Speciation and Determination of Inorganic Antimony by Solidified Floating Organic Drop Microextraction and ETV-ICP-MS

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INTRODUCTION

In recent years, antimony (Sb) has been extensively used in dyestuffs, alloys, glass, flame retardants, pharmacy, and semiconductors (1-2). As a ubiquitous and cumulative toxic element, Sb may cause a wide variety of adverse health effects such as respiratory tract irritation, dermatitis, conjunctivitis, suppuration of the nasal septum, gastritis, and cellular damages in the lungs (3). In particular, the physicochemical and toxic properties of Sb strongly depend on its chemical forms. In the environment, Sb mainly occurs in two oxidation states as Sb(III) and Sb(V). The inorganic species of Sb are more toxic than its organic ones (4). The toxicity of Sb(III) is 10 times higher than that of Sb(V) (5, 6). Therefore, a reliable and accurate method is necessary for the inorganic speciation of Sb in environmental samples.

Several detection techniques for elemental speciation mainly include atomic absorption spectrometry, inductively coupled plasma atomic emission spectrometry, inductively coupled plasma mass spectrometry (ICP-MS), and atomic fluorescence spectrometry (7-14). However, an effective separation and preconcentration method for elemental speciation is required before analysis by these techniques. It is worth noting that liquid phase microextraction (LPME) has attracted considerable interest since it was reported in the

ABSTRACT

In this work, a novel method was developed for the speciation of inorganic antimony by solidified floating organic drop microextraction (SFODME) and electrothermal vaporization inductively coupled plasma mass spectrometry (ETV-ICP-MS). Ammonium pyrroinedithiocarbamate (APDC) was used as both a chelating reagent in SFODME and a chemical modifier in ETV. Sb(III) could react with APDC to form complexes at pH 6.0, and the complexes were quantitatively extracted into the organic phase of 1-dodecanol, whereas Sb(V) remained as free species in the aqueous phase. Sb(III) was directly determined by ETV-ICP-MS. Total Sb was determined by the same method after reducing Sb(V) to Sb(III). The concentration of Sb(V) was obtained by subtracting Sb(III) from total Sb. The main factors affecting the separation and determination were examined in detail. Under optimized conditions, the detection limits were 0.54 pg mL^{-1} and 0.71 pg mL^{-1} for Sb(III) and Sb(V), respectively. The relative standard deviations for Sb(III) and Sb(V) were 5.3% and 4.6% ($c=1.0 \text{ ng mL}^{-1}$, $n=9$), respectively. This method was applied for the speciation of inorganic antimony in natural water samples and a standard reference material with satisfactory results.

analytical sciences (15, 16). LPME has different extraction modes, including single drop microextraction, hollow fiber liquid phase microextraction, and dispersive liquid-liquid microextraction (15, 17-

19). The major idea behind LPME techniques is a great reduction in the volume ratio of acceptor to donor phase. However, there are still some inherent drawbacks, such as instability of droplet, formation of air bubble, and use of toxic reagent in the sample pretreatment process. In order to overcome the problems mentioned above, a new LPME technique, namely solidified floating organic drop microextraction (SFODME), was proposed for the analysis of analytes. Owing to its unique advantages of simplicity, speed, low cost, consumption of small organic solvent, and high enrichment factor, SFODME has been successfully employed for the determination of trace elements and their speciation in various samples (20-28).

It is well known that ICP-MS is a most favorable method for elemental analysis owing to its high sensitivity, wide linear range, and rapid multielement detection capability. It is predicted that SFODME coupled with ICP-MS may be a powerful detection tool for elemental speciation. Unfortunately, the liquid nebulization sample introduction procedure for conventional ICP-MS is not compatible with SFODME because of its large sample consumption. In addition, organic solvents used in SFODME may lead to destabilization or extinction of the ICP discharge owing to relatively high solvent vapor pressure and solvent loading (29). Thus, the development of a suitable sample introduction technique with small amounts of sample consumption and *in situ* removal of the organic solvent is a promising and prospective work

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for extending the application of the SFODME technique. Electrothermal vaporization (ETV), as a sample introduction device for ICP-MS, has the merits of high introduction efficiency, small sample requirement, and low absolute detection limit. Moreover, use of a chemical modifier in ETV could greatly improve the analytical performance of the method (30-35). As described previously, SFODME is a miniaturized sample pretreatment technique, and ETV is a microamount sample introduction device. Therefore, SFODME coupled with ETV for ICP-MS may be a perfect combination. However, to the best of our knowledge, the study on SFODME-ETV-ICP-MS for elemental speciation has received little attention so far (36, 37).

