Preconcentration and Separation of Trace As(III) and Sb(III) by Carbon Nanofibers Loaded With Ammonium Pyrroinedithiocarbamate Prior to ICP-MS Determination

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INTRODUCTION

Owing to the rapid growth in technology and the industries, the elemental levels in the environment have received considerable attention in recent years. Arsenic (As) and antimony (Sb) are treated as potential chemical hazards by the World Health Organization (1). There is much epidemiological evidence that shows that arsenic causes diseases such as skin, lung, bladder, and kidney cancers (2, 3). Excessive exposure to antimony may lead to a wide variety of adverse health effects, including respiratory tract irritation, dermatitis, conjunctivitis, suppuration of the nasal septum, gastritis, and cellular damage in the lung, heart, and kidneys (4). Consequently, a reliable and accurate analytical procedure is necessary for the determination of trace/ultra-trace arsenic and antimony in environmental and biological samples.

Current analytical techniques for the determination of trace/ultra-trace elements mainly include atomic absorption spectrometry, inductively coupled plasma atomic emission spectrometry, inductively coupled plasma mass spectrometry (ICP-MS), isotope dilution spark mass spectrometry, neutron activation analysis, and differential pulse anodic stripping voltammetry (5-9). Although some of these techniques are very sensitive, there is still the need for a separation and preconcentration procedure before the

ABSTRACT

Based on carbon nanofibers (CNFs) loaded with ammonium pyrroinedithiocarbamate (APDC) as an adsorbent, a novel method is described for the preconcentration, separation, and determination of trace As(III) and Sb(III) by inductively coupled plasma mass spectrometry (ICP-MS). The adsorption behavior of the analytes on CNFs-APDC was investigated under dynamic conditions. The effects of pH, sample flow rate and volume, elution solution and interfering ions on the preconcentration and separation of the analytes were examined in detail. The adsorption capacity of CNFs-APDC for As(III) and Sb(III) was 3.6 mg g^{-1} and 2.8 mg g^{-1} , respectively. Under the optimum conditions, the detection limit (3σ) of this method was 0.065 ng mL^{-1} of As(III) and 0.012 ng mL^{-1} of Sb(III), and the relative standard deviation (RSD) was 3.1% and 5.4%, respectively ($n=9$, $c=1.0 \text{ ng mL}^{-1}$). This method was applied to the determination of trace As(III) and Sb(III) in natural water samples with recoveries of 95.3–104%. In order to validate this method, a certified reference material of human hair (GBW 07601) was analyzed, and the determined values were in good agreement with the certified values.

measurement step due to matrix effects and low levels of the analytes in real samples. To date, the widely used techniques for the separation and preconcentration of trace/ultra-trace elements include coprecipitation, solvent extraction,

cloud point extraction, solid phase extraction (SPE), ion exchange, hydride generation, and chromatography (10-16). Among these techniques, SPE for the preconcentration and separation of trace elements has achieved increasing application because of its simplicity, speed, high enrichment factors, rapid phase separation, and ability to combine with different detection techniques.

In the SPE technique, selection of an appropriate sorbent is of importance for the elaboration of an analytical procedure. Thus, the development of a new adsorbent material with high selectivity and sensitivity is forever of interest to analysts (17, 18). Recently, a nanostructure material as a new adsorbent for the preconcentration and separation of substances has drawn growing attention in the analytical sciences (19-26). As a novel and interesting material, carbon nanofibers (CNFs) have been used for hydrogen storage and the separation/preconcentration of trace elements due to their high chemical stability and large specific surface area (27-30). Some investigations showed that an important strategy for elemental enrichment is the incorporation of complexing reagents in solid supports (31-34). To the best of our knowledge, however, studies on the separation and preconcentration of trace elements have received little attention using CNFs loaded with APDC.

In this study, a novel method was developed for the separation and preconcentration of trace As(III) and Sb(III) by a microcolumn

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packed with immobilized APDC on CNFs before ICP-MS determination. This method validation was performed and applied for the determination of trace As(III) and Sb(III) in environmental and biological samples.

EXPERIMENTAL

Instrumentation

A Thermo Elemental X-7 ICP-MS (Thermo Elemental Corporation, USA), equipped with a standard low-volume glass impact-bead spray chamber, a concentric glass nebulizer and Fassel-type torch, was used in this work. The samples and standards were spiked with 2.0 ng mL⁻¹ of indium internal standard before measurement. The ion lens settings, nebulizer flow rate, and torch position of the instrument were optimized daily in order to obtain the maximum ¹¹⁵In count rate. The operating parameters for ICP-MS are listed in Table I.

