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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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ABSTRACT

A new magnetic solid phase extraction (MSPE) method using octyl-immobilized silica-coated magnetic Fe_3O_4 (C8-Fe_3O_4@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 C8-Fe_3O_4@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 C8-Fe_3O_4@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 μg L^{-1} and 0.004 μg 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 μg 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.

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 μg 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 HNO_3 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 Fe_3O_4 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 Fe_3O_4 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 Fe_3O_4 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 Fe_3O_4 nanoparticles or their derivatives. In the present work, a novel adsorbent named octyl-immobilized silica-coated magnetic Fe_3O_4 (C8-Fe_3O_4@SiO_2) 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 Fe_3O_4 and C8-Fe_3O_4@SiO_2 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 an ARL X'TRA diffractometer with Cu Kα 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 × 6.0 mm × 1.6 mm) was used for magnetic separation.

2.2. Reagents and materials

Ferric trichloride ($FeCl_3 \cdot 6H_2O$) and ferrous chloride ($FeCl_2 \cdot 4H_2O$) were purchased from Nanjing Chemical Regent Company (Nanjing, China). Tetraethyorthosilicate (TEOS), n-octyltrimethoxysilane (C8-TEOS) and ammonium pyrrolidine dithiocarbamate (APDC) were obtained from Alfa Aesar (Tianjing, China). HNO_3 and $NH_3 \cdot H_2O$ 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 MΩ 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) HNO_3 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 $K_2Sb_2(C_4H_2O_6)_2$ and $K_2H_2Sb_2O_7 \cdot 4H_2O$ (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 μm membrane (Tianjing Jinteng Instrument Factory, Tianjin, China) before analysis.

2.3. Synthesis of C8-Fe_3O_4@SiO_2 nanoparticles

The procedure for the preparation of C8-Fe_3O_4@SiO_2 nanoparticles is illustrated in Fig. 1, which involved two steps, the preparation of naked Fe_3O_4 nanoparticles and its surface modification with Si-OH and octyl. The naked Fe_3O_4 nanoparticles were prepared through a co-precipitation method [34]. The obtained naked Fe_3O_4 nanoparticles were further coated with silica and functionalized with C8- group by the hydrolysis and condensation of TEOS and C8-TEOS. Briefly, Fe_3O_4 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 HNO_3 or 0.1 M $NH_3 \cdot H_2O$. After 20 mg of the prepared C8-Fe_3O_4@SiO_2 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 HNO_3 was added into the beaker as eluent and the new mixture was ultrasonicated for 5 min. Finally, the adsorbent was removed through an external magnet and the supernatant was collected for determination of Sb(III) by ICP-MS.

The MSPE procedure for total Sb was nearly the same as that of Sb(III) except the pH of sample solution was adjusted to 2.0 prior to extraction. The concentration of Sb(V) was then calculated by the difference between total Sb and Sb(III).

3. Results and discussion

3.1. *Characterization of C8-Fe_3O_4@SiO_2 nanoparticles*

3.1.1. *TEM images*

In order to get direct information on particle size and morphology, the typical TEM images for naked Fe_3O_4 and C8-Fe_3O_4@SiO_2 nanoparticles are shown in Fig. 2. The diameter of naked Fe_3O_4 (A) was about 10 nm, while the average diameter of C8-Fe_3O_4@SiO_2 nanoparticles (B) was 15 nm. It can be clearly observed that the SiO_2 layers with thickness of ca. 5 nm were uniformly coated on Fe_3O_4 core for all the particles. To study the influence of surface decoration on the magnetic behavior of Fe_3O_4 nanoparticles, the magnetization measurement was performed using vibration sample magnetometry (VSM). Fig. S1 shows VSM curves of naked Fe_3O_4 and C8-Fe_3O_4@SiO_2 nanoparticles at room temperature. They both exhibit typical superparamagnetic behavior with the maximal saturation magnetizations of 34.6 and 21.0 emu g^{-1}, respectively.

