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Speciation of antimony(III) and antimony(V) by electrothermal atomic absorption spectrometry after ultrasound-assisted emulsification of solidified floating organic drop microextraction

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A simple, sensitive and efficient method of ultrasound-assisted emulsification of solidified floating organic drop microextraction (USE-SFODME) coupled to electrothermal atomic absorption spectrometry for the speciation of antimony at different oxidation state Sb(III)/Sb(V) in environmental samples was established. In this method, the hydrophobic complex of Sb(III) with sodium diethyldithiocarbamate (DDTC) is extracted by 1-undecanol at pH 9.0, while Sb(V) remains in aqueous phase. Sb(V) content can be calculated by subtracting Sb(III) from the total antimony after reducing Sb(V) to Sb(III) by L-cysteine. Various factors affecting USE-SFODME including pH, extraction solvent and its volume, concentration of DDTC, sonication time, and extraction temperature were investigated. Under the optimized conditions, the calibration curve was linear in the range from 0.05 to 10.0 ng mL^{-1}, with the limit of detection (3σ) 9.89 ng L^{-1} for Sb(III). The relative standard deviation for Sb(III) was 4.5% (n=9, c=1.0 ng mL^{-1}). This method was validated against the certified reference materials (GSB 07-1376-2001, GBW07441), and applied to the speciation of antimony in environmental samples (soil and water samples) with satisfactory results.

1. Introduction

Antimony (Sb) is a ubiquitous and cumulative toxic element in the environment with unknown biological functions [1]. It has extensive applications in pharmaceutical products, alloys, flame retardants, ceramics, semiconductors, and dyestuffs [1,2]. The physicochemical and toxic properties of antimony strongly depend on its binding and oxidation state rather than total concentration. Antimony mainly occurs in two oxidation states as Sb(III) and Sb(V) in the environment, which could form various inorganic and organic species with different toxicity and bioavailability. Inorganic antimony compounds are more toxic than its organic forms, and the toxicity of Sb(III) is 10 times greater than that of Sb(V) [3–5]. The International Agency for Research on Cancer (IARC) has reported that there is sufficient evidence for the carcinogenicity of Sb_2O_3 in experimental animals [5]. Antimony and its compounds are listed as priority pollutants by the U.S. Environmental Protection Agency (USEPA) and the European Union (EU), and the maximum admissible levels of Sb are 6.0 and 5.0 ng mL^{-1} for drinking water, respectively [6]. Excessive exposure to antimony may cause a wide variety of adverse health effects such as respiratory tract irritation, dermatitis, conjunctivitis, suppuration of the nasal septum, gastritis, or cellular damage in the lungs, heart, and kidneys [7]. Selective determination of antimony species is of growing interest in environmental analysis because of the implications in human health. Consequently, reliable and accurate analytical procedures are necessary for the speciation of Sb(III)/Sb(V) in different environmental samples.

Several techniques for Sb(III)/Sb(V) determination in real samples include UV–visible spectrophotometry (UV–vis) [8], inductively coupled plasma mass spectrometry (ICP-MS) [9–11], inductively coupled plasma atomic emission spectrometry (ICP-AES) [2,12], hydride generation atomic fluorescence spectrometry (HG-AFS) [13,14], flame atomic absorption spectrometry (FAAS) [15–17], and electrothermal atomic absorption spectrometry (ETAAS) [1,18]. Considered the poor sensitivity of FAAS and the high cost of ICP-MS, ETAAS is a well-established and sensitive technique with a relative small injection volume (5–50 μL), and a partially eliminated matrix during the pyrolysis step [1]. However, the effective and direct speciation of Sb(III)/Sb(V) with ETAAS is still a challenging task because of their low concentrations and matrix interferences in environmental and geological samples. Preliminary preconcentration of antimony species and matrix separation prior to analysis are therefore needed. Many miniaturized techniques involving cloud point extraction (CPE) [1,5,19], single drop micro-extraction (SDME) [20,21], and dispersive liquid phase microextraction (DLLME) [22]

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have been proven simple and inexpensive for separation and/or preconcentration antimony species. Ionic liquid-based liquid phase microextraction (IL-LPME) [23,24] has also been reported for the enrichment of metal species with satisfactory results, avoiding the usage of hazardous organic solvents, and it could be as an alternative approach before ETAAS test.

