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Cloud point extraction combined with electrothermal atomic absorption spectrometry for the speciation of antimony(III) and antimony(V) in food packaging materials

Xiuming Jiang, Shengping Wen, Guoqiang Xiang*

School of Chemistry and Chemical Engineering, Henan University of Technology, South Song Shan Road No. 140, Zhengzhou City 450001, PR China

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ABSTRACT

A simple, sensitive method for the speciation of inorganic antimony by cloud point extraction combined with electrothermal atomic absorption spectrometry (ETAAS) is presented and evaluated. The method based on the fact that formation of a hydrophobic complex of antimony(III) with ammonium pyrrolidine dithiocarbamate (APDC) at pH 5.0 and subsequently the hydrophobic complex enter into surfactant-rich phase, whereas antimony(V) remained in aqueous solutions. Antimony(III) in surfactant-rich phase was analyzed by ETAAS after dilution by 0.2 mL nitric acid in methanol (0.1 M), and antimony(V) was calculated by subtracting antimony(III) from the total antimony after reducing antimony(V) to antimony(III) by L-cysteine. The main factors affecting the cloud point extraction, such as pH, concentration of APDC and Triton X-114, equilibrium temperature and incubation time, sample volume were investigated in detail. Under the optimum conditions, the detection limit (3σ) of the proposed method was 0.02 ng mL^{-1} for antimony(III), and the relative standard deviation was 7.8% (c = 1.0 ng mL^{-1}, n = 7). The proposed method was successfully applied to speciation of inorganic antimony in the leaching solutions of different food packaging materials with satisfactory results.

1. Introduction

Antimony is a cumulative toxic element with unknown biological function and its physicochemical and toxic properties depend on its binding form and oxidation state [1–3]. The toxicity of antimony(III) ion is 10 times higher than that of antimony(V) ion, and antimony(III) has been shown to cause lung cancer [4,5]. Among several industrial applications of antimony compounds, antimony trioxide (Sb_2O_3) is largely employed in the production of glassware and ceramics. Moreover, Sb_2O_3 is added to molten glass as a clarifying reagent and is employed as a pigment in dyes and paints as well as in the textile industry. Several antimony compounds are used as additives to metal coatings and rubber, and others are added to textiles as flame retardants [3]. Therefore, there is a great risk of antimony leaching from these food packaging materials (such as plastic, enamel and porcelain containers) into our food chain [6]. Recently, an Sb(V) complex, Sb(V)-citrate, was identified for the first time in no spiked orange juice contained in poly(ethyleneterephthalate) (PET) bottles [7]. All this information emphasizes the importance of identifying and quantifying the chemical forms of antimony to provide comprehensive information about its toxicity and human health relevance.

Several atomic spectrometric techniques such as flame and electrothermal atomic absorption spectrometry (FAAS and ETAAS) [8–10], atomic fluorescence spectrometry (AFS) [11], inductively coupled plasma atomic emission spectrometry (ICP-OES) [12], inductively coupled plasma mass spectrometry (ICP-MS) [13] have been proposed for the determination of antimony species in different samples. Since the leaching quantity of antimony from food packaging materials is very small, of the order of a few ng mL^{-1}, various separation and preconcentration procedures have been used in combination with the above mentioned techniques for accurate, reliable and sensitive results. These procedures include liquid–liquid extraction [14], solid phase extraction [15], single-drop extraction [16], and cloud point extraction [17].

Nowadays, cloud point extraction (CPE) using non-ionic surfactants has attracted considerable attention as an alternative to other techniques for separation and preconcentration [18–20]. Briefly, above the cloud point temperature, the surfactant solution easily separates into two distinct phases: a surfactant-rich phase with small volume and a diluted aqueous phase, in which the surfactant concentration is close to the critical micelle concentration. Metallic elements can be extracted to the surfactant-rich phase, trapped in the hydrophobic micelle core, as the hydrophobic complexes formed between metal ion and an appropriate chelating reagent

* Corresponding author. Tel.: +86 371 67756733; fax: +86 371 67756718.
E-mail address: xianggq@haut.edu.cn (G. Xiang).

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Table 1
Instrumental parameters and temperature program for antimony analysis.

Spectrometer				
Wavelength/nm	217.6			
Current/mA	4			
Bandwidth/nm	0.2			
Background correction	Deuterium			
Sample volume/μL	10			
Graphite furnace				
Step	Temperature/°C	Ramp time/s	Step time/s	Flow rate of argon (mL min^{-1})
Drying	60	5	10	450
Ashing	400	10	15	450
Atomization	2200	0	4	0
Cleaning	2300	0	1	450

under adequate conditions. As a new separation technique, CPE offers many advantages over traditional liquid–liquid extraction, such as simple, cheap, rapid, no use of organic solvents, high capacity to concentrate a wide variety of analytes with high recoveries and high concentration factors [21].

