Dispersive Micro-solid Phase Extraction Coupled With Dispersive Liquid-liquid Microextraction for Speciation of Antimony in Environmental Water Samples by Electrothermal Vaporization ICP-MS

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INTRODUCTION

It is well known that antimony (Sb) is a ubiquitous and cumulative toxic element. It may cause a wide variety of adverse health effects, including respiratory tract irritation, dermatitis, and suppurative of the nasal septum, gastritis, and cellular damage in the lungs (1, 2). In particular, the physicochemical and toxic properties of Sb strongly depend on its chemical forms. The inorganic species of Sb are more toxic than its organic ones (3). The toxicity of Sb(III) is 10 times higher than that of Sb(V) (4, 5). Therefore, it is necessary not only to determine total Sb, but also to determine Sb speciation in real samples to evaluate its human health risk.

The problems of Sb speciation analysis in environmental samples lie in its low concentration level and the complex matrix interference. Therefore, a separation and pre-concentration technique for the different species is usually required prior to their determination. As a classical sample pretreatment technique, solid phase extraction (SPE) has been used widely for an element and its speciation analysis (6-8). However, this technique suffers from certain shortcomings such as solvent loss, large secondary waste, and a long procedure (9, 11). To overcome these problems, a new method named dispersive micro-solid phase extraction (DMSPE) has received increasing attention in the analytical sciences

ABSTRACT

A new method based on the dispersive micro-solid phase extraction (DMSPE) and dispersive liquid-liquid microextraction (DLLME) is described for the speciation of inorganic antimony (Sb) by electrothermal vaporization inductively coupled plasma mass spectrometry (ETV-ICP-MS). In DMSPE, titanium dioxide nanofibers were used as an adsorbent for the preconcentration and separation of the analytes. The upper aqueous phase and elution solution from DMSPE were used for further preconcentration and separation of Sb(III) and Sb(V) by DLLME without any pre-oxidation or pre-reduction operation, respectively. The extracts from DLLME were used for ETV-ICP-MS determination. The main factors affecting DMSPE and DLLME were examined in detail. Under the optimal conditions, the detection limits of this method were 0.025 and 0.041 pg mL^{-1} with relative standard deviations of 6.3% and 5.4% for Sb(III) and Sb(V) ($c = 1.0 \text{ ng mL}^{-1}$, $n=9$), respectively. This method was successfully applied for the analysis of Sb speciation in environmental water samples. A certified reference material of water sample was analyzed by this method, and the results of total Sb obtained were in agreement with the certified values.

owing to its major advantages of simple operation, short extraction time, high extraction efficiency, less adsorbent consumption, and bulk solution extraction (10-12). It is worth noting that an adsorbent

material plays a crucial role in DMSPE (13). Various substances have been developed for DMSPE adsorbents (11, 12-16). Titanium dioxide nanofibers (TDNFs) possess some unique properties such as large specific surface area, high chemical stability, corrosion-resistance, non-toxicity and low cost, which make them a promising candidate as adsorbents. However, the study on TDNFs as a solid phase extraction adsorbent for elemental speciation has received little attention (17).

In recent years, a series of liquid phase microextraction (LPME) procedures have emerged in the analytical sciences, including single-drop microextraction, hollow fiber liquid phase microextraction, dispersive liquid-liquid microextraction (DLLME), cloud point extraction, continuous-flow microextraction, and solidified floating organic drop microextraction (18-24). Despite the many benefits of LPME such as simplicity, low cost, rapid phase transfer and high enrichment factor (EF), its application is considerably limited because of the complex or "dirty" sample matrix. Thus, the majority of works by LPME in the literature are focused on the analysis of elemental speciation in water samples with simple matrices (25). It should be pointed out here that each technique has its advantages and disadvantages. Recently, some investigations showed that an important strategy is the coupling of different pretreatment techniques for the determination of the analytes at an extremely low concentration level in real samples (26-31). To the best of our

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knowledge, the use of DMSPE coupled with DLLME for Sb speciation has never been reported in the literature.