Ultrasound-assisted emulsification of solidified floating organic drop microextraction (USE-SFODME) has attracted much attention for sample preparation due to its simplicity, low cost, less organic solvent consumption, and achievement of high enrichment factor [25]. It avoids using high density and toxic extraction solvents compared to the conventional DLLME. For USE-SFODME, ultrasonic waves are a powerful aid in the extraction procedure because it facilitates emulsification phenomenon and accelerates mass transfer between immiscible phases [26,27]. Analytes extraction can be achieved rapidly since the extraction solvent is highly dispersed in the aqueous phase resulting in a large interface among the extraction solvent and the aqueous sample. The proposed USE-SFODME has been successfully applied to concentrate organic substances and metals [25,28–31]. To the best of our knowledge, the USE-SFODME as a separation/preconcentration of Sb(III) and Sb(V) prior to ETAAS determination has not been explored.

The aim of this work was to examine the possibility of implementation of USE-SFODME in combination with ETAAS for the speciation of Sb(III) and Sb(V) in environmental samples. Several main variables affecting the USE-SFODME were investigated in detail. The proposed method was applied to the extraction and determination of antimony species in water and soil samples.

2. Experimental

2.1. Apparatus

A ZEEnit 700 electrothermal atomic absorption spectrometer (Analytik Jena Instrument Co., Ltd., Germany) equipped with a Zeeman-based background corrector and a transverse heated graphite furnace atomizer was used for antimony determination. All measurements were performed in the peak area mode. Pyrolytic platform graphite tubes were used. An antimony hollow cathode lamp was operated at 9 mA and a wavelength of 217.6 nm with a spectral bandwidth of 0.5 nm. The graphite furnace temperature program are listed as follows: (1) Drying 1, 90 °C, 10 °C/s, hold time 10 s; (2) Drying 2, 105 °C, 10 °C/s, hold time 10 s; (3) Drying 3, 110 °C, 5 °C/s, hold time 15 s; (4) Pyrolysis, 400 °C, 250 °C/s, hold time 40 s; (5) Atomization, 2000 °C, 1500 °C/s, hold time 4 s; (6) Cleaning, 2300 °C, 500 °C/s, hold time 4 s. A model TU-1810 UV–visible spectrophotometer (Beijing Purkinje General Instrument Co., Ltd., Beijing, China) and a KQ-50E ultrasonic bath (Kunshan Ultrasonic Instruments Co., Ltd., Suzhou, China) were used. All pH values were measured by a PHS-25B pH-meter (Shanghai Precision & Scientific Instrument Co., Ltd., Shanghai, China) and the phase separation was assisted with a TG16-WS centrifuge (Hunan Xiangyi Centifuge Instrument Co., Ltd., Changsha, China). A SHA-C constant-temperature shaker was applied to the leaching of water-soluble antimony species.

2.2. Standard solutions and reagents

All reagents used were of analytical reagent grade or higher purity, and all solutions were prepared in doubly deionized water (DDW). stock solutions of 1.0 mg mL^{-1} Sb(III) and 1.0 mg mL^{-1} Sb(V) were prepared by dissolving appropriate amounts of potassium antimony tartrate (Tianjin Reagent Company, Tianjin, China) and potassium hexahydroxyantimonate (Shanghai Reagent Company, Shanghai, China) in DDW, respectively. Working standard solutions were obtained by diluting the stock solutions with DDW. Solution (3.0%, w/v) of sodium diethyldithiocarbamate (DDTC, Sinopharm Chemical Reagent Co., Ltd., Shanghai, China) was prepared in DDW. 1-Decanol (98%, Aladdin Chemical Co., Ltd., Shanghai, China), 1-undecanol (98%, Alfa Aesar (Tianjin) Chemical Co., Ltd., Tianjin, China), 1-bromohexadecane (97%) and n-hexadecane (Aladdin Chemical Co., Ltd., Shanghai, China) were used as extraction solvents. Buffer solutions of acetic-acetate (pH 3.0–5.0), ammonium acetate (pH 7.0), and ammonia–ammonium chloride (pH 8.0–11.0) were used for pH adjustments. All glassware were stored in 10% (v/v) nitric acid for at least 24 h and washed three times with DDW before use.