When CPE technique was used for the extraction of metal chelates, atomic spectrometric techniques, including flame atomic absorption spectrometry (FAAS), electrothermal atomic absorption (ETAAS), inductively coupled plasma optical emission spectrometry (ICP-OES), and inductively coupled plasma mass spectrometry (ICP-MS) were often used as detectors [22]. Several articles have reported the combination of CPE systems with atomic spectrometric detectors for the analysis of antimony species in different samples [23–25,8]. The combination of CPE with ETAAS detection could gain much lower detection limit [23,24] than that gain by combination of CPE with FAAS [8]. The low detection limit gained by CPE-ETAAS was at the same level with that gained by CPE-ETV-ICP-MS [25]. Considered the poor sensitivity of FAAS and expensive price and analysis cost of ICP-MS, ETAAS is an efficient alternative. Besides of the excellent detection limits, the need of a very small sample injection volume is another advantage of ETAAS. Furthermore, the surfactant matrix in the injection solution can be eliminated at least in part during the appropriate ashing temperature and time. In this sense, ETAAS is suitable for determination of small volume of the surfactant-rich phase obtained in CPE schemes.

The aim of this present paper is to evaluate the feasibility of combining CPE preconcentration with ETAAS for determination of inorganic antimony species in leaching solutions of different food packaging materials. In this procedure, APDC was used as chelating reagent and Triton X-114 as the extracting one. The main factors affecting CPE were investigated in detail. The developed method was applied to speciation of inorganic antimony in the leaching solution of different food packaging materials with satisfactory results.

2. Experimental

2.1. Instrumentation

A TAS-986 atomic absorption spectrometer (Beijing Purkinje General Instrument Limited Company, Beijing, China) equipped with a GFA-4A transverse heated graphite furnace atomizer was used for the determination of antimony in the surfactant-rich phase. Deuterium lamp background correction was employed to correct the non-specific absorbance. An antimony hollow cathode lamp (Beijing Shuguangming Electronic Lighting Source Instrument Limited Company, Beijing, China) was used as the radiation source. The operation conditions of antimony hollow cathode lamp were those recommended by the manufacture. Pyrolytic graphite-coated and transverse heated platform graphite tubes were used throughout. Argon 99.999% (Beijing Praxair Inc., Beijing, China) with 450 mL min^{-1} was used as a protective and purge gas. Measurements were performed in the peak area mode. The detailed instrumental parameters and graphite furnace temperature program used for the determination of antimony were shown in Table 1. A thermostatic bath (Jintan Instrument Limited Company, Jiangsu, China) was used for cloud point preconcentration experiments and phase separation was assisted by a centrifuge (80-1 model, Jintan Instrument Limited Company, Jiangsu, China) in 10 mL calibrated centrifuge tubes. All pH measurements were carried out using a PHS-25B digital pH meter equipped with a combined glass-calomel electrode (Shanghai Dapu Instrument Limited Company, Shanghai, China).

2.2. Reagents and solutions

A stock standard antimony(III) and antimony(V) solution (1000 μg mL^{-1}) were prepared by dissolving appropriate amounts of potassium antimony tartrate (Tianjin Reagent Company, Tianjin, China) and potassium hexahydroxyantimonate (Shanghai Reagent Company, Shanghai, China) in double distilled water, respectively. All stock standard solutions were stored in polyethylene bottles in a refrigerator at 6 °C. These solutions were stable for at least 6 months. Working standard solutions were obtained by appropriate dilution of the stock standard solution just before use. Solution (1.0%, v/v) of Triton X-114 (Sigma, USA) was prepared in double distilled water and was used without further purification. Solution (2.5%, w/v) of APDC (Shanghai Reagent Company, Shanghai, China) was prepared fresh daily in double distilled water. Solution (3.0%, w/v) of L-cysteine (Shanghai Huixing Biochemical Reagent Company, Shanghai, China) was prepared in double distilled water. The buffer solution of pH 4.0 acetic–acetate was used to control pH of the solutions. All chemicals and reagents used in this study were of analytical-reagent grade or higher purity.

2.3. Procedure for CPE

For the cloud point extraction, aliquots of 6.00 mL of sample or standard solution, 0.50 mL 2.5% (w/v) APDC and 1.00 mL 1.0% (v/v) Triton X-114 were added into a 10 mL centrifuge tube, and the mixture was buffered to pH 5.0 with acetic–acetate, and then diluted to 10 mL with double distilled water. The resultant solution was kept in a thermostatic water bath at 50 °C for 15 min, separation of the aqueous and surfactant-rich phase was accomplished by centrifugation for 5 min at 3500 rpm. After cooling in an ice bath, the surfactant-rich phase becomes viscous and the supernatant aqueous phase was then separated completely by a syringe centered in the tube. To decrease the viscosity of the surfactant-rich phase, 0.2 mL nitric acid in methanol (0.1 M) was added, and then 10 μL of the resultant solution was directly introduced into graphite tube for determination of antimony.

