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Talanta

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Magnetic solid phase extraction for the determination of trace antimony species in water by inductively coupled plasma mass spectrometry

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ARTICLE INFO

Article history:

Received 3 August 2014

Received in revised form

4 November 2014

Accepted 13 November 2014

Available online 20 November 2014

Keywords:

Magnetic nanoparticles

Antimony

Speciation

Solid phase extraction

ICP-MS

ABSTRACT

A new magnetic solid phase extraction (MSPE) method using octyl-immobilized silica-coated magnetic Fe_3O_4 ($\text{C8-Fe}_3\text{O}_4@\text{SiO}_2$) nanoparticles as the MSPE adsorbent combined with inductively coupled plasma mass spectrometry (ICP-MS) has been developed for speciation analysis of Sb(III) and Sb(V). At pH 5.0, Sb(III) forms a hydrophobic complex with ammonium pyrrolidine dithiocarbamate (APDC) and is retained on $\text{C8-Fe}_3\text{O}_4@\text{SiO}_2$ nanoparticles, whereas Sb(V) remains as free species in aqueous solution. At pH 2.0, both Sb species (total Sb) form hydrophobic APDC complexes, being retained on the adsorbent. Thus, sensitive speciation analysis of Sb(III) and Sb(V) could be achieved by selective SPE of either Sb(III) or total Sb under different pH on $\text{C8-Fe}_3\text{O}_4@\text{SiO}_2$ nanoparticles. The experimental parameters, such as pH of solution, concentration of APDC, eluent type and sample volume were optimized in detail. The limits of detection (LOD, 3δ , $n=10$) of this MSPE method was $0.001 \mu\text{g L}^{-1}$ and $0.004 \mu\text{g L}^{-1}$, respectively, for Sb(III) and Sb(V). The precision of the method (Relative standard deviation, RSD, $n=6$) for Sb(III) and Sb(V) at $1.0 \mu\text{g L}^{-1}$ was 3.4% and 4.6%, respectively. In order to verify the accuracy of the method, certified reference material (GSB 07-1376-2001) of environmental water was analyzed and the result obtained was in good agreement with the certified values. This proposed method is simple, accurate and sensitive, and can be applied to the speciation of Sb(III) and Sb(V) in environmental waters without any pre-reduction or pre-oxidation operation.

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1. Introduction

Antimony (Sb) is a ubiquitous element in the environment that has been extensively used for various industrial applications for a long time, for example, batteries, semiconductors and fireproof textiles. Due to its toxicity and biological effects, antimony has been considered as a priority pollutant [1–3]. The permissible limit of antimony in drinking waters prescribed by the US Environmental Protection Agency (EPA) is $6 \mu\text{g L}^{-1}$ [4,5]. However, the speciation studies have demonstrated that the impact of antimony in an environmental or biological system depends critically on its chemical forms [6]. For example, inorganic antimony species are more toxic than the organic ones, and inorganic trivalent species (Sb(III)) are 10 times more toxic than pentavalent species (Sb(V)). In the majority of environmental matrices, such as natural water and soil, antimony is mainly found in its inorganic species and usually present at trace levels. Therefore, it is highly desirable to

develop efficient speciation approaches to determine the individual antimony species in order to estimate its environmental impacts and health risks.

Several modern analytical techniques, including atomic absorption spectrometry [7], atomic emission spectrometry [8], atomic fluorescence spectrometry [9,10], spectrophotometry [11], and mass spectrometry [12,13], have been employed for the quantitative determination of antimony species after their preconcentration or speciation. Among them, inductively coupled plasma mass spectrometry (ICP-MS) has been proved to be the most powerful technique for the determination of trace elements in various matrices due to its attractive features: high sensitivity, wide linearity, multi-element capability and good precision. Nevertheless, ICP-MS based quantification of metal species usually requires the application of a separation procedure prior to detection, because the element-specific techniques including ICP-MS cannot discriminate the species of a given element [14].