Inductively coupled plasma mass spectrometry (ICP-MS) has been proven to be one of the most powerful analysis tools for elements and their speciation due to its merits of high sensitivity, wide linear dynamic range, and rapid multielement detection capability (32-38). However, a liquid nebulization sample introduction procedure for conventional ICP-MS is not compatible with LPME because of its large sample consumption. For these reasons, the application of LPME for elements and their speciation has been done by AAS in most cases (39). Electrothermal vaporization (ETV), as a sample introduction device for ICP-MS, has the advantages of high introduction efficiency, low absolute detection limits, and partial or complete removal of the organic/inorganic solvent/matrix (40-42). Moreover, the microamount of sample requirement with ETV matches that of LPME well. In addition, the use of a chemical modifier in ETV, especially an organic chelating reagent, could change refractory elements to their volatile species and greatly improve the analytical performance of ETV-ICP-MS (43-45).

In this work, a novel method based on DMSPE and DLLME was developed for the Sb speciation by ETV-ICP-MS. In DMSPE, TDNFs were used as an adsorbent for the concentration and separation of the analytes. The upper aqueous phase and elution solution from DMSPE were used for further preconcentration and separation of Sb(III) and Sb(V) by DLLME without any pre-oxidation or pre-reduction operation, respectively. In DLLME, ammonium pyrroinedithiocarbamate (APDC) and CHCl_3 were used as a chelating reagent and as an extraction solvent, respectively.

The extracts from DLLME were used for ETV-ICP-MS determination with APDC as a chemical modifier. This method was applied successfully for the analysis of Sb speciation in environmental water samples.

EXPERIMENTAL

Instrumentation

A Series-7 ICP-MS system (Thermo Fisher Scientific Corporation, USA), equipped with a modified commercially available WF-4C graphite furnace (Beijing Second Optics, P.R. China) as the electrothermal vaporizer, was used for the determination of the analytes. The operating parameters of the 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 working conditions of ETV-ICP-MS are summarized in

Table I. The pH value of the solution was controlled with a pH meter (Thermo Orion Corporation, USA) supplied with a combined electrode. An Ethos T microwave digestion device (Milestone, Italy) was used for sample digestion. A KQ-50E ultrasonic bath (Kunshan Ultrasonic Instrument Co., Ltd., Suzhou, P.R. China) was used for obtaining fine droplets. A TG16-WS centrifuge (Hunan Xiangyi Centrifuge Instrument Co., Ltd., Changsha, P.R. China) was used to accelerate phase separation.

Reagents and Solutions

Unless otherwise stated, all reagents were of high purity or at least of analytical grade. The stock standard solutions of 1.0 mg mL^{-1} Sb(III) and 1.0 mg mL^{-1} Sb(V) were prepared by dissolving appropriate amounts of $\text{K(SbO)C}_4\text{H}_4\text{O}_6$ (Tianjin Reagent Factory, P.R. China) and $\text{K}_2\text{H}_2\text{Sb}_2\text{O}_7$ (Shanghai Reagent Fac-

TABLE I
Instrumental Operating Parameters for ETV-ICP-MS

ICP-MS Plasma Conditions	
Plasma Power	1300 W
Plasma Argon Flow Rate	14.5 L min^{-1}
Auxiliary Argon Flow Rate	0.91 L min^{-1}
Nebulizer Argon Flow Rate	0.95 L min^{-1}
Sampler Orifice (nickel)	1.1 mm
Skimmer Orifice (nickel)	0.7 mm
Acquisition Mode	Peak-jumping
Number of Sweep	100
Dwell Time	10 ms
Acquisition Time	40 s
Number of Measurements per Peak	3
Isotopes	^{121}Sb
ETV Conditions	
Sample Volume	10 μL
Carrier Gas Flow Rate	0.45 L min^{-1}
Drying Step	100 °C, ramp 10 s, hold 10 s
Ashing Step	200 °C, ramp 10 s, hold 20 s
Vaporization Step	2000 °C, hold 4 s
Clear-out Temperature	2600 °C

