Elimination of Memory Effects and Simultaneous Determination of B, Br, I, Hg, Bi, and Sb in Groundwater Samples by Inductively Coupled Plasma Mass Spectrometry

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INTRODUCTION

Water, especially groundwater, is a versatile and important solvent. Because of the large area that groundwater covers, as well as the extensive contact with the surrounding geological environment and a long contact time, many rock and mineral components can dissolve in groundwater, which provides a variety of micronutrients to humans. However, in addition to providing beneficial mineral content and bio-essential elements, groundwater may also give rise to undesirable or toxic properties when various elements are either present in excess or in very low concentrations (1). Therefore, the evaluation and determination of the concentration of micronutrients in groundwater is important.

Several instrumental analytical techniques can be adopted for the analysis of micronutrients in groundwater, such as atomic absorption spectrometry (2,3), atomic fluorescence spectrometry (4,5), inductively coupled atomic emission spectrometry (ICP-AES) (6,7), and inductively coupled plasma mass spectrometry (ICP-MS) (8,9). ICP-MS has been widely used

ABSTRACT

In this study, elimination of the memory effects of B, Br, I, Hg, Bi, and Sb and their simultaneous determination in groundwater samples were studied in detail by inductively coupled plasma mass spectrometry (ICP-MS). The memory effects were eliminated with a wash run of 4.5 minutes with a 0.5% $\text{NH}_3 \cdot \text{H}_2\text{O}$ /0.5% NaF/10 mg L^{-1} Au solution. Good agreement between the measured and the reference values of the CRM samples indicated the effectiveness of this method. A good linear calibration curve was obtained with a correlation coefficient of 0.9999. Therefore, a method for the simultaneous determination of B, Br, I, Hg, Sb, and Bi in groundwater samples by ICP-MS was established.

for the simultaneous determination of trace elements in groundwater because of its high sensitivity, good precision, analysis speed, and the ability to perform multi-element measurements. However, in the analysis of B, Hg, Br, I, Bi, and Sb, various problems are encountered when conventional 2% HNO_3 solution is used, such as a long washout time, non-linear calibration curves, and decreasing sensitivity over time, because these elements can adhere to the walls of the spray chamber and the transfer tubing of the sample introduction system (10-12) causing the memory effect.

Several scholars have conducted research in order to eliminate the memory effect of B, Hg, Br, I, Bi, and Sb. For B, the memory effect could be eliminated by performing wash runs between sample runs using $\text{NH}_3 \cdot \text{H}_2\text{O}$, NaF, and Mannitol blanks (11,13-15). To effectively eliminate the memory effect for Br and I, washing with a dilute ammonia solution is required (16-18). For Hg, a number of methods have been proposed to eliminate its memory effect, such as washing with hydrobromic acid (19), addition of gold (20,21), 2-mercaptoethanol (ME) (22), Triton® X-100/ammonia/ethylenediaminetetraacetic acid (EDTA) (23), L-cysteine (24-26), and salts (27). For Sb and Bi, the memory effect could be eliminated by washing with 0.1% HF or 6% HNO_3 (28). However, elimination of the memory effects of B, Hg, Br, I, Bi, and Sb and their simultaneous determination has not been reported.

This paper describes a method used for elimination of the memory effects of B, Br, I, Hg, Sb, and Bi and their simultaneous determination in groundwater samples by ICP-MS, verified by using reference materials BCR-11, ERM-CA011, ERM-CA615, and GBW09114.

EXPERIMENTAL

Instrumentation

A PerkinElmer® ELAN® DRC-e™ (Dynamic Reaction Cell™) ICP-MS instrument was used (PerkinElmer Corporation, Shelton, CT, USA).

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The sample introduction system is comprised of a cyclonic spray chamber (PC3, Elemental Scientific, USA) with a 1.0-mm i.d. alumina injector. The typical operating parameters of the DRC™-ICP-MS used for this work are summarized in Table I. Under the operating conditions, the sensitivity of ^{115}In was $>25,000 \text{ cps/ng}\cdot\text{mL}^{-1}$, and the oxide production rate, calculated as the ratio of CeO/Ce , was $<3\%$.

Reagents and Standards

High-purity water ($18.2 \text{ M}\Omega \text{ cm}^{-1}$) used in the preparation of the blanks, standards, and sample solutions was obtained from a Millipore® water purification system (Millipore® Corporation, France). The single-element stock solutions (B, Br, I, Hg, Sb, Bi, and Au) were purchased from the National Center for Analysis and Testing of Steel Materials, P.R. China. Nitric acid (HNO_3 , 65–70%, w/w, 99.9999%) and ammonium hydroxide (NH_4OH , 28–30%, w/w, 99.9999%) were purchased from Beijing Chemical Reagent Research Institute.