2.3. Procedure for USE-SFODME

A 40.0 mL of the working standard solution (or sample solution) containing 1.0 ng mL^{-1} of Sb(III), 0.60 mL 3.0% (w/v) DDTC, 8.0 mL buffer solution (pH 9.0) and 50.0 μL of 1-undocanol was placed in a screw cap ployethylene tube with conical bottom, sonicated at 35 °C for 20 min and the cloudy solution was centrifuged for 10 min at 6500 rpm, keeping in an ice bath for 10 min. The solidified 1-undocanol was transferred to a conical vial for melting and dissolved in 0.50 mL of methanol containing nitric acid (0.10 mol L^{-1}). A 20 μL of resultant solution was injected by the autosampler (MPE-60) into the ETAAS nebulizer for quantification.

2.4. UV–visible absorption spectra

Aliquots of 5.0 mL solution containing 2.0 μg mL^{-1} of Sb(III) [or Sb(V)] and 0.60 mL 3.0% (w/v) DDTC were adjusted to pH 9.0 and were introduced into the 1-cm quartz cell for UV–visible absorption spectra measurements. Absorbance of the blank solutions was deducted for all experiments.

2.5. Sample preparation

The Slender West Lake surface water (Yangzhou, China) was filtered through a 0.45 μm membrane filter immediately and kept at 4 °C before use. A certified reference material of water (GSB 07-1376-2001, No. 204906, Institute for Environmental Reference Materials of State Environmental Protection Administration, Beijing, China) was diluted properly with DDW prior to analysis.

The soil sample was collected from the campus at Yangzhou University (Yangzhou, China). 5.0 g of soil sample (100 Mesh) and 40.0 mL of DDW (pH=7.0) were transferred into a 250 mL polyethylene flat-bottomed flask and shaken at 200 rpm for 2 h at 25 °C. After centrifugation (5000 r min^{-1} for 20 min), the bulk aqueous phase was filtered through a 0.45 μm membrane filter for further analyzing as described above. A certified reference material for elemental forms in soil [GBW07411 (GSF-1), National Research Center for Certified Reference Materials, Beijing, China] was treated as the real soil sample.

2.6. Determination of antimony species

After the extraction, a 20 μL resultant solution was introduced into graphite for Sb(III) determination. Total Sb was determined after the reduction of Sb(V) to Sb(III), and the concentration of Sb(V) was calculated by the difference between the total Sb and Sb(III). Prereduction of Sb(V) to Sb(III) was carried out in 0.20% (w/v) L-cysteine and 0.4 mol L^{-1} hydrogen chloride in a water bath at 50 °C for 30 min.

3. Results and discussion

3.1. Optimization of graphite furnace conditions

The influence of pyrolysis temperature (200–600 °C) and atomization temperature (1800–2200 °C) on the absorbance (A) of antimony was investigated. The matrix was sufficiently eliminated and A reached maximum at the pyrolysis temperature of 400 °C and then decreased at higher pyrolysis temperature due to antimony loss. The highest atomic signal was observed at 2000 °C. So, the optimal pyrolysis and atomization temperature was 400 °C and 2000 °C, respectively.

3.2. Optimization of extraction conditions

3.2.1. Effect of pH

pH plays a unique role in Sb-DDTC complex formation and its subsequent extraction. The effect of pH on the extraction efficiency of Sb(III) was investigated in the range of pH 3.0–10.0. As shown in Fig. 1, the maximum extraction efficiency of Sb(III) was observed at pH 9.0, while Sb(V) was not extracted in the tested pH range. The reason for the extraction of Sb(III) was the formation of the hydrophobic complexes Sb(III)–DDTC [10], which could be demonstrated with UV–visible absorption spectra (Fig. 1, inset). There was a strong absorption band at 398 nm in Sb(III)–DDTC system (curve 1), which was not found in the Sb(V)–DDTC system (curve 2). It illustrated that Sb(III)–DDTC complex was formed and Sb(V) did not form a complex with DDTC. Thus, pH 9.0 was adopted for selective separation of Sb(III) and Sb(V).