tory, P.R. China) in high purity deionized water, respectively. The working solutions were prepared daily by appropriate dilution of the stock solutions. The APDC solution was prepared by dissolving proper amounts of APDC (Shanghai Reagent Factory, P.R. China) in high purity water. Chlorobenzene, carbon tetrachloride, 1,2-dichloroethane, chloroform, acetonitrile, acetone, ethanol, and methanol were purchased from Shanghai Reagent Factory (Shanghai, P.R. China). High purity deionized water obtained from a Milli-Q® A10 system (Millipore Corporation, USA) was used throughout this work. 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. TDNFs were fabricated by a facile electrospinning and subsequent annealing method, and the diameter of the TDNFs was mainly in the range of 350–450 nm.

Sample Pretreatment

The water samples (Wuhan, P.R. China) were collected in 50-mL polyethylene containers, then filtered through a 0.45-μm membrane filter, and stored in polyethylene bottles at 4 °C for future use. The storage period was kept as short as possible. The blanks were prepared exactly as the samples except that no analytes were added.

Dispersive Micro-solid Phase Extraction

A 5.0-mL sample solution (pH=5.0) spiked with the target analytes was placed in a 10-mL screw cap test tube with a conic bottom. A 6.0-mg amount of TDNFs was added to the test tube, followed by sonication for 6 seconds. After extraction, the mixture was centrifuged at 6000 rpm for 5 minutes to separate the TDNFs from the aqueous solution. The upper aqueous

phase containing Sb(III) was carefully removed into a 10-mL centrifuge tube. The Sb(V) retained on the TDNFs was desorbed with 2.0 mL of 0.5 mol L⁻¹ HNO₃ by vortex for 2 minutes. The obtained desorption solution was transferred into another 10-mL centrifuge tube.

Dispersive Liquid-liquid Microextraction

Two aliquots of 100 μL APDC (as chelating reagent) solution were added into the upper aqueous phase (pH=5.0) containing Sb(III) and the desorption solution (pH=0.5) containing Sb(V), respectively, then calibrated to 5.0 mL. The two solutions were shaken for 1 minute and sonicated for 2 minutes to mix the sample solutions and to promote the formation of the APDC-Sb(III) and APDC-Sb(V) complexes. Then, the two aliquots of 0.2 mL ethanol (as dispersive solvent) containing 15 μL CHCl₃ (as extraction solvent) were added to the aforementioned solutions, respectively, and cloudy solutions formed immediately. Phase separation was achieved by centrifugation at 5000 rpm for 3 minutes. After the end of the centrifugation cycle, a small droplet of CHCl₃ containing the analytes was sedimented at the bottom of the conical test tube. Finally, an amount of 10 μL of the sedimented phase was injected into the ETV device for ICP-MS analysis.

ETV-ICP-MS Procedure

After the ETV unit was connected to the ICP-MS, 10 μL of the analytes in the organic solvent was injected into the graphite furnace. During the drying step, 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 within 5–10 seconds before 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 determination of the analytes.

RESULTS AND DISCUSSION

Optimization of DMSPE Parameter

Effect of pH

The pH of the sample solution plays a key role in speciation separation and adsorption efficiency. It proved to be a primary parameter in the following experiments. Therefore, the effect of sample pH on the adsorption of the analytes on the TDNFs was investigated in the pH range of 1.0–8.0. The results in Figure 1 show that in the pH range of 3.0–6.0, Sb(V) was retained on the TDNFs with an adsorption percentage above 90%, while Sb(III) was not retained on the TDNFs in the tested pH range. This fact reveals that Sb(V) could be effectively separated from Sb(III) on the TDNFs by selection of a proper pH. In this work, a pH of 5.0 was selected for the separation of Sb(V) and Sb(III).