Analytical Procedure

In order to determine the blank, different washing solutions were introduced to the ICP-MS system for 1 minute. The mixed standards in 2% nitric acid medium were then continuously introduced into the ICP-MS for ~1 minute (2 runs); no rinse was performed between the individual runs. Then the system was cleaned using different washing solutions.

RESULTS AND DISCUSSION

Subdivision of B, Br, I, Hg, Sb, and Bi into Groups

It is known that the memory effects of B, Br, I, Hg, Sb, and Bi increase the blank counts and worsen the analytical performance of ICP-MS. Al-Ammar et al. (11)

TABLE I
Instrumental Operating Parameters

ICP-MS	PerkinElmer ELAN® DRC™-e
Sample Introduction	PFA-400 Micro Flow Nebulizer
Spray Chamber	Cyclonic Spray Chamber (PC3 Peltier Chiller), Room Temperature
Injector Tube	1.0 mm i.d. Quartz
RF Power	1300 W
Plasma Gas Flow	16 L min ⁻¹
Auxiliary Gas Flow	1.0 L min ⁻¹
Nebulizer Gas Flow	0.80 L·min ⁻¹
Auto Lens	On
Dwell Time	50 ms
Sweeps	20
Readings	1
Replicate	3
Cones	Ni

and Farhat et al. (29) considered that it originates from the tendency of B to volatilize as boric acid from the sample solution layer that covers the inside surface of the spray chamber, while Hg can adhere to the walls of the spray chamber and the transfer tubing of the sample introduction system (10,22). Similarly, Br, I, Sb, and Bi can also adhere to the walls of the spray chamber (28,30-32). To reduce the blank counts due to memory effects, prolonged washing of the sample introduction system is often necessary. However, a simple way for minimizing memory effects is to rinse the system with a flush solution.

In order to find a suitable washing solution, B, Br, I, Hg, Sb, and Bi were divided into three groups: the first group comprised B, Br, and I; the second group contained Hg; and the third group included Sb and Bi.

Elimination of Memory Effects of B, Br, and I

Samples with high halogen (Br, I) and B concentrations can produce a critical memory effect, which reduces the sensitivity and

stability of the ICP-MS signals in subsequent samples. In the preliminary study, B, Br, and I solutions ($100 \mu\text{g L}^{-1}$) were introduced to the instrument for ~1 minute (2 runs), and then removed using different washing solutions for an additional 6 minutes. The effects of the different washing solutions used are shown in Figure 1. It can be seen that a lower concentration (0.25%) of ammonia solution ($\text{NH}_3\cdot\text{H}_2\text{O}$) is less effective than a higher concentration (0.5%). Also, the washing effect of 0.5% $\text{NH}_3\cdot\text{H}_2\text{O}$ mixed with 0.5% sodium fluoride (NaF) solution was better than that of 0.5% $\text{NH}_3\cdot\text{H}_2\text{O}$ alone. The memory effect of B, Br, and I could be reduced to the blank value within 0.5, 2.0, and 4.0 minutes, respectively.

Elimination of Memory Effect of Hg

The memory effect of Hg increases the blank count and deteriorates the analytical performance of ICP-MS (25). To reduce the blank count, prolonged washing of the sample introduction system is often necessary. It has been suggested that adding an Au solution to the system is effective in reducing the

memory effect of Hg (20,21). We compared the washing effects of 0.5% $\text{NH}_3 \cdot \text{H}_2\text{O}$ /0.5% NaF, 3% HNO_3 , 0.5% $\text{NH}_3 \cdot \text{H}_2\text{O}$ /0.5% NaF/10 mg L^{-1} Au, and 3% HNO_3 /10 mg L^{-1} Au solutions (Figure 2). The results clearly showed that the washing effect of the $\text{NH}_3 \cdot \text{H}_2\text{O}$ solution was superior to that of the nitrate solution, and that the washing effect of the Au-containing solution was superior to that without Au. Under the experimental conditions used, the memory effect of Hg could be

reduced to the blank value within 3 minutes by using the 0.5% $\text{NH}_3 \cdot \text{H}_2\text{O}$ /0.5% NaF/10 mg L^{-1} Au solution (the background value of B, Hg, Br, I, Sb, and Bi in Au stock solutions has been tested, and it can be ignored), which was also the most effective washing solution.

Elimination of Memory Effects of Sb and Bi

Hu et al. (28) studied the memory effects of Sb and Bi in ICP-MS in

detail and found that the washout effect of 0.1% HF was better than that of 6% HNO_3 and 0.1% HClO_4 . However, for non-HF-resistant systems, washout with 0.1% HF was not applicable. In the next study, the washing effect of diluted HNO_3 , diluted HNO_3 /10 mg L^{-1} Au, and 0.5% $\text{NH}_3 \cdot \text{H}_2\text{O}$ /0.5% NaF/10 mg L^{-1} Au solutions were compared. Figure 3 showed that the amount of Bi adsorbed by the sample introduction system was much larger than the amount of Sb adsorbed by the

Fig. 1 (a,b,c). Washing curves illustrating the removal of 100 $\mu\text{g L}^{-1}$ B, Br, and I, respectively, with different washing solutions.