2.4. Leaching procedure

(1) The ceramic containers for food: The containers were washed by double distilled water. After natural drying, 400 mL (nearly the maximum volume of the containers) double distilled water with pH = 6.0 was added into the containers, and then the containers were covered with 24 h standing.
(2) The plastic drinking cups (made by two different materials, acrylonitrile-styrene resin, AS and polycarbonate, PC): After cleaned by double distilled water, the cups were filled with 750 mL double distilled water and the contacting time was kept for 24 h with a lid.
(3) The plastic drinking-water pipes (made by polypropylene, PP): The pipes were cut into small pieces after cleaned, and then the leaching of 2.5 g pipe fragment was carried out with 100 mL double distilled water with pH 6.0 for 24 h.

All the food packaging materials for leaching procedure were bought in the supermarket. The leaching solutions were collected in volumetric flasks and stored at 4 °C.

2.5. Determination of Sb(III) and Sb(V)

(1) Sb(III): After the CPE procedure, a 10 μL the resultant solution was directly introduced into graphite tube for determination.
(2) Total Sb: When total antimony was to be determined, 0.5% (w/v) L-cysteine at pH 3.00 had to be added and heated for 25 min in boiling water bath prior to CPE procedure, then determined by ETAAS.
(3) Sb(V): The content of Sb(V) was calculated by subtraction of Sb(III) from the total Sb.

3. Results and discussion

3.1. Optimization of the ETAAS conditions

The selection of an appropriate pyrolysis temperature is very important for removing the matrix as much as possible and preventing pyrolysis loss of the analytes prior to atomization. This decreases the possibility of chemical interference and reduces the magnitude of the background signal. The influence of pyrolysis temperature (200–600 °C) on the absorbance of the antimony in surfactant-rich phase was investigated. The results showed that maximum absorbance of obtained when the pyrolysis temperature was near 400 °C. However, when pyrolysis temperature was higher than 450 °C, the absorbance of antimony was decreased rapidly with the increasing pyrolysis temperature. Therefore, 400 °C was selected as the optimized pyrolysis temperature for the determination of antimony. The effect of pyrolysis time on the absorbance of antimony was also investigated at the selected pyrolysis temperature of 400 °C. The results showed that the signal of the background decreased when the pyrolysis time (hold time) changed from 5 to 15 s and no appreciable improvements were observed for longer time. As a result, a pyrolysis time of 15 s was chosen.

With the selected pyrolysis temperature of 400 °C and pyrolysis time 15 s, the effect of the atomization temperature on signal of antimony was studied in the temperature range of 1700–2400 °C, and the results showed that the maximum analytical signal of antimony was obtained when the atomization temperature varied from 2100 to 2300 °C. The experiment results showed that atomization time has little effect on the atomic signal of antimony. Therefore, an atomization temperature of 2200 °C and an atomization time of 4 s were selected for atomization of antimony.

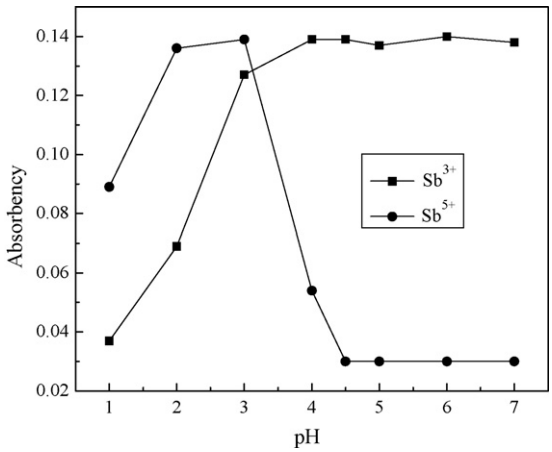

Fig. 1. Effect of pH on the signal intensity of antimony(III) and antimony(V) in surfactant-rich phase. Condition: Sb(III) or Sb(V) standard solutions (1.0 ng mL^{-1}, 6.00 mL), 0.5 mL 2.5% (w/v) APDC, 1.0 mL 1.0% (v/v) Triton X-114, pH 1.0–7.0, equilibrium temperature 50 °C and incubation time 15 min.

3.2. Selective extraction of Sb(III) and Sb(V)

The pH plays an important role on metal-chelate formation and subsequent extraction. In this part of study, the effect of pH on the signal intensity of Sb(III) and Sb(V) in the surfactant-rich phase was evaluated at pH values varying between 1.0 and 7.0. As can be seen from Fig. 1, Sb(III) was completely extracted in the pH range of 3.0–7.0, but there is virtually no extraction of Sb(V) in the pH range of 4.5–7.0. The reason for the extraction of Sb(III) was that Sb(III) can form hydrophobic Sb(III)–APDC complex with APDC and therefore was extracted into surfactant-rich phase. However, when pH larger than 4.0, Sb(V) does not form a dithiocarbamate complex with APDC and is not extracted into surfactant-rich phase. Based on these results, pH 5.0 was used for selective separation of Sb(III) and Sb(V).

