# On-line preconcentration and determination of trace amounts of bromate in drinking water

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## ABSTRACT

A simple, accurate, sensitive method was proposed for on-line preconcentration and determination of trace amount of bromate in drinking water. Based on the decolorizing reaction resulting from the oxidation of methyl orange with bromate in 3.6mol $L^{-1}$ hydrochloric acid medium, the decrease percentage in color was directly proportional to the bromate amount at 510nm. The optimal experimental conditions, including reaction conditions and preconcentration conditions had been obtained. The liner range of the proposed method was between 2.5 to 100μg $L^{-1}$ and the detection limit was 0.76μg $L^{-1}$. The relative standard deviation was 1.67% for 10μg $L^{-1}$ bromate(n=12). The method has been applied successfully to bromate determination in drinking water samples and the recoveries were 96.5% ~106.5%.            © 2008 Trade Science Inc. - INDIA

## INTRODUCTION

Bromate is a disinfection byproduct(DBP) anion produced from the ozonation of source water containing bromide. Bromate has been judged as a potential carcinogen by both the World Health Organization (WHO) and the US Environmental Protection Agency (EPA) and has been classified as a group 2B probable human carcinogen[1]. Research shows that the rate of cancer-causing is 0.1% and 0.01% respectively if people chronically drink water containing 5.0μg $L^{-1}$ and 0.5μg $L^{-1}$ of bromate[2]. The EPA has proposed a maximum contaminant level (MCL) of 10μg $L^{-1}$ of bromate in drinking water and the WHO also set a guideline of 10μg $L^{-1}$ of bromate in drinking water[3]. Therefore, determination of bromate in drinking water has become a grave concern for people[4-6]. Up to now, there are some methods for bromate determination including extractive flotation photometric method[6], ion chromatography method[7,8] and decolorizing spectrophotometric method[9-12]. Yet, some of them are instrument-expensive; some are time-consuming; some are operation-troublesome; others are solvent-toxic while decolorizing spectrophotometric method was applied differently because of its simple operation and fast analysis.

Decolorizing spectrophotometric methods can not directly determine bromate in drinking water because of very low concentration. Therefore, a new method of flow injection preconcentration online was proposed for the spectrophotometric determination of low concentration bromate in drinking water. The method was based on the decolorizing reaction which resulted from

the oxidation of methyl orange by preconcentrated bromate in 3.6mol L$^{-1}$ hydrochloric acid medium and was applied successfully to the determination of bromate in drinking waters. Compared with existing decolorizing spectrophotometry of determination of bromate in drinking water (sample preconcentration treatment by adopting direct heat or microwave heat), the proposed method was proved to be simple and easy to perform.

## EXPERIMENTAL

### Apparatus

A model ZJ-la automatic metallic element analyzer[13] developed and produced successfully by Professor Zhang xinshen of our own laboratory was used. The analyzer has the functions of flow injection analysis (FIA), and ion chromatography and automatic sample injection.The function flow injection analysis was applied to determine bromate. Two analytical pumps of flow injection analysis were used to deliver all solutions. One was used to deliver eluant and reagent solution. The other pump is used to deliver sample solution. Polytetrafluoroethylene(PTFE) tubing of 0.5mm in internal diameter was used as the channels for all solutions to circulate.

Ultraviolet and visible spectra were obtained using a Spectrum lab S54. The absorbance intensity was recorded at 510nm on an IBM-PC. Data acquisition and processing were performed with HW-2000 Chromatography software running under Windows XP.

### Preparation of solution

Stock standard solution of bromate: 1000mg L$^{-1}$; Methyl orange solution: 0.001mol L$^{-1}$ ; Sodium chloride(NaCl) solution: 0.5mol L$^{-1}$; Hydrochloric acid (HCl): 6mol L$^{-1}$; Reagent solution(R): mixture of $4\times10^{-5}$mol L$^{-1}$ methyl orange and 3.6mol L$^{-1}$ HCl. All solutions were prepared with deionized water.

### Preparation of preconcentration column

The preconcentration column developed by our laboratory was filled with whole exchange capacity of strong-base anion exchange resin with quaternary amine functional group. The exchange capacity of resin was 3-4mmol g$^{-1}$; filling granularity was 30-50μm.The preconcentration column length was 40mm and its in-

ternal diameter was 5mm.

