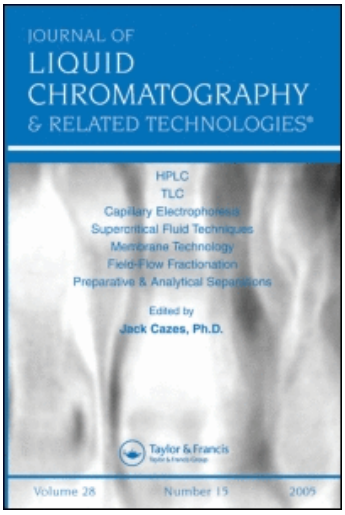

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DETERMINATION OF BROMATE IN DRINKING WATER AT THE LOW μg/L LEVEL BY COLUMN SWITCHING ION CHROMATOGRAPHY

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ABSTRACT

A simplified "heart-cut" column switching technology was used for the determination of bromate in drinking water at the low μg/L level. A simplified two-step procedure for finding the time window was established. By using sodium hydroxide as the eluent and a 150 μL sample loop, detection limits of 2.5μg/L can be obtained for bromate even if 30 mg/L of chloride is present. Spike recoveries of tap waters collected from three different areas of China were in the range 94~103%. Principles and other applications of this technique are also discussed.

INTRODUCTION

Bromate is a disinfection by-product formed during the ozonization of drinking water.[1] It was also reported that bromate forms in waters containing bromide ion in the presence of UV radiation. In addition, Macalady reported that seawater containing bromide treated with chlorine in the presence of sunlight forms bromate. Thus, bromate is a potential by-product of various disinfection processes.[2]

As bromate is a potential carcinogen, the World Health Organization (WHO) and the U.S. Environmental Protection Agency (EPA) favor the limit of 25 μg/L[3] and 10 μg/L[4] in drinking water, respectively. Both values are determined by the inability to reliably quantify lower concentrations. In the future, limitations below the low μg/L level are to be expected.

Although chlorination is the major treatment technology applied in China at present and bromate ion formation is believed not to occur in waters containing bromide when treated with chlorine dioxide,[2] it is still very necessary to find sensitive, simple, and fast analytical methods for bromate determination at low μg/L levels, so as to aid in researching ozonization process design options to minimize this contaminant.

Because chlorination of drinking water produces other carcinogens, such as the trihalomethanes and ozonization is still one of the most promising alternatives to chlorination. Development of the analytical method for this contaminant will undoubtedly speed up the innovation of the water treatment technology.

The most widely used analytical method for measuring BrO_3^- in drinking water is ion chromatography. Typically, BrO_3^- peak resolution is not a problem with standard solutions. However, drinking water can contain appreciable amounts of chloride ion that can interfere with the BrO_3^- measurement.

The inability to efficiently separate BrO_3^- in the presence of even 25 mg/L Cl^- is a major concern when the IC procedure is used for bromate measurement at the low μg/L level. Pretreatment with Ag^+ cartridges was used to precipitate Cl^- prior to sample injection,[5] however, as the efficiency of the commercially available cartridges is inconsistent. Ag^+ sample pretreatment is at times impractical and expensive for routine analysis.

An alternative procedure is to dilute the eluent and thereby increase the separation between the bromate and chloride ions, but this method is too time-consuming because of the long elution times of common anions such as sulfate ion. Moreover, the sensitivity of the bromate will decrease with the dilution of the eluent.

Post column derivation detection is another alternative for measuring bromate in water, but it can not solve the interference from nitrite.[6-8] Recently, a new promising post ion chromatography derivation method was developed for the determination of bromate. But the ion content of the sample was still restrained by the column capacity.[9]

By coupling IC with MS,[10-14] good results can be obtained. By means of on-line coupling IC-ICP-MS, the limit of detection for bromate can reach to ng/L level. However, ICP-MS is extremely expensive.

Since the concentration of chloride in tap water is always in the range of 20 to 30 mg/L and since the detection limits of bromate can reach to 2.5 μg/L in the presence of 1 mg/L chloride by using sodium hydroxide of proper concentration as the eluent, bromate of high concentration in the tap water can be determined by diluting the samples. However, this method can not be applied to determine bromate of low concentrations, especially when the concentration is lower than 100 μg/L.

In recent years, liquid chromatography matrix elimination employing "heart-cut" column-switching techniques has been demonstrated to be a powerful analytical tool.[15-19] It has universal applicability, does not suffer from the limitations associated with classical matrix elimination in liquid chromatography, and markedly reduces the column abuse that can occur when the capacity of the column has been significantly exceeded. However, it needs a time-consuming six-step procedure to optimize the heart-cut timing parameters (H-C time window) for every specific matrix.