Up till now, the chromatographic techniques including liquid chromatography (LC) [15,16], gas chromatography (GC), [17] and capillary electrophoresis (CE) [18], and non-chromatographic techniques including solid phase extraction (SPE) [19–22], liquid-liquid

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extraction (LLE) [23] and cloud point extraction (CPE) [24] have been exploited for the separation of antimony species, followed by element-specific determination. Among these techniques, SPE features simple device and can enrich the species of interest, making it desirable procedure for speciation analysis [25–27]. Recently, Mendil et al. [28] developed a SPE method for the determination of Sb(III) and Sb(V) in water samples by graphite furnace atomic absorption spectrometry (GFAAS). The separation method of these species was established using a micro-column packed with tetraethylenepentamine bonded silica gel phase, and Sb(III) was retained on the adsorbent, whereas Sb(V) passed through. For the determination of total Sb, a reduction step of Sb(V) is made using L-cysteine. Shakerian et al. [29] described a method for the determination of Sb(III) based on selective adsorption of Sb(III) on an antimony ion imprinted polymer (IIP) sorbent. The adsorbed Sb(III) was eluted by 4.0 M HNO₃ and subsequently determined by GFAAS. The determination of total inorganic antimony was achieved after the reduction of Sb(V) to Sb(III) using potassium iodide and ascorbic acid. However, applications of these traditional adsorbents in speciation of antimony are being limited owing to lengthy pretreatment duration per sample and tedious pre-reduction or pre-oxidation process.

Magnetic materials, particularly super paramagnetic Fe₃O₄ nanoparticles, provide a novel biomedical and environmental purification technique because of their specific magnetic separation characteristics [30,31]. Considering the special advantages of high adsorption capacity of nanoparticles and the separation convenience of magnetic Fe₃O₄ nanoparticles, the surface modification of these magnetic nanoparticles with a specific ligand has been proven to be a selective, quick, simple, and efficient way for preconcentration of trace elements and their species [32,33]. For example, Jiang et al. reported a zincon-immobilized silica-coated magnetic Fe₃O₄ nanoparticles which has been successfully used for determination of trace lead [34] and speciation of chromium [35].

The utilization of magnetic materials in the area of trace elements and their species is attracting much attention. To the best of our knowledge, there is still no research on speciation of antimony using magnetic Fe₃O₄ nanoparticles or their derivatives. In the present work, a novel adsorbent named octyl-immobilized silica-coated magnetic Fe₃O₄ (C8-Fe₃O₄@SiO₂) nanoparticles has been prepared and used for preconcentration and separation of Sb(III) and Sb(V) in different pH range. Compared with previously reported works, the proposed method here needs no pre-reduction or pre-oxidation operation, and is suitable for analyzing samples in batches as it is simple and convenient operation, high reproducibility, no special and expensive reagents and equipments.

2. Experimental

2.1. Apparatus

A Perkin-Elmer SCIEX ELAN 9000 ICP-MS (Perkin-Elmer, Inc., Wellesley, MA, USA) equipped with a glass concentric nebulizer and a cyclonic spray chamber (Glass Expansion, Romainmotier, Switzerland) was used for determination of antimony. The instrumental operating conditions selected are summarized in Supplementary Material (Table S1).

The pH values were controlled by a Mettler Toledo SevenMulti pH meter (Mettler-Toledo, Shanghai, China) supplied with a combined electrode. The transmission electron microscopy (TEM) images of naked Fe₃O₄ and C8-Fe₃O₄@SiO₂ nanoparticles were obtained using a JEM-200CX high-resolution transmission electron microscope (HRTEM) (JEOL, Tokyo, Japan). Fourier transform infrared (FT-IR) spectra (4000–400 cm⁻¹) in KBr were recorded on a NEXUS870 spectrometer (Nicolet, Madison, WI, USA). The X-ray diffraction (XRD) patterns were collected on a ARL X'TRA diffractometer with Cu K α radiation (ARL,

Lausanne, Switzerland). The magnetism measurement of nanoparticles was carried out using a superconducting quantum interference device (SQUID) magnetometer (Quantum Design, San Diego, CA, USA) at room temperature. A KQ3200DE ultrasonic bath with temperature control (Kunshan Shumei Ultrasonic Instrument, Suzhou, China) was employed to disperse the nanoparticles in solution. An Nd-Fe-B magnet (10 mm \times 6.0 mm \times 1.6 mm) was used for magnetic separation.