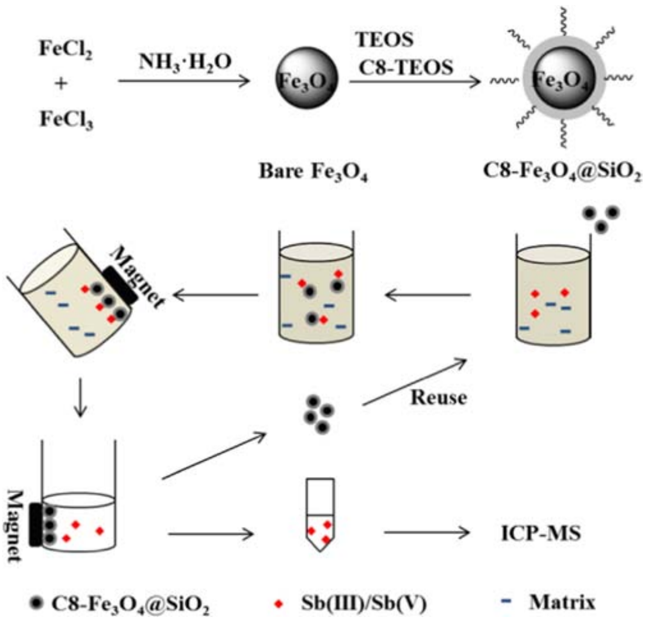

Fig. 1. Synthesis route of C8-Fe_3O_4@SiO_2 nanoparticles and their use for MSPE for determination of Sb(III) and total Sb.

3.1.2. *FT-IR spectra*

FT-IR was employed to examine the surface functional groups of naked Fe_3O_4 and C8-Fe_3O_4@SiO_2 nanoparticles, and the obtained FT-IR spectra are shown in Fig. 3. The adsorption peak at 580 cm^{-1} is ascribed to the characteristic band of Fe-O of Fe_3O_4. The bands located at 1620 cm^{-1} and 1450 cm^{-1} can be assigned to bending vibration of the adsorbed molecular water and the structural (hydroxyl) water, respectively. A broad absorption band in the range from 900 to 1100 cm^{-1} observed in the FT-IR spectrum of C8-Fe_3O_4@SiO_2 nanoparticles (B) can be attributed to Si-O stretching, and absorption bands at 2918.6 and 2960.8 cm^{-1} are ascribed to stretching vibration of C-H bond. The above results indicated that the octyl (C8-) functional group was present and chemically bound to the surface of nanoparticles.

3.1.3. *XRD patterns*

The structures of naked Fe_3O_4 and C8-Fe_3O_4@SiO_2 nanoparticles were analyzed by wide-angle XRD and the results are showed in Fig. S2. The six characteristic peaks occurred at 2θ region of 20–70° were marked by their corresponding indices (220), (311), (400), (422), (511), and (440), respectively, which match well with the standard XRD data cards of Fe_3O_4 crystal (JCPDS No. 19-06290), suggesting that the Fe_3O_4 nanoparticles are well retained after the functionalization. Consistent with the TEM and FI-IR results, the extra band of C8-Fe_3O_4@SiO_2 nanoparticles occurred round $2\theta = 23$ is the diffraction peaks of amorphous silica.

3.2. *Optimization of MSPE parameters*

3.2.1. *Effect of pH*

pH of sample solution plays an important role on species distribution and adsorption efficiency, and therefore is proved to be a primary parameter for speciation analysis. Moreover, a proper

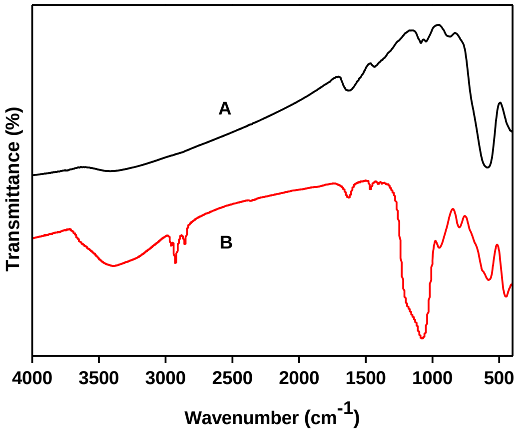

Fig. 3. FI-IR spectra of naked Fe_3O_4 (A) and C8-Fe_3O_4@SiO_2 (B).