A Model HL-2 peristaltic pump (Shanghai Qingpu Huxi Instrument Factory, P.R. China), coupled to a self-made polytetrafluoroethylene (PTFE) microcolumn (20 mm × 3.0 mm i.d.) packed with CNFs-APDC, was used for the preconcentration and separation process. A minimum length of PTFE tubing with an i.d. of 0.5 mm was used for all connec-

tions. The pH values of the solutions were controlled with a pH meter (Thermo Orion Corporation, USA), supplied with a combined electrode. A Model Ethos T microwave system (Milestone, Italy) was used for sample digestion.

Standard Solutions and Reagents

The As(III) and Sb(III) stock solutions (1.0 mg mL⁻¹) were purchased from the National Analysis Center of Iron & Steel (Beijing, P.R. China). The working solutions of the analytes were prepared by mixing and diluting the stock solutions. All other reagents used were of ultra-pure or at least of analytical grade. High-purity water obtained from a Milli-Q®A-10 system (Millipore Corporation, USA) was used throughout this work. The pH values of the solution were adjusted by adding an appropriate amount of HCl. The CNFs were kindly provided by the Shenyang Metal Institute of the Chinese Academy (Shenyang, P.R. China).

Preparation of Microcolumn with APDC

The microcolumn was prepared by placing 20 mg of CNFs into an empty conical column using the dry packing method. To avoid loss of CNFs, a small amount of quartz

wool was filled into both ends of the column. The microcolumn was then connected to a peristaltic pump with PTFE tubing to form the preconcentration system.

Before its use, 0.1 mol mL⁻¹ HCl solution was passed through the column for cleaning, then it was washed with high purity water to pH 7; and finally, 1.0×10⁻⁴ mol L⁻¹ APDC solution was passed through the column at a flow rate of 0.2 mL min⁻¹. The filtrate was collected and analyzed for un-adsorbed APDC with a UV-vis spectrophotometer at 275 nm. The retained amount of APDC on the CNFs was 0.94 mg g⁻¹.

Sample Decomposition

A 0.1000 g sample of GBW 07601 Human Hair (from the Institute of Geophysical and Geochemical Prospecting, Langfang, P.R. China) was accurately weighed into 100-mL Teflon® vessels, and 3.0 mL of concentrated HNO₃ and 1.0 mL of 35% H₂O₂ (m/V) were added. After about 5 minutes, when the first vigorous reaction had taken place, the digestion vessels were closed and placed into the microwave oven. Then, the samples were digested in the microwave oven at 180 °C (ramp, 10 minutes; hold, 15 minutes) at 1.0 kW power. After cooling and adding 0.5 mL of concentrated HClO₄, the solution was transferred into a Teflon beaker and heated to near dryness on a hot plate at 200 °C. The residues were dissolved with 1.0 mL of 0.1 mol L⁻¹ HCl, and diluted to 10 mL with deionized water.

The waste sample was collected from Dongxi Lake (Wuhan, P.R. China), filtered through a 0.22-μm membrane filter, and analyzed as soon as possible after collection. The blank was prepared exactly as the samples.

TABLE I
ICP-MS Operating Parameters

Plasma Power	1.3 kW
Plasma Argon Flow Rate	14.5 L min ⁻¹
Auxiliary Argon Flow Rate	0.71 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 Sweep	100
Dwell Time	10 ms
Acquisition Time	40 s
Number of Measurements per Peak	3
Isotopes	⁷⁵ As, ¹²² Sb, and ¹¹⁵ In

Recommended Procedure

Aliquots of 20-mL solutions containing As(III) and Sb(III) were prepared, and the pH was adjusted to the desired value with HCl. The solution was passed through the microcolumn by using a peristaltic pump at a desired flow rate. Afterwards, the retained metal ions were eluted with 0.6 mol L⁻¹ NaOH solution. The analytes in the effluents were determined by ICP-MS. The column could be used repeatedly after regeneration with 0.6 mol L⁻¹ NaOH solution and high purity water, respectively.