The adsorption behaviors of Sb(V) and Sb(III) on the TDNFs may be explained in terms of the surface charge of the TDNFs (46). When the pH is in the range of 3.0–6.0, Sb(III) mainly exists as H₃SbO₃ and Sb(OH)₃, while Sb(V) exists predominantly as H₂SbO₄⁻ and Sb(OH)₆⁻. At an acidic condition, the surface of the TDNFs is electro-positive (TiOH₂⁺) which favors the adsorption of H₂SbO₄⁻ and Sb(OH)₆⁻.

In addition, the adsorption capacity was investigated by the method recommended in the literature (47). In the particle size range of 350–450 nm, the adsorption capacity of Sb(V) on the TDNFs was 3.1 mg g⁻¹.

Effect of Adsorbent Amount

To obtain an optimum TDNF dosage necessary for the separation and preconcentration of the ana-

lytes, the amount of TDNFs was varied from 1.0 to 10 mg per sample solution (5.0 mL). It was found that the quantitative adsorption of Sb(V) was achieved with amounts ranging from 5.0–10 mg. Thus, a 6.0-mg amount of TDNFs was used for further experiments.

Effect of Concentration and Volume of Eluent

Due to the low adsorption efficiency of Sb(V) at $\text{pH} < 2.0$, the diluted HNO_3 solution was employed for the fast and quantitative elution of Sb(V) retained on the TDNFs by vortex. The effect of HNO_3 concentration on the recovery of Sb(V) was studied in its concentration range of 0.1–1.5 mol L^{-1} . The experimental results show that the retained Sb(V) could be eluted quantitatively with a 0.5- mol L^{-1} HNO_3 solution. Furthermore, the effect of eluent volume on the recovery of the analytes was also studied with a 0.5- mol L^{-1} HNO_3 solution. The experimental results indicated that quantitative recoveries (>90.0%) could be obtained with 2.0 mL of a 0.5- mol L^{-1} HNO_3 solution.

Influence of Sonication and Centrifugation Time

In DMSPE, mass transfer takes place during the dispersive step. The effect of sonication time was evaluated in the range of 3–20 seconds. The results showed that the recovery of the analytes increased within the first 5 seconds, and then the recovery of the analytes remained approximately constant after exceeding 5 seconds. Hence, a sonication time of 6 seconds was chosen for further study. In addition, the recovery of the analytes was also investigated as a function of centrifugation time at 5000 rpm. The experiments were performed in the range of 1–10 minutes. With increasing centrifugation time, the recovery of the analytes increased rapidly. Over 4 minutes, the recovery of the analytes was constant. Thus, 5 minutes was selected as the final centrifugation time.

Effect of Desorption Time

The effect of desorption time on the recovery of the analytes was investigated in the time range of 1–5 minutes by vortex. The experimental results showed that the analytes could be quantitatively

recovered in the whole investigated time range, indicating a fast desorption dynamics. Therefore, 2 minutes was used as the desorption time.

Selection of DLLME Conditions

Effect of Sample pH

For DLLME, the sample pH is a very important factor in the separation and concentration of the analytes since it affects the formation of the Sb(III)-APDC and Sb(V)-APDC complex by using necessary hydrophobicity and their subsequent extraction. Therefore, the effect of sample pH on the signal intensities of the analytes was investigated in detail and the results are shown in Figure 2. As can be seen, the maximal signals of Sb(V) and Sb(III) were recorded in the pH range of 0–1.0. It is worth noting that Sb(III) was also quantitatively determined in the pH range of 3.0–7.0. The reason for the facts mentioned above is that at the corresponding pH range, Sb(V) and Sb(III) could form the stable and hydrophobicity complexes with APDC. Based on these results, the upper aqueous phase ($\text{pH}=5.0$) containing Sb(III) and the desorp-

Fig. 1. Effect of pH on the adsorption of analytes on TDNFs in DMSPE. Sb(III) and Sb(V): 1.0 ng mL^{-1} ; sample volume: 5.0 mL.

