Authority treatment plant, Carrboro, NC. 500-ml samples placed in a 1-l

Table 2
Method detection limits of bromate

	Synthetic water	Natural water
Mean concentration (μg/l) [a]	0.514	0.628
Standard deviation S (μg/l)	0.098	0.069
Statistical MDL (μg/l) [b]	0.31	0.22
Height at t_R = 5.97 min in blank (noise)	2148	3977
3 × noise	6444	11931
Noise detection limit (μg/l) [c]	0.13	0.35
Recovery of 5 μg/l spike (%)	107	95

[a] Mean value of 7 repeated injections of 0.5 μg/l bromate spiked into each matrix.
[b] Determined as 3.143s + blank.
[c] Bromate detection limit at signal-to-noise ratio of 3:1.

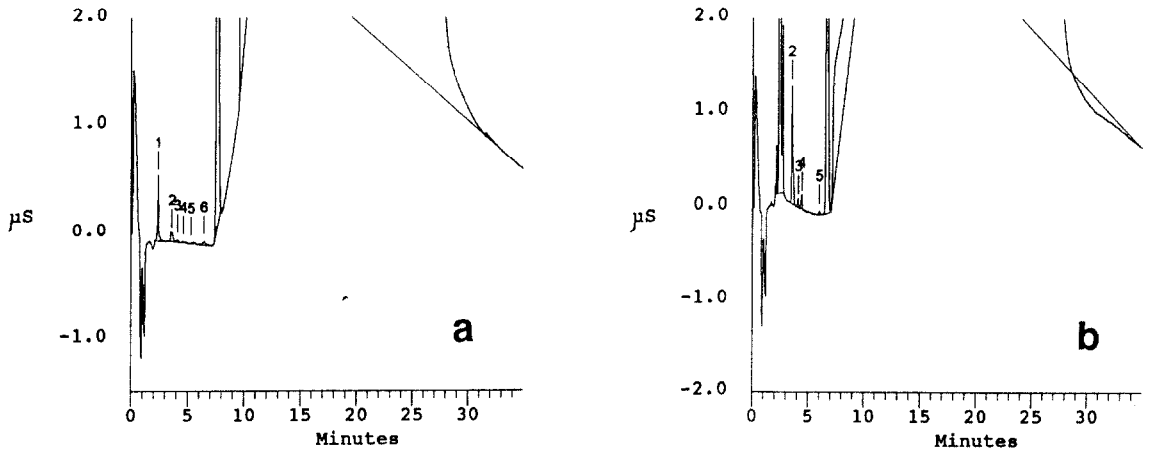

Fig. 3. Chromatogram of bromate; (a) at 1.28 μg/l in synthetic water: retention time of peak no. 6 = 6.45 min; peak area = 745 756; peak height = 35 625); (b) in ozonated University Lake water: retention time of peak no. 5 = 5.97 min; concentration of bromate found (peak no. 5) = 1.1 μg/l; peak area = 336 216 peak height = 36 708.

washing bottle were attached to a Model 200 Sander ozonizer (Erwin Sander, Vetze-Eltze, Germany) supplied by air. Ozone was supplied to the sample so that an approximate transfer of 1 mg ozone to 1 mg TOC was achieved. After ozonation, a sample was poured into a 100-ml Erlenmeyer flask and purged gently with pure nitrogen (99.9%) to remove any residual ozone from the solution. The sample was then filtered through an Ag^+ resin cartridge and into two clean autosampler vials for duplicate analysis.

For quality control purposes a sample of the raw surface water was similarly treated without ozonation. The resulting chromatogram using the stated analytical conditions and the plumbing of Fig. 1 is shown in Fig. 3b for the ozonated sample. Utilizing a calibration curve in the range of 0.5–5 μg/l bromate in synthetic water, bromate was quantified in the ozonated water at 1.1 μg/l. A 5 μg/l spiked sample of the ozonated water produced the chromatogram in Fig. 4 illustrating a recovery of 105%.