The aim of this work was to examine the possibility of implementing SFODME in combination with ETV-ICP-MS for the speciation of inorganic antimony. Ammonium pyrroinedithiocarbamate (APDC) was used as both a chelating reagent in SFODME and a chemical modifier in ETV for the separation, preconcentration, and volatilization of Sb(III) and Sb(V) prior to their determination by ICP-MS. The main factors affecting the determination of the analytes were investigated in detail. This method was assessed by its application for speciation of inorganic Sb in natural water samples and a standard reference material.

EXPERIMENTAL

Instrumentation

An X-7 ICP-MS system (Thermo Elemental Corporation, USA), equipped with a modified commercially available WF-4C graphite furnace (Beijing Second Optics, P.R. China) as an electrothermal vaporizer, was used for the determination of the analytes. The operating parameters of ICP-MS were optimized with a concentric glass

nebulizer prior to connection with the ETV device. A pyrolytic graphite tube was used throughout this work. The pH value of the solution was controlled with a pH meter (Thermo Orion Corporation, USA) supplied with a combined electrode. The working conditions of ETV-ICP-MS are summarized in Table I.

Standard Solutions and Reagents

Stock standard solutions (1.0 mg mL⁻¹) of Sb(III) were obtained by dissolving appropriate amounts of K(SbO)C₄H₄O₆ (Tianjin Reagent Factory, P.R. China) in high purity deionized water. Stock standard solutions (1.0 mg mL⁻¹) of Sb(V) were prepared by dissolving appropriate amounts of K₂H₂Sb₂O₇ (Shanghai Reagent Factory, P.R. China) in boiling water. Working solutions were prepared daily by appropriate dilution of the stock solutions. APDC solution was pre-

pared by dissolving proper amounts of APDC (Shanghai Reagent Factory, P.R. China) in 1-undecanol (Shanghai Reagent Factory). All glass and polypropylene wares were kept in 2.0 mol L⁻¹ HNO₃ solution for at least one night, then rinsed with 0.1 mol L⁻¹ HNO₃ solution, and subsequently with deionized water before use. All other reagents used in this study were of high purity or at least of analytical grade. High purity deionized water obtained from the Milli-Q® A10 system (Millipore Corporation, USA) was used throughout this work.

Sample Preparation

Water samples, including river water (Yangtze River, Wuhan, P.R. China) and lake water (Dongxi Lake, Wuhan, P.R. China), were collected in 50-mL polyethylene containers, respectively. All water samples were filtered through a 0.45 μm membrane filter, and then stored in polyethylene bottles at

TABLE I
Operating Parameters for ETV-ICP-MS

ICP-MS Plasma	
Plasma Power	1300 W
Plasma Argon Flow Rate	14.5 L min ⁻¹
Auxiliary Argon Flow Rate	0.89 L min ⁻¹
Nebulizer Argon Flow Rate	0.94 L min ⁻¹
Sampler Orifice (nickel)	1.1 mm
Skimmer Orifice (nickel)	0.7 mm
Acquisition Mode	Peak-jumping
Number of Sweeps	100
Dwell Time	10 ms
Acquisition Time	40 s
Number of Measurements per Peak	3
Isotope	¹²¹ Sb
ETV	
Sample Volume	10 μL
Carrier Gas Flow Rate	0.45 L min ⁻¹
Drying Step	100 °C, ramp10 s, hold 10 s
Ashing Step	200 °C, ramp10 s, hold 20 s
Vaporization Step	2000 °C, hold 4 s
Clear-out Temperature	2600 °C

4 °C for future use. The storage period was kept as short as possible. Blanks were prepared exactly as the samples except no addition of analytes.