By filling the preconcentration column, mix resin and deionized water into pasty matter drop slowly into column with burette. After sedimentating for a moment, resin was dropped slowly until the preconcentration column became full. Then cover strainer and cover on the column and wash a few minutes with deionized water for further work.

### Analytical procedure

The FIA manifold used was outlined in figure 1 with PTFE pipes. The sample solution was injected into preconcentration column to preconcentrate. When the instrument was put into analyzing position, the preconcentrated bramote eluted by eluant was pushed to the three-way cock and mixed with the reagent (admixture of methyl orange solution and hydrochloric acid) in the reaction coil. The methyl orange was then oxidated and carried into the flow cell. The absorbance intensity of the decolorizing complex was determinedat 510nm by detector and transformed to a signal of the peak which was recorded by HW-2000 software on a PC.

## RESULTS AND DISCUSSION

### Choice of reaction conditions

### 1. Choice of pH

In the flow injection analysis, the absorbance of decolorizing complex was affected by pH of the reaction medium. The effect of pH on oxidation of methyl orange was tested in the hydrochloric acid concentration ranging from1.2 to 4.8mol L$^{-1}$. The test results in the figure 2 showed that the peak height increased when concentration of hydrochloric acid changed from 1.2mol L$^{-1}$ to 3.6mol L$^{-1}$ and that the peak height decreased when concentration of hydrochloric acid changed from
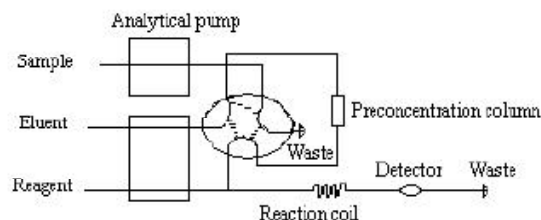


**Figure 1 : Schematic diagram of the flow injection concentration online**
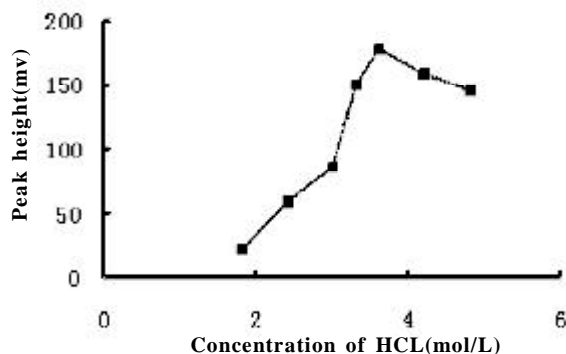
*Full Paper*



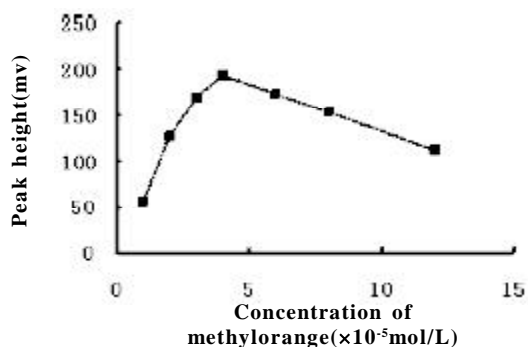**Figure 2 : Effect of concentration of HCl on the peak height**



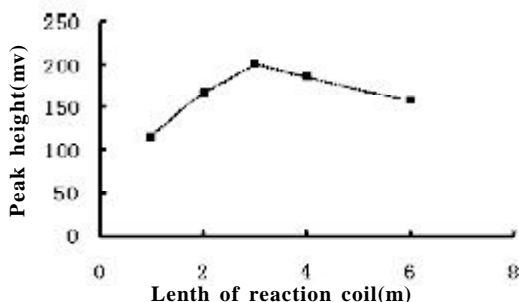**Figure 3 : Effect of concentration of methyl orange on the peak height**



**Figure 4 : Effect of length of reaction coil on the peak height**

$3.6$mol $L^{-1}$ to $4.8$mol $L^{-1}$. In low concentration of hydrochloric acid, oxidation capability of bromate augmented while hydrochloric acid concentration increased and its decolorizing complex was red. In high concentration of hydrochloric acid, bromate was deoxidized in excess and its decolorizing complex was yellow. The results also showed that the maximum peak height could be obtained when concentration of hydrochloric acid was $3.6$mol $L^{-1}$. Thus, $3.6$mol $L^{-1}$ of hydrochloric acid was selected as the optimal concentration for the further work.