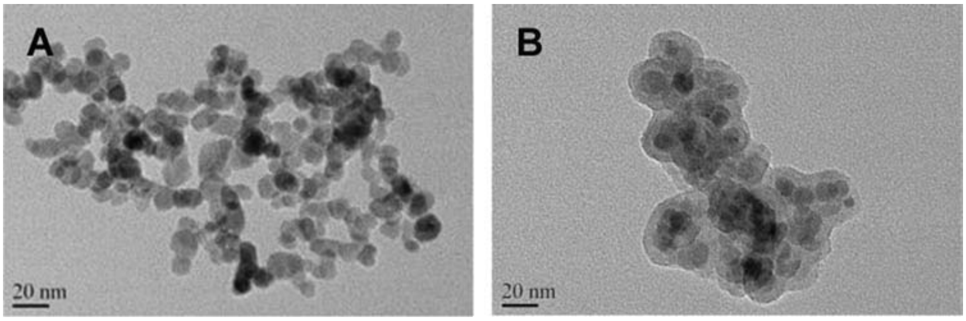

Fig. 2. TEM images of naked Fe_3O_4 (A) and C8-Fe_3O_4@SiO_2 (B).

pH can bring down the interference of the matrix and increase the selectivity of the method. The influence of pH on the adsorption behavior of Sb(III) and Sb(V) in presence and absence of APDC was investigated over the pH range of 2.0–6.0. As can be seen in Fig. 4, in the absence of APDC, there was only ca. 40–60% Sb(III) retained on C8-Fe_3O_4@SiO_2 nanoparticles in the tested pH range, and virtually no retention of Sb(V) on the nanoparticles in the same pH. However, in the presence of APDC, Sb(III) was quantitatively retained on the adsorbent in the whole pH range, while Sb(V) could be quantitatively retained only in the pH range of 2.0–3.0. The dramatic differences in the adsorption of Sb(III) and Sb(V) with and without APDC could be attributed to their different complexation abilities under different pH conditions. For Sb(III), it is mainly present as less water soluble uncharged species $Sb(OH)_3$ in the pH range of 2.0–6.0, while it could form the stable complex Sb(III)–APDC with APDC in the examined pH range. The hydrophobicity of Sb(III)–APDC is much higher than $Sb(OH)_3$ [8,19], so when APDC exists, Sb(III)–APDC could be efficiently retained by the hydrophobic C8- group on C8-Fe_3O_4@SiO_2 nanoparticles. For Sb(V), it could form complex with APDC only in strongly acidic solutions ($pH \leq 3.0$) [13,21], while existed as water soluble species $H[Sb(OH)_6]$ or $Sb(OH)_5^-$ in weak acidic solutions, so Sb(V) was retained in the presence of APDC in the pH range of 2.0–3.0.

According to above results, it can be found that in the presence of APDC, both Sb(III) and Sb(V) are quantitatively retained on C8-Fe_3O_4@SiO_2 nanoparticles in the pH range of 2.0–3.0, while only Sb(III) is retained on the adsorbent in the pH range of 4.5–6.0. So, speciation of Sb(III) and Sb(V) can be attained by adjusting pH of sample solution. Notably, no pre-reduction and pre-oxidation process is needed prior to MSPE operation. For further study, pH 5.0 was selected for speciation of Sb(III) and pH 2.0 was chosen for preconcentration of total Sb. Sb(V) was then calculated by difference between total Sb and Sb(III).

3.2.2. Effect of amount of APDC

An appropriate APDC concentration should be used to ensure the effective complexation of Sb(III) and Sb(V) with APDC. So the influences of APDC concentration on the retentions of Sb(III) and Sb(V) were studied and the results are summarized in Fig. 5. It can be seen that efficient preconcentration of Sb(III) at pH 5.0, and simultaneous retention of Sb(III) and Sb(V) at pH 2.0 were achieved at APDC concentration of 2.5 mM. Considering that the interfering substances (e.g. Pb and As, etc.) in real samples may form complexes with APDC, and that excessive APDC may compete with Sb(III)/Sb(V)–APDC complexes for C8- active sites on the surface of C8-Fe_3O_4@SiO_2 nanoparticles, finally, an appropriate APDC concentration of 5 mM was used throughout the work.

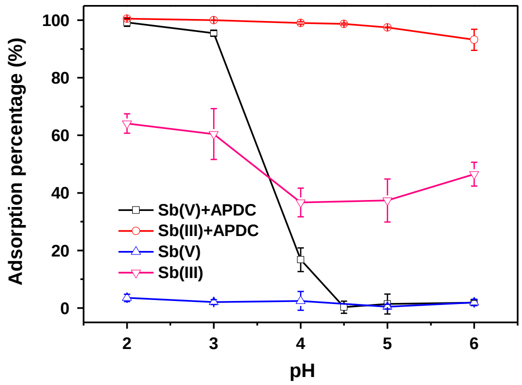

Fig. 4. Effect of pH on the adsorption of 10 μg L^{-1} Sb(III) and Sb(V) on C8-Fe_3O_4@SiO_2 nanoparticles.