3.2.2. Extraction solvent and its volume

An appropriate extraction solvent for USE-SFODME should have low water solubility and volatility, lower density than water, a melting point close to or below room temperature (10–30 °C), high extraction capability of interested analytes, and no interference [32]. In the present work, four extraction solvents including 1-decanol (m.p. 6 °C), 1-undecanol (m.p. 13–15 °C), 1-bromohexadecane (m.p. 17.3 °C), and n-hexadecane (m.p. 17–19 °C) [25,28] were investigated for the extraction of Sb(III). As shown in Fig. 2, both 1-decanol and 1-undecanol were with high extraction efficiency, while 1-bromohexadecane and n-hexadecane gave the extraction efficiency of 59.0% and 20.0%, respectively. Furthermore, 1-bromohexadecane and n-hexadecane produced high backgrounds during the determination of Sb(III) by ETAAS. It should be noted that 1-undecanol solidified more easily than 1-decanol in ice bath, and was conveniently collected from the aqueous solution. Consequently, 1-undecanol was chosen as the extraction solvent.

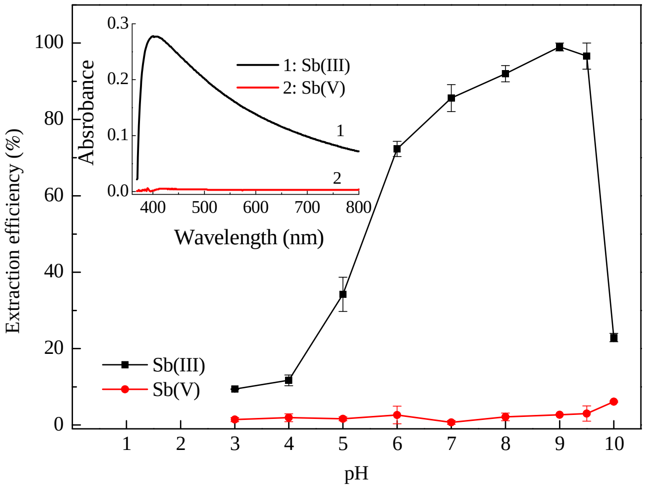

Fig. 1. Effect of pH on the extraction efficiency of Sb(III) and Sb(V). Conditions: 1.0 ng mL^{-1} Sb(III) or Sb(V), pH 3.0–10.0 buffer solutions, 0.60 mL 3.0% (w/v) DDTC. Inset shows UV–visible absorption spectra of (1) Sb(III)+DDTC and (2) Sb(V)+DDTC. Conditions: 2.0 μg mL^{-1} Sb(III) or Sb(V), pH 9.0, 0.60 mL 3.0% (w/v) DDTC.

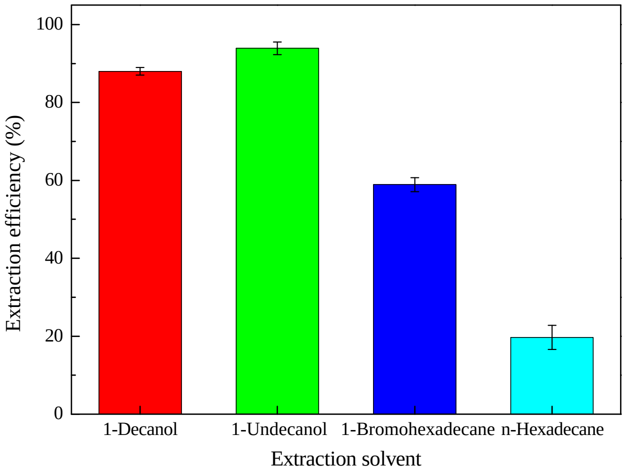

Fig. 2. Influence of extraction solvent on the Sb(III) extraction. Conditions: 1.0 ng mL^{-1} Sb(III), pH 9.0 buffer solution, 50 μL extraction solvent, 0.60 mL 3.0% (w/v) DDTC.