RESULTS AND DISCUSSION

Influence of pH on Adsorption

In the SPE procedure, the pH value of the aqueous sample plays an important role with respect to the adsorption of the analytes on the CNFs-APDC. In order to evaluate the effect of pH, a series of sample solutions was adjusted to the pH range of 1.0–10 with HCl and processed according to the recommended procedure. The effect of pH value on the recoveries of the analytes was investigated. The recoveries were calculated based on the difference between the amounts of the analytes in the starting sample and in the solution flowing out from the column. The results shown in Figure 1 indicate that quantitative recoveries (>90%) for As(III) and Sb(III) were obtained in the pH range of 2.0 to 4.0. Thus, all other experiments in this work were carried out at pH 3.0.

Choice of Eluent

The choice of eluent is very important for the successful coupling of a microcolumn preconcentration system to the ICP-MS. From Figure 1, it can be seen that the adsorption of the analytes on the CNFs-APDC is negligible at pH >10. The reason for this may be that extra NaOH results in the decomposition of the As(III)/Sb(III)-APDC

complex and the formation of soluble AsO₃³⁻/SbO₃³⁻. Thus, various concentrations of the NaOH solutions were studied for desorption of the retained analytes from the microcolumn. The results in Table II show that 0.4 mol L⁻¹ NaOH was sufficient for the quantitative elution of the analytes (>90%). As a result, a 0.6 mol L⁻¹ NaOH solution was selected for the elution of As(III) and Sb(III) in the following experiments.

In addition, the effect of eluent volume on the recoveries of the analytes was also investigated with 0.6 mol L⁻¹ NaOH solution (Table III). The experimental results demonstrated that quantitative recoveries (>90%) were obtained with 1.5 mL of 0.6 mol L⁻¹ NaOH solution. Taking the required sampling volume for ICP-MS into account, a 2.0-mL eluent volume was adopted for this work.

Effect of Flow Rate of Sample Solution

Retention of the analytes on the adsorbent depends on the flow rate of the sample solution. Therefore, the flow rate of the sample solution was optimized in the range of 0.2 and 2.0 mL min⁻¹ by passing 20 mL of solution through the microcolumn with a peristaltic pump. The experimental results in Figure 2 show that quantitative recoveries of the studied ions (>90%) were obtained in the flow rate range of 0.2–1.2 mL min⁻¹. However, the recoveries of the analytes will decrease by further increasing the flow rate above 1.2 mL min⁻¹ because of a decrease in adsorption kinetics. In this work, a flow rate of 1.2 mL min⁻¹ was used for subsequent determination.

Fig. 1. Effect of pH on the adsorption of As(III) and Sb(III) on CNFs-APDC. As(III) and Sb(III): 5.0 ng mL⁻¹; sample volume: 20 mL.

TABLE II
Effect of Eluent Concentration on the Recovery of Analytes

Concentration (NaOH, mol L ⁻¹)	Recovery (%)	
	As(III)	Sb(III)
0.1	42.3	50.2
0.2	68.9	71.3
0.4	90.1	91.4
0.6	98.3	98.7
0.8	96.5	96.5

TABLE III
Effect of Eluent Volume on the Recovery of Analytes

Eluent Volume (NaOH, mL)	Recovery (%)	
	As(III)	Sb(III)
0.5	50.9	45.9
1.0	70.2	75.4
1.5	91.2	92.3
2.0	96.4	94.7
2.5	97.3	98.3
3.0	95.8	95.7

Effect of Sample Volume

High preconcentration factors are necessary for the determination of lower analyte levels in real environmental and biological samples. Hence, the effect of sample volume on the recovery of the analytes was examined in the range of 20–250 mL sample volume containing 10 ng of the analytes. The above sample solutions were passed through the microcolumn at an optimum flow rate according to the recommended procedure. As can be seen in Figure 3, the analytes could be recovered quantitatively (>90%) up to 150 mL of sample solution. Because the elution volume was 1.5 mL of 0.6 mol L⁻¹ NaOH solution, an enrichment factor of 100 was achieved in this work.

Interference Study

The effects of common coexisting ions on the adsorption of the analytes were investigated. The tolerance limit of coexisting ions is defined as the largest amount that makes the recovery of the analyte less than 90%. In the present experiments, 5.0 ng mL⁻¹ solutions of the analytes containing the added interfering ions were treated according to the recommended procedure. Table IV shows that the coexisting foreign ions did not interfere in the

determination within the range of their amounts tested.