SFODME Extraction

The SFODME device for extraction of the analytes was similar to that reported in the literature (38). Sample solutions containing analytes were adjusted to pH 6.0 using diluted nitric acid or ammonium hydroxide. Then 10 mL of the resulting solution was transferred into an 11-mL vial, and a stir bar and 20 μ L of APDC in 1-dodecanol were added. The magnetic stirrer was turned on and the solution stirred for a fixed time. In this step, the analytes reacted with APDC to form hydrophobic complexes, and were extracted into 1-undecanol. After the extraction process, the sample vial was transferred into an ice bath until the organic solvent was solidified. The solidified solvent was then transferred into a conical vial where it immediately melted at room temperature. The extract was diluted to 100 μ L with tetrahydrofuran (THF). Finally, 10 μ L of the extract was injected into the ETV for ICP-MS determination.

ETV-ICP-MS Procedure

After the ETV unit had been connected to the ICP-MS, 10 μ L of the analytes in the organic solvent was injected into the graphite furnace. During the drying and charring process, the dosing hole of the graphite furnace was kept open to remove the water and the organic vapor. Then it was sealed with a graphite probe for 5-10 seconds prior to the vaporization step, the vaporized analytes were swept into the plasma excitation source by a carrier gas, and the peak-hop transient mode for data acquisition was used for the detection of the analytes.

Data Analysis

Sb(III) was directly determined by this method. Total Sb was determined after the reduction of Sb(V) to Sb(III), and the concentration of Sb(V) was calculated by the respective difference between the total Sb and Sb(III) concentration. Prereduction of Sb(V) to Sb(III) was carried out with 0.5% (w/v) L-cysteine media for 30 minutes in a boiling water bath (39).

RESULTS AND DISCUSSION

Investigation of Vaporization Behavior for Sb(III)

The vaporization behavior of Sb(III) was investigated with and without APDC as a chemical modifier. It can be seen from Figure 1 that Sb(III) was partly vaporized at 2000 °C without APDC (b), and its severe memory signal was recorded (c). However, the intensive signal of Sb(III) was detected at the same vaporization temperature with APDC (d), and no memory signal was observed for Sb(III) even at 2600 °C (e). In addition, the blank signal was not found in this experiment (a). The possible reason for this is that Sb(III) can form thermally stable and volatile Sb(III)-APDC complexes. Thus, APDC was selected as the suitable chemical modifier for improving the volatility of Sb in ETV.

Influence of pH on SFODME

Due to its effect on the complex formation and subsequent extraction, the pH value of the sample solution plays an important role in SFODME. Therefore, the effects of pH value on the signal intensity of Sb(III) and Sb(V) were investigated in the pH range of 1.0–7.0. As is shown in Figure 2, the maximum

Fig. 1. Signal profiles of Sb(III). a: APDC in 1-undecanol and THF; b: Sb(III) aqueous solution; c: residual signal from b at 2600 °C; d: Sb(III) with APDC in 1-undecanol and THF; e: residual signal from d at 2600 °C. Conditions: Sb(III): 5 ng mL⁻¹ (b); Sb(III): 2.0 ng mL⁻¹ (d); vaporization temperature: 2000 °C.

Fig. 2. Effect of pH on signal intensity. Conditions: Sb(III) and Sb(V): 2.0 ng mL⁻¹; vaporization temperature: 2000 °C.

signal intensity Sb(III) was obtained in the pH range of 2.0–7.0, whereas the signal intensity of Sb(V) was hardly detected in the pH range of 5.0–7.0. The reason for this is that Sb(III) can react with APDC to form 1-dodecanol extractable Sb(III)–APDC complexes, but Sb(V) does not form APDC complexes extracted by 1-dodecanol. Based on the results mentioned above, a pH of 6.0 was used for the separation of Sb(III) and Sb(V).