The effect of 1-undecanol volume on the extraction of 1.0 ng mL^{-1} Sb(III) was also examined. The extraction efficiency initially increased with an increase of 1-undecanol volume from 10.0 to 40.0 μL, became constant (> 90.0%) up to 60.0 μL, and then decreased slightly after this volume. 1-Undecanol is a viscous solvent and must be diluted before injection to ETAAS [31]. The higher volume of 1-undecanol would make the sample injection to ETAAS more difficult. It could be not completely eliminated at the stage of pyrolysis, resulting in high background. Therefore, a volume of 50.0 μL of 1-undecanol was chosen for further studies.

3.2.3. Effect of DDTC concentration

The extraction efficiency of Sb(III) is dependent on DDTC concentration. The effect of DDTC concentration was studied in the range from 0.5% to 4.0% (w/v). The extraction efficiency was increased with the DDTC concentration up to 2.0% (w/v), and quantitative extraction results were from 2.0% to 4.0% (w/v). Therefore, a DDTC concentration of 3.0% (w/v) was used.

3.2.4. Sonication time and extraction temperature

Sonication produces fine droplets of extraction solvent into the aqueous phase and results in vast contact areas between the aqueous phase and the extraction solvent [30]. The influence of sonication time on the determination of 1.0 ng mL^{-1} Sb(III) was evaluated in the range of 5–30 min. The extraction efficiency increased as the sonication time increased from 5 to 10 min, and kept stable (> 94.0%) above 10 min. Hence, 20 min of sonication time was selected.

The extraction temperature influences the solubility of organic solvent in water as well as emulsification [25]. It also affects the mass-transfer process and then the extraction efficiency. The effect of extraction temperature on the extraction efficiency of Sb(III) was studied over different temperatures ranging from 15 to 50 °C at the interval of 5 °C. Quantitative extraction (> 90.0%) was found for Sb(III) in the range of 30–50 °C. Emulsification was easily achieved and remained intact in the extraction temperature range of 30–50 °C. Accordingly, the extraction was performed at 35 °C.

3.2.5. *Salt addition*

The influence of ionic strength on the extraction was studied by varying the concentration of NaCl in the range of 0–6% (w/v). The results disclosed that a concentration of NaCl up to 5% (w/v) had no significant impact on the extraction of Sb(III). No addition of salt was chosen in this study.

3.2.6. *Effect of sample volume*

To explore the possible enrichment of low concentrations of antimony from a large sample volume, the effect of sample volume (10.0–40.0 mL) on the extraction of 40.0 ng of Sb(III) from different sample volume was examined. It was found that the extraction efficiency (> 90.0%) was obtained up to a sample volume of 40.0 mL.

3.2.7. *Speciation of Sb(III) and Sb(V)*

Under the specified conditions, mixtures of Sb(III) and Sb(V) in different Sb(V)/Sb(III) concentration ratios were examined. The experimental results showed that the recoveries were 90.0–109.0% for Sb(III) and 91.5–109.4% for Sb(V) with Sb(V)/Sb(III) ratio varying from 1 to 20. It demonstrated that Sb(III) and Sb(V) can be selectively extracted and quantitatively recovered. Therefore, the proposed methodology was suitable for the speciation of Sb(V) and Sb(III) within the concentration ratio of 20-fold.

3.2.8. *Potential interference of coexisting ions*

Possible interferences of common coexisting ions were assessed. The tolerance limit was defined as the largest amount varying analyte absorbance less than ±5% ($C_{\mathrm{Sb(III)}}=1.0$ ng mL^{-1}). According to the results, Sb(III) determination was not interfered by 5000-fold of K(I) and Na(I); 3000-fold of Ca(II) and Mg(II); 400-fold of Zn(II); 300-fold of Sn(IV) and Al(III); 200-fold of Pb(II), Cd(II), Co(II), Mn(II) and Cr(III); 150-fold of Ni(II), Fe(III) and Se(IV); and 100-fold of Cu(II), respectively. The obtained results clearly indicated that this method has good tolerance to matrix interference.

3.3. *Reduction of Sb(V) to Sb(III)*

The reduction of Sb(V) to Sb(III) was required for Sb(V) quantification. The efficiency of reduction reaction of Sb(V) to Sb(III) was examined for 100.0 ng mL^{-1} Sb(V) subjecting to the USE-SFODME procedure. Several factors affecting reduction efficiency of Sb(V) such as concentrations of L-cysteine and hydrochloric acid, reduction temperature and time were studied.