Fig. 2. Effect of sample pH on signal intensity of analytes in DLLME. Sb(III) and Sb(V): 1.0 ng mL^{-1} ; vaporization temperature: 2000 °C.

tion solution (pH=0.5) containing Sb(V) from DMSPE were used for the direct determination of Sb(III) and Sb(V) by DLLME without any pre-oxidation or pre-reduction operation, respectively.

Effect of Extraction Solvent and Its Volume

In general, the extraction solvent should have low solubility in water and excellent extraction ability for the target analytes. In addition, it should have higher density than water to make the phase separation easy. For this purpose, chlorobenzene, 1,2-dichloroethane, and chloroform were investigated as the extraction solvents. The experimental results show that chloroform (CHCl_3) has better extraction efficiency among the tested solvents. Thus, CHCl_3 was selected as the optimal extraction solvent.

The effect of extraction solvent volume on the extraction efficiency was also investigated in the range of 10–50 μL . The experimental results illustrate that the signal intensity of the analytes kept almost constant when the extraction solvent volume varied from 10 to 30 μL . However, the signal intensity of the analytes decreased by further increasing the volume above 30 μL . In order to get a high enrichment factor, 15 μL of CHCl_3 was used as the extraction solvent in this work.

Effect of Type and Volume of Dispersive Solvent

In order to form the stable emulsion, the dispersive solvent in DLLME should be miscible with both water and extraction solvent. For this purpose, acetone, ethanol, and methanol were studied as the dispersive solvents. The experimental results show that the recovery of the analytes for acetone, ethanol, and methanol was 94.1%, 96.3%, and 97.5%, respectively. The higher recovery was obtained using methanol, but ethanol has low toxicity and cost and was, therefore, selected as the disperser solvent.

In addition, the effect of ethanol volume on the signal intensity of the analytes was investigated in the range of 0.2–0.5 mL. The experimental results show that a relatively high signal intensity and better reproducibility for the analytes were obtained with 0.2 mL ethanol as the dispersive solvent. Therefore, 0.2 mL of ethanol was selected as the optimum volume to achieve a stable cloudy solution.

Influence of APDC Concentration

The effect of APDC concentration on the signal intensity of the analytes was studied in the concentration range of 0.1×10^{-2} – 3.0×10^{-2} mol L^{-1} . The experimental results show that the signal intensity of the analytes increased with the increase of APDC concentration from 0.1 to 1.0×10^{-2} mol L^{-1} , and is then nearly constant when the concentration of APDC exceeds 1.0×10^{-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 2.0×10^{-2} mol L^{-1} APDC was used in subsequent work.

Effect of Extraction and Centrifugation Time

The effect of extraction time was evaluated in the range of 5 seconds to 2 minutes. The experimental results show that the extraction time has no significant effect on extraction efficiency. This fact reveals that the interface area between the extraction solvent and the aqueous phase is extremely large due to the formation of a cloudy solution, resulting in the very fast mass transfer of the analytes from the aqueous phase to the extraction phase. Hence, the extraction time can be kept very short, which is the remarkable advantage of DLLME. Consequently, 5 seconds was selected for the extraction of the analytes. Besides, the effect of the centrifugation time was studied from 1 to 5 minutes at 5000 rpm. Satisfactory results were

achieved within 3 to 5 minutes. Thus, 3 minutes was selected as the centrifugation time for this work.

Effect of Potential Interference Ions

The effect of various cations and anions commonly existing in biological samples on the extraction and determination of the analytes was examined based on the typical concentrations of these ions in real natural water samples. The tolerance limit of coexisting ions is defined as the largest amount making variation of less than 10% in the recovery of the analytes. The results show that 2000 mg L^{-1} Cl^- and NO_3^- , 1500 mg L^{-1} SO_4^{2-} , SiO_3^{2-} and PO_4^{3-} , 3000 mg L^{-1} K^+ and Na^+ , 2000 mg L^{-1} Ca^{2+} and Mg^{2+} , 2.0 mg L^{-1} Al^{3+} and Fe^{3+} had no significant effect on the extraction and determination of the analytes.