Fig. 2. Washing curves illustrating the removal of 100 $\mu\text{g L}^{-1}$ Hg using different washing solutions.

low nitric acid medium (2% HNO_3). For Bi, the washout effect of diluted HNO_3 /10 mg L^{-1} Au was better than that of diluted HNO_3 , and the memory effect could be reduced to the blank value within 3.5 minutes with the 6% HNO_3 /10 mg L^{-1} Au solution or within 4.5 minutes with the 0.5% $\text{NH}_3\cdot\text{H}_2\text{O}$ /0.5% NaF /10 mg L^{-1} Au solution. As for Sb, the memory effect could be reduced to the blank value within 0.5 minutes with all of the washing solutions except water, and the

blank value of the nitric acid solution was higher than that of the $\text{NH}_3\cdot\text{H}_2\text{O}$ solution. From these results, it is clear that the 0.5% $\text{NH}_3\cdot\text{H}_2\text{O}$ /0.5% NaF /10 mg L^{-1} Au solution showed best results.

In summary and as can be seen from Figures 1, 2, and 3, when the simultaneous determination of B, Hg, Br, I, Bi, and Sb in groundwater samples is performed by ICP-MS, the memory effects of these elements can be eliminated with a

wash run of 4.5 minutes with 0.5% $\text{NH}_3\cdot\text{H}_2\text{O}$ /0.5% NaF /10 mg L^{-1} Au solution. For verification, a mixed standard solution containing 100 $\mu\text{g/L}$ B, Br, I, Hg, Sb, and Bi was measured six times consecutively based on the experimental methods. Figure 4 shows that the memory effects of these six elements can be effectively eliminated by the selected washing solution and confirms that the method established is effective and reliable.

Fig. 3 (a and b). Washing curves illustrating the removal of 100 $\mu\text{g L}^{-1}$ introduced Sb and Bi, respectively, using different washing solutions.

Fig. 4. Washing curves illustrating the removal of 100 $\mu\text{g L}^{-1}$ B, Br, I, Hg, Sb, and Bi, using 0.5% $\text{NH}_3\cdot\text{H}_2\text{O}$ /0.5% NaF /10 mg L^{-1} Au solution.

TABLE II
Analysis Results of Reference Materials

		B ($\mu\text{g L}^{-1}$)	Br ($\mu\text{g L}^{-1}$)	I ($\mu\text{g L}^{-1}$)	Hg ($\mu\text{g L}^{-1}$)	Sb ($\mu\text{g L}^{-1}$)	Bi ($\mu\text{g L}^{-1}$)
BCR-611	TM ^a		94 $\pm$ 3				
	RV ^b		93 $\pm$ 4				
ERM-CA011b	TM ^a	950 $\pm$ 46				5.1 $\pm$ 0.22	
	RV ^b	952 $\pm$ 48				5.1 $\pm$ 0.23	
ERM-CA615	TM ^a				0.036 $\pm$ 0.003		
	RV ^b				0.037 $\pm$ 0.004		
GBW09114	TM ^a			61 $\pm$ 5			
	RV ^b			61 $\pm$ 6			
GBW(E)080271	TM ^a						100 $\pm$ 1
	RV ^b						100 $\pm$ 1

^a TM = This method.

^b RV = Reference value.

Analytical Characteristics

The method's limit of detection (LOD) and a good linear calibration curve with a correlation coefficient of 0.9999 ($n=6$) were obtained. The LOD for B, Hg, Br, I, Bi, and Sb was 0.5, 0.01, 0.2, 0.04, 0.005, and 0.06 $\mu\text{g L}^{-1}$, respectively. The LODs were determined from three sets of standard deviations (SD) from 20 consecutive measurements of the reagent blanks.

To investigate the accuracy and precision of the proposed method, similar matrix reference materials were analyzed, i.e., BCR-11 Groundwater: low-level bromide, ERM-CA011 Hard drinking water: metals, ERM-CA615 Groundwater: trace elements (obtained from the Institute for Reference Materials and Measurements, Geel, Belgium), and GBW09114 Water standard material: iodine, GBW(E)080271 Water standard material: bismuth (obtained from the Institute of the National Standard Substances, P.R. China). As shown in Table II, the analytical results were in good agreement with the certified values for the studied trace elements.

CONCLUSION

A method for the elimination of the memory effects of B, Br, I, Hg, Bi, and Sb and their simultaneous determination in groundwater samples by ICP-MS was established. The memory effects of the elements could be eliminated by washing for 4.5 minutes with 0.5% $\text{NH}_3 \cdot \text{H}_2\text{O}$ /0.5% NaF/10 mg L^{-1} Au solution. Good agreement was found between the measured and reference values of the CRM samples, indicating the effectiveness of this method.

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