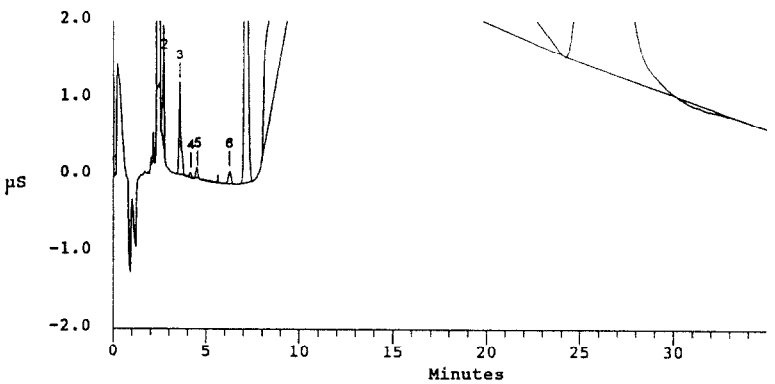

Fig. 4. Chromatogram of ozonated University Lake water with a 5 μg/l bromate spike; concentration of recovered bromate (peak no. 6) = 5.25 μg/l.

3.3. Quenching of residual disinfectant

Water treatment plants and consumers' drinking water will often contain residual disinfectants such as free chlorine, chloramines, or chlorine dioxide. Residual ozone could also be present in samples collected for bromate analysis drawn immediately after ozonation. If samples containing these oxidants were injected onto an ion exchange column, the oxidant would attack the active sites on the column causing irreversible damage. Similarly, if oxidants remain in the sample at the time of collection, bromate concentration might change as a result of continued reaction. It is therefore essential to quench such samples from residual disinfectant and such a procedure in ion chromatography should involve non-ionic reagents that will not interfere with the chromatography. In the case of ozone and chlorine dioxide, it is usually sufficient to purge the sample with nitrogen gas for 5 min. Experiment has shown that this does not cause any loss in bromate from the sample. Chlorinated samples cannot be quenched by purging and consequently require the addition of a quenching reagent. Moreover, when bromide is present in the sample, both chlorine and ozone can react with it to produce the hypobromite ion. It is this species that is directly responsible for the formation of bromate in aqueous solution [14] and thus it is essential that it be removed from the sample at the time of collection. The reagent of choice was ethylene diamine (EDA) and Fig. 5 illustrates the effectiveness of a 50 mg/l addition of EDA to natural water containing spiked bromide to 0.2 mg/l and ozonated at a 1:1 ozone:TOC level. In the absence of EDA, bromate continues to grow in concentration with time (Fig. 5a), whereas its presence appears to stabilize bromate concentration (Fig. 5b).

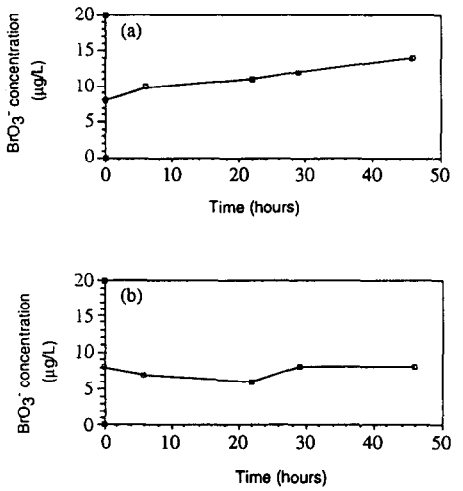

Fig. 5. Change in bromate concentration in ozonated spiked surface water; (a) without EDA quench (b) in the presence of 50 mg/l EDA.

3.4. Analysis of ozonated waters from treatment plants

Water samples were collected at various points in the treatment plants in 40-ml glass vials (Pierce, Rockford, IL, USA) equipped with polypropylene screw caps that had Teflon-faced silicone septa. Prior to dispatching these bottles to the plants, a few drops of an EDA solution (equivalent to 2 mg) were placed in the bottom of each. For the purpose of quality control, one vial was filled with reagent water and EDA solution and sent with the collection vials to each plant. This particular study focussed on analyzing samples taken prior to and following ozonation in order to quantify trace amounts of bromate. In order to characterize the sampled water, applied ozone dose and raw water TOC data were supplied by the plant and ambient bromide levels were measured with direct injection ion chromatography of a separate sample [6]. The bromate content was analyzed first using direct injection of a 100-μl sample using the same analytical conditions as previously described without chelation and pre-concentration. The purpose was to identify if bromate concentrations were in excess of 5 μg/l. If they were, the sample was diluted with synthetic water to bring the concentration in the range 0.5–5 μg/l and then the sample was reanalyzed using the pre-concentration technique. If no chromatographic response was detected by direct injection of the sample, pre-concentration was applied without dilution. The results of these