In this paper, a "heart-cut" column switching technology, which employed a simplified two-step H-C time window determination procedure was applied to eliminate the interference of chloride. Results showed that this method can effectively eliminate the interference in tap water. Detection limits for bromate can reached to 2.5 μg/L in the presence of 30 mg/L chloride by direct injection. It is a cheap, sensitive, and fast IC method suited for the routine analysis for bromate lower than 150 μg/L in tap or related waters.

EXPERIMENTAL

Instrumentation

The brand of all the systems and columns is Dionex (Sunnyvale, CA, USA). A Model DX-300 ion chromatograph equipped with a 150 μL sample loop was employed along with a AL-450 chromatography workstation for instrument control, as well as, data acquisition and processing. AG11 guard column and AS11 separation column were used for separation. Two high-pressure 4-way valves and a concentrator column (AG-11-HC 4 mm) were utilized for the "heart-cut" column switching technique.

Detection was performed by a PED electrochemical detector in conductivity detection mode. Chemical suppression was achieved by a ASRS-I anion self-regenerating suppressor. The installation is illustrated in Figure 1. A CTC-1 column and a Model DQP-1 pump were employed to eliminate the cations in the samples.

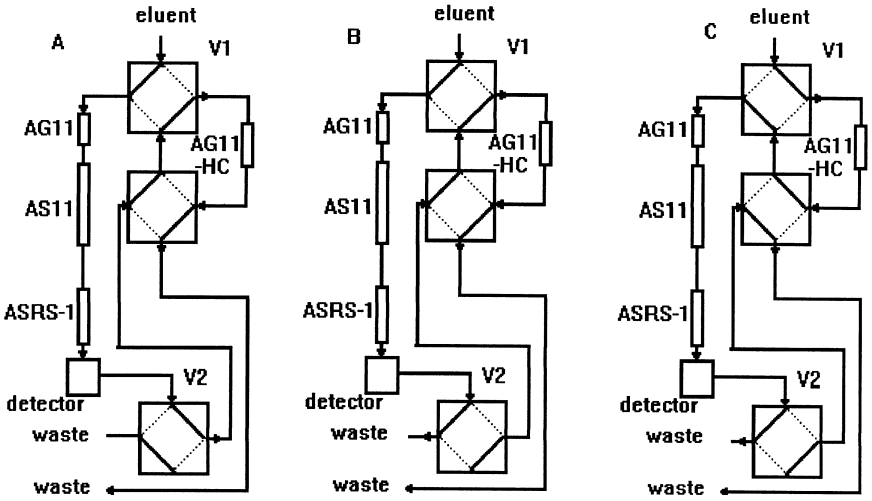

Figure 1. System configuration. The passway is shown as the bold line.

Reagents

All reagents used were of analytical reagent grade. Distilled deionized water was used throughout. All the sample solutions were pumped through CTC-1 column by Model DQP-1 pump to eliminate the cations. CTC-1 column was regenerated by 50 mmol/L HCL after every 50 mL sample solution was pumped through. All solutions were filtered through a 0.45 μm membrane filter and degassed before use. All bromate standard solutions were prepared from sodium bromate (Beijing Xinguang Chemical Reagent Factory, China). All standard solutions were made daily or refrigerated at 4 deg. centigrade for a maximum of 14 days. The eluents were: E_1: 2 mmol/L sodium hydroxide and E_2: 20 mmol/L sodium hydroxide, respectively. The flow rate was 0.8 mL/min. Regenerant was 50 mmol/L H_2SO_4. (As the Dionex equipment was made of polyether ketone (PEEK), it was not damaged by the eluent and regenerant.)

Experimental Procedure

This two-stage procedure consisted of a matrix elimination run and a bromate analysis run. In the matrix elimination run from 0 to 6.9 min, the effluent was introduced to a concentrator column (Figure 1A). Since the eluent (sodium hydroxide) was neutralized to water in the suppressor and had lost its eluent power, the effluent was collected onto the concentrator column. After

Table 1

Program for the Two-Stage Procedure

Time (min)	E_1 (%)	E_2 (%)	V_1	V_2
0.0	100	0	on	on
6.9	100	0	on	off
7.0	100	0	on	off
15.0	0	100	on	off
15.1	100	0	on	off
25.0*	100	0	off	off
35.0	100	0	on	off

Note: 1. Begin data collection. 2. The passway is shown as the bold l line in Figure 1. 3. No equilibrium is needed before the next injection. 4. E_1: 2 mmol/L $NaOH_2$; E_2: 20 mmol/L NaOH; flow rate = 0.8 mL/min.

column switching, by switching a four-way valve (V2, Figure 1B), the majority of the matrix and strong retained anions in the samples were eluted from the column to waste using gradient eluent. When all the anions in the sample were eluted from the separation column (15 minutes), the system was equilibrated for 10 min to 2 mmol/L NaOH, then the bromate analysis run (Figure 1C) was begun. The isolated bromate was then eluted from the concentrator column. The configuration of the different valves and columns are illustrated in Figure 1. The program for the two-stage procedure is list in Table 1.