Quantitative Vaporization of Analytes

For ETV-ICP-MS, quantitative vaporization of Sb(III) and Sb(V) was investigated with the addition of APDC at pH 6.0. The results in Figure 3 show that the signal for Sb(V) can hardly be detected with APDC (f). In the presence of APDC, however, the intense and symmetrical signals for total Sb were recorded due to the formation of the Sb(III)–APDC complex (g). It is worth noting that the signal intensity of total Sb (g) is about 50% of that for total Sb after reduction by L-cysteine (h). The reason for this is that Sb(V) was reduced into Sb(III) to result in the increase of its concentration. In addition, a blank sig-

nal was not observed in the experiment (i). These facts indicate that the analytes can be quantitatively vaporized and transported from ETV to ICP for their determination.

Effect of APDC Amount

The effect of APDC concentration on the signal intensity of the analytes was studied in the concentration range of 0.1×10^{-2} – 4.0×10^{-2} mol L⁻¹. The results are shown in Figure 4. It is obvious that the signal intensity of Sb(III) increased with an increase in APDC concentration up to 2.0×10^{-2} mol L⁻¹, and is then nearly constant when the concentration of APDC exceeds 2.0×10^{-2} mol L⁻¹. Taking into account that APDC could be consumed by the matrix in a real sample analysis, a relatively high concentration of 3.0×10^{-2} mol L⁻¹ APDC was used in subsequent work.

Influence of Extraction Time

Extraction time is a considerable factor influencing extraction efficiency and analysis speed. For this reason, the effect of extraction time on signal intensity of Sb(III) was investigated by varying the extraction time between 5 and 50 min-

utes. The experimental results show that the signal intensity of Sb(III) was increased firstly with an increase in extraction time, and then reached a plateau after 25 minutes. Thus, an extraction time of 30 minutes was used for the subsequent experiment.

Effect of Stirring Rate

In order to accelerate mass-transfer of the analytes from the aqueous phase to the organic phase, the effect of the stirring rate on the extraction efficiency of the analytes was investigated with a sample solution of 20 mL at different stirring rates from 100 to 1200 rpm. The experimental results show that the signal intensities of the analytes increased rapidly with an increase in the stirring rate up to 900 rpm. However, the signal intensity decreased obviously when the stirring rate exceeded 1000 rpm owing to the loss of floating solvent drop. Hence, a stirring rate of 900 rpm was selected in this work.

Effect of Sample Volume

To explore the possible enrichment of low concentrations of the analytes in a large sample volume, the effect of sample volume on the

Fig. 3. Quantitative vaporization of analytes. f: Sb(V) with APDC in 1-undecanol and THF; g: total Sb with APDC in 1-undecanol and THF; h: total Sb with APDC in 1-undecanol and THF after reduction by L-cysteine; i: APDC+L-cysteine in 1-undecanol and THF; total Sb: Sb(III) + Sb(V); Sb(III) and Sb(V): 2.0 ng mL^{-1} ; vaporization temperature: 2000°C ; pH: 6.0.

Fig. 4. Effect of APDC concentration on SFODME. Sb(III): 2.0 ng mL^{-1} ; vaporization temperature: 2000°C ; pH: 6.0.

extraction of the analytes was examined using different sample volumes (10–50 mL). The results indicated that the extraction was quantitative (recovery >90%) with an aqueous phase volume in the range of 10–20 mL. However, a decrease was observed with a further increase in sample volume. Based on the organic phase volume (20 μ L) and the maximum sample volume (20 mL), an enrichment factor of 1000 was obtained for the analytes. Considering the two factors of analysis time and enrichment fold, the sample volume of 10 mL was used for further experiments.

Effect of Interfering Ions

The effect of various cations and anions commonly existing in natural water on the extraction of the analytes was examined. The tolerance limit of coexisting ions is defined as the largest amount making a variation of less than 10% in the recovery of the analytes. The results in Table II show that the selected ions had no significant effect on the extraction and determination of the analytes in the range of their tested concentration. Thus, this method may be applied for the speciation of inorganic Sb in natural water samples.

Optimization of ETV Conditions

A temperature of 100 °C and a time of 10 seconds were used as

the drying conditions in this work. To remove the extraction solvent from the furnace and to avoid the signal loss of the analytes at the same time, the effect of pyrolysis temperature on signal intensity was studied in the range of 100–400 °C with a pyrolysis time fixed at 20 seconds. The results show that the signal of the analytes decreased with an increase in pyrolysis temperature above 250 °C. Thus, a pyrolysis temperature of 200 °C and a pyrolysis time of 20 seconds were selected for this work.