Table 3
Bromate formation in ozonated natural waters

Treatment plant	O_3:TOC (mg/mg)	Ambient Br^- (mg/l)	BrO_3^- formed (μg/l)
A	3:2.8	0.02	5
B [a]	9.2:11.6	0.18	10
C [a]	2.5:2.9	0.05	8
D_1 [a]	1.5:2.6	0.28	10
D_2 [a]	1.4:3.2	0.22	18
E	6:5.4	0.03	1.1
F	4:7.6	0.04	0.8

[a] Samples diluted 1:10 with synthetic water prior to analysis.

analyses are shown in Table 3 and in no case was bromate detected prior to ozonation. Fig. 6 illustrates the chromatogram obtained for plant F where bromate elutes at 3.47 min. This analysis was performed using the same analytical conditions as described earlier except that the run eluent was adjusted to a 10 m*M* borate mix and the regenerant flow adjusted upwards to maintain a background conductivity of 4–8 μS. Under these conditions, the analytical run time was reduced to 30 min.

4. Conclusions

Although the pre-concentration technique described here succeeded in most of the plants surveyed, highly colored surface waters analyzed prior to ozonation created some analytical problems. These raw waters contain high levels of dissolved humic materials which occupy active sites on the analytical column. This causes poor resolution of bromate from chloride in spite of pre-treatment to reduce chloride concentration and renders bromate detection impossible in highly colored raw waters. However, following ozonation of such waters, this interference is removed and resolution between the two anions is accomplished. If these colored waters are mistakenly injected onto the analytical or concentration columns, the columns are best regenerated by cleaning for about 1 h with a 4:1 mixture of acetonitrile and 1 *M* sodium chloride.

The method described in this paper has been validated for the analysis of bromate in ozonated waters at a detection limit of 0.5 μg/l which is about an order of magnitude less than currently available using traditional direct injections of samples. In practice, this method should be applicable to most aqueous samples containing bromate from as low as 0.5 μg/l to sub mg/l levels. It is important, however, to demonstrate the recovery of bromate from the matrix under investigation by analyzing samples spiked with bromate at concentration in the range expected to be found in the samples. Sample treatment and analysis using this analytical technique can be automated to an extent that total analysis

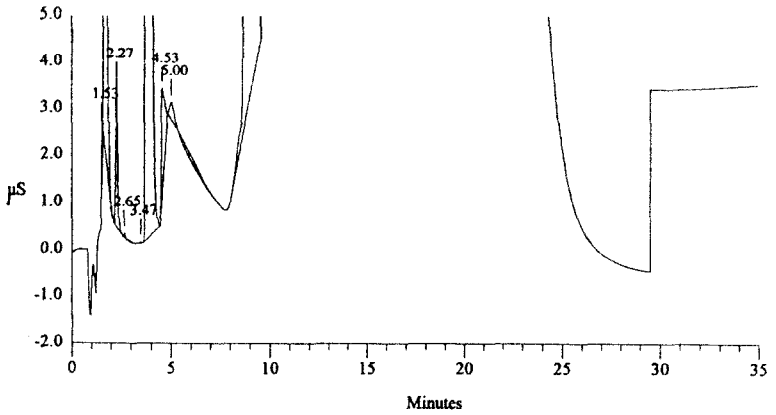

Fig. 6. Chromatogram of bromate formed in plant F at $t_R = 3.47$ min using a 10 m*M* borate eluent.

time is less than 45 min per sample making this method viable for laboratory monitoring of bromate in drinking water.

5. Acknowledgements

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