3.2.3. Effect of eluent

An appropriate eluent is not only important for the quantitative elution of the retained targets, but also important for the subsequent ICP-MS determination. Organic solvents such as methanol, ethanol, and acetone have been demonstrated effective in desorbing APDC complexes from the SPE adsorbent. However, high contents of organic solvents were not directly compatible with the sample introduction system of ICP-MS, because they may cause unexpected interferences for ICP-MS determination, or even plasma extinction. Although this problem can be solved by evaporating organic solvents away and a suitable dilution by diluted HNO_3 before introducing in ICP-MS, we found that the procedure was time consuming and affected the precision of results. For this reason, HNO_3 solutions, which are often used as carrier solution for ICP-MS detection, were subsequently tested as eluent with different concentration. With the fixed volume of 2 mL, the experiment results indicated that 2 M HNO_3 was sufficient for the complete desorption of Sb(III) and total Sb. Considering there was a signal depression with increasing HNO_3 concentration (Fig. S3), finally, 2 mL of 2 M HNO_3 was used to elute Sb(III) and total Sb in this work.

3.2.4. Effect of sample volume and ultrasonic time

In order to examine the possibility of enriching low concentrations of analyte from large volumes, the effect of sample volume on the recovery of antimony was studied. The results showed that the recoveries of Sb(III) and Sb(V) were not affected by sample volumes between 20–100 mL, and a decrease of recovery (< 90%) was examined when sample volumes were larger than 150 mL. Therefore, the sample volume of 100 mL was selected with respect of maximum recoveries of analytes, and an enrichment factor of 50 was achieved by using 2 mL eluent.

The effect of ultrasonic time for extraction and elution was also examined. The results indicated that both species can be adsorbed on C8-Fe_3O_4@SiO_2 nanoparticles within 15 min and also desorbed quantitatively with HNO_3 in 5 min.

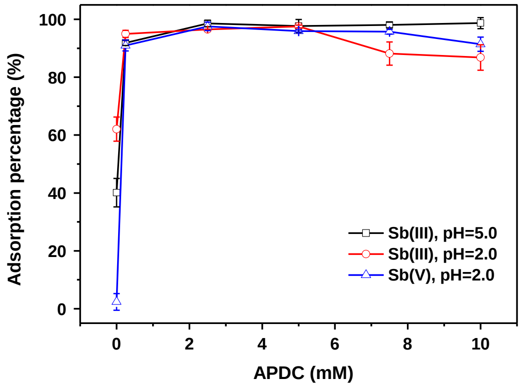

Fig. 5. Effect of APDC on the adsorption of 10 μg L^{-1} Sb(III) and Sb(V) on C8-Fe_3O_4@SiO_2 nanoparticles.

Table 1
Analytical results of antimony species in certified reference material (mean ± SD, $n=3$).

Sample	Certified (μg L^{-1}, Total Sb)	Found (μg L^{-1})		
		Total Sb	Sb(III)	Sb(V)
GSB 07-1376-2001	25.00 ± 2.40	25.26 ± 1.58	0.38 ± 0.07	24.88 ± 1.65

Table 2
Determination of antimony species in real water samples (mean ± SD, $n=3$).

Sample	Sb concentration (μg L^{-1})		Spiked result (μg L^{-1})					
	Sb(III)	Sb(V)	Sb(III)			Sb(V)		
			Added	Found	Recovery (%)	Added	Found	Recovery (%)
Yangtze River	0.015 ± 0.003	1.090 ± 0.025	1.0	1.035 ± 0.065	104	1.0	2.057 ± 0.170	97
Waste water	0.063 ± 0.005	2.183 ± 0.061	1.0	1.029 ± 0.079	97	1.0	3.284 ± 0.152	110
Tap water	ND	1.277 ± 0.054	1.5	1.361 ± 0.070	91	2.0	3.178 ± 0.127	95
Lake water	0.023 ± 0.008	1.391 ± 0.033	1.5	1.603 ± 0.068	105	2.0	3.372 ± 0.063	99