## 2. Concentration of methyl orange

The reagent concentration was an important factor in flow injection analysis. The effect of methyl orange concentration on the peak height were tested from $1 \times 10^{-5}$ mol $L^{-1}$ to $1.2 \times 10^{-4}$ mol $L^{-1}$ in figure 3 .The results showed that the peak height rose when concentration of methyl orange changed from $1 \times 10^{-5}$ mol $L^{-1}$ to $4 \times 10^{-5}$ mol $L^{-1}$ and the peak height declined when concentration of methyl orange changed from $4 \times 10^{-5}$mol$L^{-1}$ to $1.2 \times 10^{-4}$ mol $L^{-1}$. The tested results also showed that the maximum peak height could be obtained at the methyl orange concentrations of $4 \times 10^{-5}$mol $L^{-1}$.

## 3. Choice of reagent flow rate

In the FIA, the reagent flow rate could affect sensitivity of method. In the study, the reagent flow rate was adjusted by pump pipe internal diameter. Therefore, the effect of flow rate of reagent solution on the peak height was studied from $0.10$L min$^{-1}$ to $0.72$mL min$^{-1}$. The test results showed that the best result could be obtained when the flow rate of reagent was set at $0.23$ mL min$^{-1}$.

## 4. Choice of the reaction coil length

If reaction coil was too short, the reagents would react incompletely. If reaction coil was too long, it would be time consuming. Therefore, reaction coil length was tested from 1 to 6m. The study results in figure 4 showed that 3m of the reaction coil length was the optimum and further increase of reaction coil length did not increase peak height. Thus, 3m of the reaction coil length was chosen as optimal parameter.

### Choice of preconcentration condition

### 1. Choice of filling granularity and length of precon centration column

Filling granularity and length of preconcentration column could affect the effect of preconcentration. In the study, filling granularity of $30 \sim 50 \mu m$ was selected and length of preconcentration column from 20mm to 80mm was tested. The results showed that the shorter the length of preconcentration column the higher the sensitivity. However, if the length of concentration column was too short, the concentration of preconcentration bromate was not adequate, which lowered the sensitivity. The highest sensitivity was obtained when the
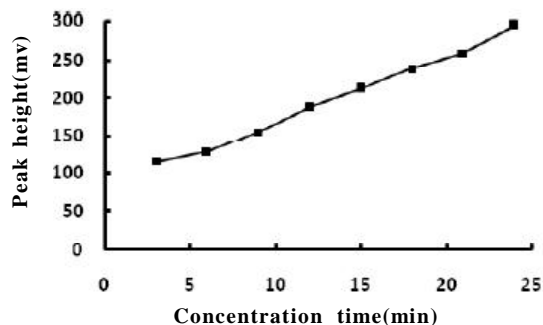
**Figure 5 : Effect of preconcentration time on the peak height**

length of concentration column was 40mm. Thus, 40mm of concentration column length was selected for further study.

## 2. Choice of preconcentration time

Preconcentration time can affect analysis sensitivity and sampling frequency. Preconcentration time was tested from 3min to 24min. The results in figure 5 showed that the longer the preconcentration time, the higher the analysis sensitivity, but the lower the sampling frequency.

Taken a comprehensive consideration of analysis sensitivity and sampling frequency, preconcentration time of 10min was decided for further work.

## 3. Choice of preconcentration rate

Either too high or too low concentrated rate was not proper. Too high preconcentration rate would increase analysis sensitivity but augment pressure of preconcentration column which would cause leakage or pump pipes rupture. Too low preconcentration rate would reduce analysis sensitivity and sampling frequency but augment the preconcentration time. Taken a comprehensive consideration of analysis sensitivity and sampling frequency, preconcentration rate of 3min $L^{-1}$ was chosen for further work.

## 4. Choice of eluant concentration

If eluant concentration was too low, bromate in preconcentration column would elute incompletely. If eluant concentration was too high, it would waste reagent. In the study, sodium chloride was selected as eluant and its concentration was 0.5mol $L^{-1}$.