RESULTS AND DISCUSSION

Principle

Suppressor plays an important role in this method. In the matrix elimination run (Figure 1A), suppressor reduces the eluent power so that the analyte anions can be retained on the concentration column. While in the bromate analysis run (Figure 1C), suppressor greatly reduced background conductance as it does in normal IC.

Sodium hydroxide was used as the eluent, because the hydroxide ion can be neutralized completely by the suppressor. Thus both the eluent power in the matrix elimination run and the background conductance in the bromate analysis run can be reduced as low as possible.

To improve the sensitivity, a large sample loop should be used. A 150 μL sample loop was used in the experiment because it was found that when injecting a larger sample the chromatographic efficiency was eroded while LOD was not significantly improved.

Separation Conditions for Bromate and Chloride

Undoubtedly, in the switching time window, separation conditions for better resolution of analyte and matrix ions can result in less residual matrix introduced to the concentration column and, thus, can reduce the interference of the matrix more effectively. However, analysis time is also an important factor that should be considered when trying to choose the separation conditions. To compromise these two factors, 2 mmol/L sodium hydroxide (flow rate = 0.8 mL/min) was chosen as the separation condition, in which baseline resolution of 1 mg/L bromate and 1 mg/L chloride was obtained and bromate was eluted within 7.0 min. The same separation conditions were used in the bromate analysis run. Thus, since the system has been equilibrated in the analysis run, no equilibration procedure is needed before the next injection and hence the time required for analysis can be shortened, especially when large amounts of samples are analyzed.

The Determination of Switching Time Window

The procedure for the determination of the time window are as follows:

1. Assemble the entire system according to Figure 1A and then find the proper separation conditions for 1 mg/L chloride and 1 mg/L bromate.

2. Equilibrate the system under the separation conditions, then inject 0.5 mg/L bromate standard solution. The interval between 0.0 min and the time for the complete elution of the bromate is defined as the time window.

When a large amount of chloride exists in the matrix, it will act as an eluent for bromate. Since chloride ion has a stronger elution strength than hydroxide ion, the bromate peak will shift forward. As this shift will vary with the concentration of the matrix, a time-consuming six-step procedure is needed to find the time window in the reported "heart-cut" method for every specific sample.

In this paper, since no anions eluted before chloride are found to interfere with bromate, we define the interval between 0.0 min and the time for the complete elution of the bromate standard solution as the time window, so that

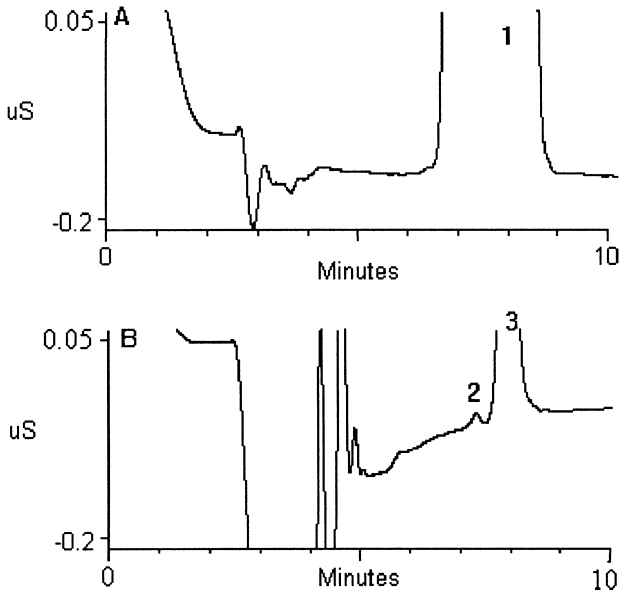

Figure 2. Bromate determination in mixed standard solution. Direct injection (sample volume 150 µL) on AG11 and AS11 column. (A) not treated with "heart-cut" technique. Conditions: 2mmol/L NaOH, flow rate = 0.8 mL/min. (B) treated with "heart-cut" technique. Conditions as in Table.1 Peaks: 1 = BrO_3^- (2.5 µL) + Cl^- (30 mg/L), 2 = BrO_3^- (2.5 µL), = Residual Cl^- (about 0.3 mg/L).

the bromate can be introduced to the concentration column complete. Considering the fact that the widespread of the peak increases with the increase of the bromate concentration, a relatively high concentration bromate standard solution (500 µg/L) was used to determine the time window.