3.2.5. *Adsorption capacity*

The adsorption capacity of C8-Fe_3O_4@SiO_2 nanoparticles was determined by a batch equilibrium technique under the optimized condition. 800 mg APDC were mixed with 1000 mL 200 μg L^{-1} Sb(III) solution at pH 5.0, Sb(III) solution at pH 2.0, and Sb (V) solution at pH 2.0, and then 10 mg C8-Fe_3O_4@SiO_2 nanoparticles were added to each solution. After equilibration and separation using an external magnet, the concentrations of the analytes remaining in solution were measured by ICP-MS. The adsorption capacities of C8-Fe_3O_4@SiO_2 nanoparticles were found to be 3.5 mg g^{-1} for Sb(III) at pH 5.0, 2.9 mg g^{-1} for Sb(III) at pH 2.0, and 2.3 mg g^{-1} for Sb(V) at pH 2.0.

3.2.6. *Interference study*

Generally, the coexisting substances in the solution may compete with target analyte complex for the active sites of adsorbent. Besides, the coexisting substances also may compete with the analyte ion for APDC in the present study. The effects of cations and anions on the determination of antimony were investigated under the optimized conditions. The results showed that in the presence of 1000 mg L^{-1} K^+ and Na^+, 200 mg L^{-1} Ca^{2+} and Mg^{2+}, 25 mg L^{-1} Al^{3+}, Fe^{3+}, Cu^{2+}, and Zn^{2+}, 1000 mg L^{-1} Cl^-, SO_4^{2-} and PO_4^{3-}, the recoveries of the analytes, Sb(III) and total Sb, were still above 90%. From these experimental results, it can be concluded that large numbers of ions have no considerable effect on the determination of Sb(III) and Sb(V), and the developed method has a good tolerance to the interference.

3.3. *Analytical performance*

Under above optimized conditions, the analytical performance of the method was evaluated. The limits of detection (LOD) were calculated after application of the MSPE procedure to blank solutions. Based on three times the standard deviations (SD) of the eluate signals divided by the preconcentration factor (50), the LOD was found to be 0.001 and 0.004 μg L^{-1}, respectively, for Sb(III) and Sb(V). The instrumental LOD for Sb species was also determined by using blank solutions without preconcentration and found to be 0.055 μg L^{-1} for Sb(III) and 0.073 μg L^{-1} for Sb(V) for comparison. The precision (Relative standard deviation, RSD) for six replicate measurements of 1.0 μg L^{-1} Sb(III) and Sb(V) was 3.4% and 4.6%, respectively. Good linearity of Sb(III) and Sb(V) was obtained in the concentration range from 0.05 to 10.00 μg L^{-1}, with linear correlation coefficients of 0.9994 and 0.9991, respectively. In addition, under the optimized conditions, the adsorbents could be reused at least 10 times without decreasing extraction efficiency.

3.4. *Analysis application*

The proposed method was validated by determining antimony concentration in the certified reference material GSB 07-1376-2001 (Standard environmental water sample). As can be seen in Table 1, both kinds of the inorganic antimony species were found in the sample and Sb(V) was the main species, total Sb was in good agreement with the certified value, whereas no certified values for Sb(III) and Sb(V) were available for reference.

The method was applied in the analysis of antimony species in tap, waste, river and lake waters. The results are listed in Table 2. The recoveries of Sb(III) and Sb(V) for spiked samples were also evaluated. The results showed that the recoveries in all spiked samples were in the range from 91% to 110%, demonstrating that the proposed method is suitable for determination of antimony species in environmental waters.

4. Conclusions

A novel MSPE method using octyl-immobilized silica-coated magnetic Fe_3O_4 nanoparticles as the adsorbent combined with ICP-MS was developed for the speciation of Sb(III) and Sb(V) in environmental waters. The well-characterized nanoparticles are shown to be excellent adsorbents for the APDC complexes of Sb(III) and Sb(V), which allows Sb(III) and total Sb to be easily preconcentrated and determined at different pH. By contrast with traditional SPE procedure for antimony species, the proposed C8-Fe_3O_4@SiO_2 nanoparticles based method did not need pre-reduction and pre-oxidation process. Moreover, it is simple, facile, and economic for speciation of trace antimony in real-world applications.

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Appendix A. Supporting information

Supplementary data associated with this article can be found in the online version at http://dx.doi.org/10.1016/j.talanta.2014.11.026.

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