3.3.1. *Optimization of L-cysteine concentration*

L-Cysteine has been utilized as reductant for reducing Sb(V) to Sb(III) in acidic media [1,2,19]. The effect of L-cysteine concentration (0.08–0.75%, w/v) on the reduction efficiency of Sb(V) was discussed. The highest reduction efficiency (> 97.0%) of Sb(V) was obtained in the concentration range of 0.16–0.30% (w/v), and obviously decreased by following increase of the L-cysteine concentration. It is probably that the a complex formed between Sb(V) and L-cystein avoiding the reduction of Sb(V) to Sb(III) [19]. Hereby, an L-cysteine concentration of 0.20% (w/v) was used.

3.3.2. *Selection of hydrochloric acid concentration*

The effect of hydrochloric acid concentration in the range from 0.05 to 0.45 mol L^{-1} on the reduction efficiency of Sb(V) was studied. The reduction efficiency increased along with the hydrochloric acid concentration from 0.05 to 0.40 mol L^{-1}, and leveled off (> 98.0%) at higher concentrations. So the reduction experiment of Sb(V) to Sb(III) by L-cysteine was carried out in 0.40 mol L^{-1} hydrochloric acid.

3.3.3. *Influences of reduction temperature and time*

The effect of temperature was studied in the range of 30–80 °C. The temperature of 50 °C was sufficient for complete reduction of Sb(V) to Sb(III), and further increase in reduction temperature would result in a decrease of efficiencies due to partial loss of reduction activity of L-cysteine.

The influence of time on the reduction efficiency was also investigated with the time varying from 20 to 50 min. The reduction efficiency of more than 90.0% in this temperature range was obtained. Therefore, 30 min of reduction time was selected.

3.3.4. *Effect of the concentration range of Sb(V)*

The reduction ability of L-cysteine on Sb(V) to Sb(III) was evaluated by varying the original Sb(V) concentration from 50.0 to 300.0 ng mL^{-1} in aqueous solutions. The results illustrated that a reduction efficiency over 95.0% was achieved with the concentration of Sb(V) up to 150.0 ng mL^{-1} and than decreased. The determined Sb(V) concentrations after USE-SFODME were in agreement with the initial content of Sb(V) (50.0–150.0 ng mL^{-1}) and remained unchanged at higher concentrations. Accordingly, Sb(V) within the concentration of 150.0 ng mL^{-1} could be completely converted to Sb(III) by the reductant.

3.4. *Method performance*

The analytical performance of the presented method was evaluated and summarized in Table 1 under the optimum conditions. Table 2 compares the characteristic data of the present method with those reported in literatures. As can be seen, this method is effective for the speciation of Sb(III)/Sb(V) with lower limit detection and better precision than majority of the reported methods.

Table 1
Method performance for Sb(III).

Parameters	
LOD (3σ, ng L^{-1})	9.89
RSD (C=1.0 ng mL^{-1}, n=9)	4.5%
Linear range (ng mL^{-1})	0.05–10.0
Regression equation	$A=0.0196+0.1416C$ ($R=0.995$, C: ng mL^{-1})
Preconcentration factor[a]	80

[a] $V_{\mathrm{Sample}}/V_{\mathrm{Diluted\ phase}}$.

Table 2
Comparison of analytical performance of the proposed method with other methods for the speciation of antimony.

Method	LOD [a] (ng mL^{-1})	Linear range (ng mL^{-1})	RSD (%)	Ref.
CPE-ETAAS	0.02	0.1–3.0	7.8	[1]
CPE-ICP-AES	0.09	–	4.3	[2]
CPE-FAAS	1.82	–	2.6	[15]
SPE-ICP-AES[b]	32	0.15–50.0	2.7	[12]
SPE-HG-AFS	2.1 ng L^{-1}	0.01–2.0	4.8	[13]
SPE-ETAAS	0.14	0.14–5.0	6.8	[18]
SDME-ETAAS	8.0 ng L^{-1}	0.01–50	6.6	[21]
DLLME-ETAAS	0.05	0.05–5	–	[22]
USE-SFODME-ETAAS	9.89 ng L^{-1}	0.05–10.0	4.5	This work

[a] LOD=Limit of detection for Sb(III);
[b] SPE=Solid phase extraction.