2.2. Reagents and materials

Ferric trichloride (FeCl₃ · 6H₂O) and ferrous chloride (FeCl₂ · 4H₂O) were purchased from Nanjing Chemical Reagent Company (Nanjing, China). Tetraethyorthosilicate (TEOS), *n*-octyltrimethoxysilane (C8-TEOS) and ammonium pyrrolidine dithiocarbamate (APDC) were obtained from Alfa Aesar (Tianjing, China). HNO₃ and NH₃ · H₂O were of guarantee reagent, and obtained from Merck (Darmstadt, Germany). All other chemicals were at least of analytical grade, and used without further purification. Deionized water (DIW, 18.25 M Ω cm) obtained from a Milli-Q water system (Millipore, Bedford, MA, USA) was used throughout the experiment. Plastic and glass containers and all other immersed laboratory materials that could come into contact with samples or standards were stored in 20% (v/v) HNO₃ solution, and rinsed with DIW prior to use.

Stock standard solutions (1000.0 mg L⁻¹) of Sb(III) and Sb(V) were prepared by respectively dissolving appropriate amounts of K₂Sb₂(C₄H₂O₆)₂ and K₂H₂Sb₂O₇ · 4H₂O (both purchased from J&K, Shanghai, China) in DIW. Lower concentration standard solutions were prepared daily by appropriate dilutions from their stock solutions.

The certified reference material GSB 07-1376-2001 (Standard environmental water sample) was obtained from the National Research Center for Certified Reference Materials (Beijing, China). Four water samples: tap water, waste water, Xuanwu Lake water and Yangtze River water were collected in Nanjing, China. Each water sample was filtered through a 0.45 μ m membrane (Tianjing Jinteng Instrument Factory, Tianjin, China) before analysis.

2.3. Synthesis of C8-Fe₃O₄@SiO₂ nanoparticles

The procedure for the preparation of C8-Fe₃O₄@SiO₂ nanoparticles is illustrated in Fig. 1, which involved two steps, the preparation of naked Fe₃O₄ nanoparticles and its surface modification with Si-OH and octyl. The naked Fe₃O₄ nanoparticles were prepared through a co-precipitation method [34]. The obtained naked Fe₃O₄ nanoparticles were further coated with silica and functionalized with C8- group by the hydrolysis and condensation of TEOS and C8-TEOS. Briefly, Fe₃O₄ nanoparticles (1.0 g) were homogeneously dispersed in a mixture of isopropanol (300 mL), deionized water (28 mL) and concentrated aqueous ammonia (20 mL, 28 wt%). A mixture of TEOS (7 mL) and C8-TEOS (3.5 mL) was added dropwise with continuous stirring. After the reaction had been performed at room temperature for 2 h, the product was collected with a magnet, and washed repeatedly with ethanol and water, and finally dried under vacuum.

2.4. Procedure of speciation analysis

The MSPE process is also illustrated in Fig. 1. For determination of Sb(III), 100 mL aqueous sample solution containing the studied ions was prepared with 2.0 mL of 0.25 M APDC, and the pH was adjusted to 5.0 with 0.1 M HNO₃ or 0.1 M NH₃ · H₂O. After 20 mg of the prepared C8-Fe₃O₄@SiO₂ nanoparticles were added into the beaker, the mixture was ultrasonicated for 15 min. Then, the magnetic adsorbent was magnetically separated through an external magnet and the supernatant was decanted directly. Subsequently, 2 mL of 2 M HNO₃ was added into the beaker as eluent and the new mixture

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