## 5. Choice of eluant flow rate

The sensitivity was greatly affected by flow rate of

eluent. If flow rate was too high, the sensitivity augmented and base line noises increased. If flow rate was too slow, bromate in preconcentration column would elute incompletely, which caused sensitivity decline. The result showed that flow rate of 0.5mL $min^{-1}$ of eluent was optimal for further work.

## Linearity and precision and detection limit of the proposed method

To assess the reproducibility and accuracy of the proposed method, under the selected condition above, tests of linearity and precision and detection limit were conducted. The linearity was tested by a series of working standard solutions of bromate ranging from 0.5g $L^{-1}$ to 150μg $L^{-1}$. Test showed that the peak height versus bromate concentration was linear within the range of 2.5μg $L^{-1}$ to 100μg $L^{-1}$. The curve was H=2.152C-0.7519[H: peak height; C: bromate concentration(μg $L^{-1}$)] and the correlation coefficient obtained was 0.9997 and the detection limit(3 times of base line noises) of method was 0.76μg $L^{-1}$. The test of precision was conducted by twelve injections of 10μg $L^{-1}$ bromate standard solution into tap water sample. The results showed that the RSD was calculated as 1.67%.

## Effect of interference ions

Under the selected conditions above, the effect of interference ions was tested by analyzing a standard solution of 8.0μg $L^{-1}$ of bromate, in which each foreign ion with certain concentration was added. The results of test showed that the following ions did not interfere with a relative error of less ± 5%: a great deal of $K^+$, $Na^+$, $Cl^-$, $Ca^{2+}$, $Mg^{2+}$, $Ba^{2+}$, $Zn^{2+}$, $Al^{3+}$, $NH_4^+$(20mg $L^{-1}$); $Cu^{2+}$, $Mn^{2+}$, $F^-$, $SO_4^{2-}$, $PO_4^{3-}$, $NO_3^-$, $CO_3^{2-}$, $CH_3COO^-$ (15mg $L^{-1}$); $Fe^{3+}$, $SCN^-$(5mg $L^{-1}$); $IO_3^-$, 4mg $L^{-1}$, $I^-$, $SO_3^{2-}$(2mg $L^{-1}$). However, the oxidative anion such as $MnO_4^-$, $Cr_2O_7^{2-}$, $ClO^-$, $ClO_3^-$, $ClO_2^-$ interfered. 0.02mol $L^{-1}$ HCOONa was added to eliminate interference of each interfered ion above of 5mg $L^{-1}$ respectively. Thus, the results showed that the proposed method had good selectivity.

## Application

The proposed method was applied to determine bromate in four drinking water samples on the ZJ-la automatic metallic element analyzer. The analysis results of samples were shown in TABLE 1.

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**TABLE 1 : Determination of bromate in drinking water**

| Sample | Bromate($\mu g\ L^{-1}$) | | | |
| --- | --- | --- | --- | --- |
| | Sample concentration | Added | Found by the method | Recovery (%) |
| Tap water | 0.00 | 50.00 | 53.27 | 106.54 |
| Pure water | 0.00 | 50.00 | 52.63 | 105.26 |
| 1# table water | 3.31 | 50.00 | 52.98 | 99.34 |
| 2# table water | 0.00 | 50.00 | 48.26 | 96.52 |

To prove the applicability of the method, a test of recovery was conducted by accurately adding known concentration of bromate into each sample whose original bromate had been determined. The test results in TABLE 1 showed that the recoveries varied from 96.5% to 106.5% and analytical results of the proposed method were satisfactory. Therefore, the proposed method was suitable for determination of trace amounts of bromate in drinking water.

## CONCLUSION

The proposed method was significant with regard to the development of a simple, reliable and precise flow injection method for on-line preconcentration and determination of trace amounts of bromate in drinking water samples. Higher sensitivity, selectivity and broad determination range ($2.5\mu g\ L^{-1}$ to $100\mu g\ L^{-1}$) of bromate were just some of the advantages of this method. Furthermore, the preconcentration column of whole exchange capacity of strong-base anion exchange resin was used to preconcentrate the samples. The model ZJ-la automatic metallic elements analyzer developed by our own laboratory was cheap, small and easy to move.

## ACKNOWLEDGMENT

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