Optimization of ETV Conditions

The ETV temperature program was optimized and selected in this work. A drying temperature of 100 °C and a drying time of 10 seconds were used for the removal of the water vapor during the drying step; a pyrolysis temperature of 200 °C and a pyrolysis time of 20 seconds were used for *in situ* removal of the extraction solvent from the graphite furnace. In addition, the effect of vaporization temperature on the signal intensity of the analytes was studied with a vaporization time of 4 seconds. The experimental results show that with APDC as a chemical modifier, the maximum signal was obtained at 1900 °C for the analytes, and then kept constant with a further increase of vaporization temperature to 2200 °C. Thus, a vaporization temperature of 2000 °C with a vaporization time of 4 seconds was used in this work.

Analytical Performances

Under the optimized conditions, some important parameters of this

method, including precision, linear range of the calibration curve and the detection limits, were validated. The detection limits of Sb(III) and Sb(V), based on three times the standard deviation of the blank solution, were 0.025 pg mL⁻¹ and 0.041 pg mL⁻¹, respectively. The linear dynamic range of the calibration curve covered three orders of magnitude with a correlation coefficient better than 0.9932. The relative standard deviation was 6.3% and 5.4% for Sb(III) and Sb(V) (c=1.0 ng mL⁻¹, n=9), respectively.

Sample Analysis

Water samples (Wuhan, P.R. China), including wastewater, river water, and lake water, were collected in 50-mL polyethylene containers. They were filtered through a 0.45-μm membrane filter and then stored in polyethylene

bottles at 4 °C for future use. This method was applied for the analysis of Sb(III) and Sb(V) in the water samples mentioned above. The results are listed in Table II. The recovery of the analytes was in the range of 94.0–105%. In order to validate the accuracy of this method, a certified reference material GBW(E) 080545 water sample (Institute for Reference Materials of SEPA, Beijing, P.R. China) was analyzed, and the results were in good agreement with the certified value (Table III).

CONCLUSION

In conclusion, a new method was developed based on the dispersive micro-solid phase extraction (DMSPE) coupled with dispersive liquid-liquid microextraction (DLLME) and used for the determination of Sb species in environmen-

tal water samples by ETV-ICP-MS. TDNFs were used as the adsorbent for the concentration and separation of the analytes. The upper aqueous phase and the elution solution from the DMSPE were used for further preconcentration and separation of Sb(III) and Sb(V) by DLLME, respectively. The extracts from DLLME were used for ETV-ICP-MS determination with APDC as a chemical modifier. This study may provide a potential technique for Sb speciation in real samples. In addition, this method has also the features of low detection limit, simple operation, good accuracy, and without use of a pre-oxidation or pre-reduction operation.

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TABLE II
Analytical Results and Recoveries of Analytes
in Environmental Water Sample

Sample	Species	Content (ng mL ⁻¹)	Added (ng mL ⁻¹)	Found (ng mL ⁻¹)	Recovery (%)
Lake Water	Sb(III)	0.46±0.04	1.0	1.42±0.10	96.0
	Sb(V)	1.64±0.13	1.0	2.69±0.21	105
Wastewater	Sb(III)	5.27±0.41	2.0	7.22±0.35	97.5
	Sb(V)	4.52±0.19	2.0	6.40±0.29	94.0
River Water	Sb(III)	0.69±0.04	1.0	1.65±0.11	96.0
	Sb(V)	2.14±0.11	1.0	3.12±0.21	98.0

Mean value ± standard deviation, n=5.

TABLE III
Analytical Results of Analytes in
Certified Reference Material of Water Sample

Sample	Element (μg mL ⁻¹)	Found ^a (μg mL ⁻¹)	Certified (%)
Water Sample GBW(E)080545	Total Sb	96.8±4.9	100
	Sb(III)	5.7±0.4	-
	Sb(V)	93.5±6.2	-

^a Mean value ± standard deviation, n=5.

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