Table 3
Determination of antimony species in real samples and certified reference materials for water and soil samples (Mean ± S.D., $n=3$).

Samples	Added		Found			Recovery (%)		
	Sb(III)	Sb(V)	Sb(III)	Sb(V) [a]	Total Sb	Sb(III)	Sb(V)	Total Sb
GSB 07-1376-2001 ($\mu g\ mL^{-1}$)	0	0	0.13 ± 0.01	1.48 ± 0.05	1.61 ± 0.03[b] 1.52 ± 0.05[c]	–	–	–
	1.0	1.0	1.22 ± 0.03	2.40 ± 0.16	3.62 ± 0.27	109.0	92.0	100.5
	2.0	2.0	2.35 ± 0.02	3.31 ± 0.13	5.66 ± 0.28	111.0	91.5	101.2
GBW07441 (GSF-1) ($\mu g\ kg^{-1}$)	0	0	2.03 ± 0.10	2.10 ± 0.17	4.13 ± 0.40[b] 4.50 ± 1.00[c]	–	–	–
	5.0	5.0	7.24 ± 0.74	7.33 ± 0.12	14.57 ± 0.94	104.2	104.6	104.4
	10.0	10.0	11.98 ± 1.05	11.10 ± 1.22	23.08 ± 1.57	99.5	90.0	94.8
Lake water ($ng\ mL^{-1}$)	0	0	0.37 ± 0.01	1.05 ± 0.07	1.42 ± 0.11	–	–	–
	2.0	2.0	2.48 ± 0.08	2.90 ± 0.15	5.38 ± 0.12	105.5	92.5	99.0
	4.0	4.0	4.12 ± 0.10	4.95 ± 0.40	9.07 ± 0.38	93.8	97.5	95.6
Tap water ($ng\ mL^{-1}$)	0	0	ND	ND	ND	–	–	–
	1.0	1.0	0.98 ± 0.02	1.11 ± 0.05	2.09 ± 0.08	98.0	111.0	104.5
	2.0	2.0	2.20 ± 0.06	2.14 ± 0.15	4.34 ± 0.29	110.0	107.0	108.5
Soil ($\mu g\ kg^{-1}$)	0	0	36.84 ± 1.48	255.67 ± 9.72	291.82 ± 3.25	–	–	–
	20.0	20.0	55.19 ± 3.83	278.79 ± 7.10	333.98 ± 8.58	91.8	115.6	105.4
	40.0	40.0	72.64 ± 2.92	298.03 ± 7.44	370.67 ± 4.54	89.5	105.9	98.6

ND: Not detected.

[a] The concentration of Sb(V) was calculated by subtraction of Sb(III) from the total antimony.

[b] The total antimony was obtained by USE-SFODME.

[c] The certified value was for the total antimony in the certified reference.

3.5. *Analysis of real samples*

The optimized method was validated by analyzing antimony species in two certified reference materials (GBW07441 and GSB 07-1376-2001). As shown in Table 3, the determined values for total Sb were in good agreement with the certified values. Because there are no reference materials with certified values for Sb(III) and Sb(V) available, the accuracy of Sb(III)/Sb(V) determination was evaluated by a recovery study of spike additions. The recoveries of Sb(III) and Sb(V) in the reference materials were in the range of 90.0–111.0%.

The proposed method was also used for determination of Sb(III)/Sb(V) in soil and water samples. The results along with the recoveries of Sb(III)/Sb(V) species in the spiked samples were obtained in Table 3. The content of Sb(V) was higher than that of Sb(III) in all samples except that in the tap water. The recoveries for the spiked samples ranged from 89.5% to 115.6%.

4. Conclusions

The USE-SFODME method combined with ETAAS is effective for the speciation of Sb(III) and Sb(V) in water and soil samples. The results demonstrated that the USE-SFODME technique can improve analytical sensitivity for antimony species. Compared with conventional LLE and SPE methods, this method is simpler, more sensitive, low cost, low consumption of organic solvents, and with a high preconcentration factor. Moreover, matrix interferences can be eliminated in the ETAAS analysis without addition of any matrix modifier.

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