In addition, the effect of vaporization temperature on the signal of the analytes was studied with a vaporization time of 4 seconds. The results show that the signal intensity of the analytes could only be detected at about 900 °C without APDC, and no signal plateau was obtained in the range of the tested vaporization temperature. However, the situation changed greatly after APDC was added. A weak signal for the analytes appeared at 550 °C, the signal increased gradually with an increase in vaporization temperature, maximum signal was obtained at 1900 °C for the analytes, and then maximum signal was kept constant with a further increase in the vaporization temperature to 2200 °C. Based on the above results, a vaporization temperature of 2000 °C and a vaporization time of 4 seconds were used for ETV-ICP-MS determination.

Analytical Performance

According to the definition of IUPAC, the detection limits for Sb(III) and Sb(V), based on three times the standard deviation of the blank solution, were 0.54 μ g mL⁻¹ and 0.71 μ g mL⁻¹, respectively. The relative standard deviations were 5.3% and 4.6% for Sb(III) and Sb(V) (n=9, c=0.1 μ g mL⁻¹), respectively. The linear dynamic range of the calibration curve for this method covered three orders of magnitude with a correlation coefficient better than 0.9982.

Sample Analysis

Natural water samples, including lake water and river water, were used for analysis of the analytes by this method. In addition, the recovery experiments of different amounts of analytes were carried out. The results in Table III show that the recoveries are in the range of 94.0–98.0%. In order to establish the validity of this method, a certified reference material GBW(E) 080545 Water Sample, obtained from Institute for Reference Materials of SEPA (Beijing, P.R. China), was analyzed and the results were in good agreement with the certified value (see Table IV).

CONCLUSION

In summary, a novel method is developed for the speciation of inorganic Sb in natural water samples, based on solidified floating

TABLE II
Effect of Interfering Ions

Diverse Ions	Concentration Ratio ^a
Na ⁺ , K ⁺	20,000
Ca ²⁺ , Mg ²⁺	10,000
Fe ³⁺ , Zn ²⁺ , Al ³⁺	500
SO ₄ ²⁻ , SiO ₃ ²⁻ , PO ₄ ³⁻	10,000
Cl ⁻ , NO ₃ ⁻	20,000

^a Foreign ion / analyte.

TABLE III
Analytical Results and Recoveries of Analytes in Natural Water Samples

Sample	Species	Content (ng mL ⁻¹)	Added (ng mL ⁻¹)	Found (ng mL ⁻¹)	Recovery (%)
Lake Water	Sb(III)	0.37±0.03	1.0	1.31±0.09	94.0
	Sb(V)	1.81±0.10	1.0	2.78±0.16	97.0
River Water	Sb(III)	0.54±0.04	1.0	1.52±0.13	98.0
	Sb(V)	2.31±0.16	1.0	3.26±0.19	95.0

Mean value ± standard deviation, n=3.

organic drop microextraction (SFODME) coupled with electrothermal vaporization inductively coupled plasma mass spectrometry (ETV-ICP-MS). Ammonium pyrroinedithiocarbamate (APDC) and 1-undecanol were used as the chelating reagent and an extraction solvent in SFODME, respectively. At the same time, APDC acted as a chemical modifier in ETV. The experimental results show that under the selected experimental conditions, the Sb(III)-APDC complex can be extracted effectively with 1-dodecanol, and vaporized quantitatively by ETV into ICP for its determination. In addition, this method provides advantages such as high enrichment factor, low detection limit, simple operation, low cost, good precision, and accuracy.

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TABLE IV
Analytical Results of Analytes in CRM GBW(E) 080545 Water Sample

Sample	Element	Found ^a ($\mu\text{g mL}^{-1}$)	Certified ($\mu\text{g mL}^{-1}$)
Water Sample GBW(E) 080545	Total Sb	95.7 $\pm$ 5.2	100
	Sb(III)	4.3 $\pm$ 0.2	-
	Sb(V)	91.4 $\pm$ 4.3	-

Mean value $\pm$ standard deviation, n=3.

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