Adsorption Capacity

The adsorption capacity was investigated by a method provided in the literature (35). Aliquots of 100 mL of a series of concentrations (1.0–10 µg mL⁻¹) were adjusted to the appropriate pH, then preconcentrated and eluted. The amount of metal ions adsorbed at each concentration level was determined. Breakthrough curves were obtained by plotting the metal ion concentrations (µg mL⁻¹) versus the milligram of metal ions adsorbed on per gram of adsorbent. The adsorption capacity calculated from the breakthrough curve was 3.6 and 2.8 mg g⁻¹ for As(III) and Sb(III), respectively.

TABLE IV
Tolerance Limits
of Coexisting Ions

Coexisting Ion	Concentration Ratio ^a
Na ⁺ , K ⁺	10,000
Ca ²⁺ , Mg ²⁺	5000
Al ³⁺ , Fe ³⁺	200
SiO ₃ ²⁻ , SO ₄ ²⁻ , PO ₄ ³⁻	2000

^a Concentration ratio: Foreign ion/determined ion.

Column Reuse

In order to examine the long-term stability of the microcolumn, it was subjected to successive adsorption and desorption cycles by passing 20 mL of the solutions containing the analytes through the column. The stability and potential regeneration of the column were assessed by monitoring the changes in the recoveries of the analytes. The column can be reused after regeneration with 3.0 mL of 0.6 mol L⁻¹ NaOH solution and 20 mL deionized water, respectively, and is stable up to 50 adsorption-elution cycles without any obvious decrease in the adsorption capacity and the recovery for the analytes.

Analytical Performance

The reproducibility of the preconcentration was evaluated by passing 20 mL of standard solution of the analytes through the microcolumn and repeating the procedure nine times. The obtained relative standard deviation (RSD) of As(III) and Sb(III) (c= 1.0 ng mL⁻¹) was 3.1% and 5.4%, respectively. The detection limit, defined as the concentration that produces a signal equivalent to three times the standard deviation of nine measurements of the blank, was 0.065 ng mL⁻¹ and 0.012 ng mL⁻¹ for As(III) and Sb(III), respectively.

Fig. 2. Effect of sample flow rate on the recovery of As(III) and Sb(III) on CNFs-APDC. As(III) and Sb(III): 5.0 ng mL⁻¹; pH=3.0; sample volume: 20 mL.

Fig. 3. Effect of sample volume on the recovery of As(III) and Sb(III) on CNFs-APDC. pH: 3.0; sample volume: 20 mL; As(III) and Sb(III): 10 ng.

TABLE V
Analytical Results of the Analytes
in Natural Water Sample

Element	Added (ng mL ⁻¹)	Found ^a (ng mL ⁻¹)	Recovery (%)
As(III)	0	0.38±0.04	-
	2.0	2.31± 0.15	96.5
	3.0	3.51± 0.26	104
Sb(III)	0	0.091± 0.008	-
	2.0	2.13± 0.17	102
	3.0	2.95±0.21	95.3

^a Mean value ± standard deviation, n=3.

TABLE VI
Analytical Results of the Analytes
in Standard Reference Material of Human Hair

Element	Found ^a (μg g ⁻¹)	Certified (μg g ⁻¹)
As(III)	0.31±0.02	0.28±0.04
Sb(III)	0.10±0.011	0.095±0.012

^a Mean value ± standard deviation, n=3.

Sample Analysis

In order to establish the validity of this method, the analytes were determined in a natural water sample and a biological reference material (GBW 07601 Human Hair). The obtained results are summarized in Tables V and VI, respectively. As can be seen, the determined values were in good agreement with the certified values, and the recoveries of the analytes were reasonable for trace analysis and ranged from 95.3–104%.

CONCLUSION

In this work, an effective procedure for the preconcentration and separation of trace As(III) and Sb(III) in environmental and biological samples is described using a microcolumn packed with CNFs-APDC, followed by ICP-MS analysis. The adsorption behavior of the analytes was investigated in detail. The analytes were retained in the pH range of 2.0–4.0, and desorbed quantitatively with 1.5 mL of 0.6 mol L⁻¹ NaOH solution. In addition, no carryover was observed in the next analysis. The analytes could be concentrated 100 times within a short time and recovered with high precision. The adsorption capacity for As(III) and Sb(III) was 3.6 mg g⁻¹ and 2.8 mg g⁻¹, respectively. The experimental results show that this method is applicable for the determination of trace/ultratrace

elements in natural water and hair samples.

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