It should be pointed out that the simplified two-step procedure is only suited for the described system (NaOH as eluent, and no anions eluted before chloride were found to interfere with bromate). For more complex matrices, the six-step procedures for finding the optimum time window for a specific matrix described by Killgore and Villasenor is still recommended.[15]

Matrix Elimination

Figure 2A illustrates that, when attempting to detect bromate of 2.5 µg/L in the presence of a high chloride level (i.e. 30 mg/L), the resolution is not sufficient to separate bromate from chloride. Figure 2B shows that by treating

the mixed standard solution (2.5 μg/L BrO_3^- + 30 mg/L Cl^-) with "heart-cut" technology, the majority of the chloride in the matrix was eliminated and the chloride level was reduced to less than 1 mg/L, which is sufficient to resolve bromate from chloride under the chosen separation conditions. It should be pointed out that in order to reduce the chloride level by the described procedure, the IC performance had to be at its optimum. It was found that after analyzing real samples for some time, impurities of sample matrix especially some cations were deposited on the column, then the bromate and chloride cannot be separated by the method. It is important that all the samples should be pretreated by CTC-1 column before analysis.

Efficiency of the Concentration Column

The performance of the concentration column is mainly limited by three factors: First is the efficiency of the suppressor. The residual hydroxide ions that are not neutralized completely in the suppressor can acted as an eluent, causing the loss of the bromate from the concentration column. The second is the time window. The residual chloride ion, which has a higher affinity for the resin can also act as an eluent. A proper time window can minimize the amount of the residual matrix. The third is the column capacity. That is, assuming that the concentration column can provide sufficient capacity to retain the bromate and the residual matrix ions together with the residual eluent ions that are not neutralized in the suppressor. In this work, a high capacity column, AG11-HC (4 x 50 mm) column is used as the concentration column.

To test the performance of the concentration column when samples of high concentration matrices were analyzed, a series of mixed standard solutions were analyzed according to the procedure described in the experimental procedure and the recoveries of the bromate retained on the concentration column were calculated. The mixed standard solutions consisted of 30 mg/L chloride and bromate of various concentrations from 2.5 μg/L to 150 μg/L.

Table 2 shows the recoveries of the bromate. It showed that, for 5 μg/L to 150 μg/L bromate, the concentration column retained a high percentage of the bromate. As regards to the low recovery of 2.5 μg/L bromate, we assume it is caused by the impurity of the eluent. As a result, the hydroxide is not neutralized completely in the suppressor. The residual hydroxide ion will inevitably elute some amount of the bromate from the concentration column.

The fact that the background conductance in the experiment (3~4 μS) is higher than the conductance of deionized water at the same flow rate (< 1 μS) also indicates the exists of the impurities in the eluent. The recovery of low concentration bromate can be improved by using eluent of higher purity.

Table 2

Recovery (%) of Bromate

Concentration (μg/L)	2.5	5.0	20	50	100	150
Missing Amount (μg/L)	0.46	0.33	0.48	0.85	0.40	5.25
Recovery (%)	81.4	93.4	97.9	98.3	99.6	96.5

Table 2 also shows that when concentrations were lower than 150 μg/L, an average of 0.4 μg/L of the bromate is missing. While for 150 μg/L bromate, the amount of the missing bromate increased to 5.25 μg/L, indicating the concentration column overloading.

Accuracy and Detection Limit

Mixed standard solutions consisted of 30 mg/L chloride and bromate of various concentrations from 5.0 μg/L to 150 μg/L and were analyzed according to the experimental procedure, three times each under the same conditions; we recorded the response, and then established the calibration curve according to the obtained response and the concentrations of the bromate in the standard solutions.

Results showed that, when the concentrations were from 5.0 μg/L to 150 μg/L, correlation coefficient of peak area was 0.9997. Limit of detection was found to be 2.5 μg/L. The R.S.D. based on the determination of 30 μg/L bromate (n = 7) is 3.4%.

Analysis of Samples

Three tap waters from different areas of China were analyzed. The samples are: No.1, from XinJiang Autonomous Region, which is in the northwest of China; No. 2, from AnHui province in southeast of China; No. 3, from Beijing in north of China. No bromate was found in these three tap waters.

The spike recoveries are listed in Table 3. Results showed that the matrices in these three tap waters did not interfere with the determination of bromate.

Table 3

Determination of Bromate in Tap Water

Sample	Spike (μg/L)	n	Mean Recovery (%)	R.S.D. (%)
1	25	5	94.5	3.8
2	30	6	103.4	3.5
3	40	5	97.9	2.7

CONCLUSION

The "heart-cut" technology performed accurate and precise analysis for the determination of bromate at low concentrations in the presence of high concentration chloride in a relatively short time and at a low cost without pretreatment. As bromate is a weakly retained ion and the separation for bromate and chloride is very difficult, the demand for either the concentration column or the switching time window is strict. Since the determination of bromate at the low μg/L level in the presence of high concentration chloride is a rather difficult problem, the successful application of this method indicates that the application of this versatile technique to quantify analytes of low concentration in a wide range of sample matrices is promising.

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