3.3. Effect of APDC concentration

The CPE efficiency depends on the hydrophobicity of the ligand and the complex formation, the apparent equilibrium constants in the micelle medium, the kinetics of the complex formation, and the transference between the phases. The variation of the analytical signal as a function of the concentration of APDC in the range of 0.5–3.0% (w/v) was studied, and the experimental result was demonstrated in Fig. 2. It could be seen that the analytical signal for Sb(III) increased rapidly as the concentration of APDC increased from 0.5% (w/v) to 2.0% (w/v), and kept constant with concentration of APDC up to 3% (w/v). For further studies, an APDC concentration of 2.5% (w/v) was selected.

3.4. Effect of Triton X-114 concentration

Compared with Triton X-100, Triton X-114 has lower cloud point temperature (18 °C) and higher density of the surfactant-rich phase. It makes more convenient for inducing the phase separation and collecting the surfactant-rich phase by centrifugation. The effect of Triton X-114 concentration upon sensitivity and extraction was studied within the surfactant concentration range of 0.2–2.0% (v/v). Fig. 3 showed the effect of Triton X-114 concentration on signal intensity of Sb(III) in surfactant-rich phase. It is obvious that a quantitative extraction was observed with the Triton X-114 concentration in the range of 0.5–2.0% (v/v). Therefore, a Triton X-114 concentration of 1.0% (v/v) was employed for further studies.

Table 2
Interferences of coexisting ions on extraction and determination of antimony(III).

Coexisting ions	Mass ratio[a]	Recovery (%)	Coexisting ions	Mass ratio[a]	Recovery (%)
Mg^{2+}	2000	100	Ni^{2+}	5	100
Ca^{2+}	2000	101	Al^{3+}	5	91.5
Mn^{2+}	10	102	Cu^{2+}	5	104
Pb^{2+}	10	94.9	Co^{2+}	5	95.7
Zn^{2+}	10	94.9	Cd^{2+}	5	95.7
Cr^{6+}	10	96.6	Fe^{3+}	5	102

[a]Coexisting ion/antimony(III) (the concentration of antimony(III) was 1.0 ng mL^{-1}).

Table 3
The recovery results for determination of antimony(III) and antimony(V) in the leaching solutions of food packaging materials (n = 3, mean ± SD, ng mL^{-1}).

Samples	Sb(III) added	Sb(III) found	Recovery (%)	Sb(V) added	Found		Recovery (%)
					Total	Sb(V)[a]	
Ceramic container I	0	0.68 ± 0.08	–	0	0.73 ± 0.08	0.05 ± 0.01	–
	0.5	1.23 ± 0.05	110.0	0.5	1.32 ± 0.07	0.64 ± 0.04	118.0
	1.0	1.68 ± 0.11	100.0	1.0	1.64 ± 0.11	0.96 ± 0.08	91.0
Drinking cup (AS)	0	0.44 ± 0.05	–	0	1.62 ± 0.07	1.18 ± 0.05	–
	1.0	1.44 ± 0.12	100.0	1.0	2.71 ± 0.05	2.24 ± 0.03	109.0
	2.0	2.33 ± 0.18	94.5	2.0	3.48 ± 0.12	3.04 ± 0.04	93.0

All the concentration values were normalized by the same sample volume 400 mL.
[a] The content of antimony(V) calculated by subtraction antimony(III) from the total antimony.

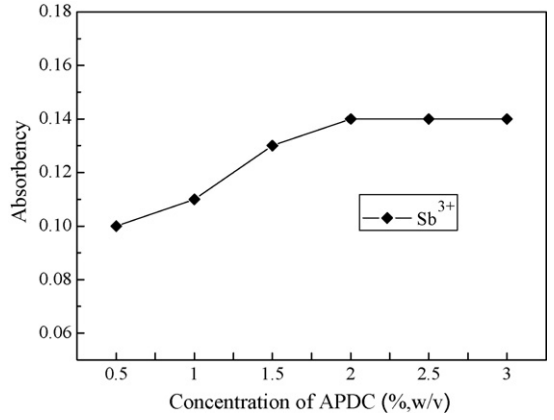

Fig. 2. Effect of APDC concentration on the analytical signal intensity of antimony(III). Condition: Sb(III) standard solutions (1.0 ng mL^{-1}, 6.00 mL), 0.5 mL 0.5–2.5% (m/v) APDC, 1.0 mL 1.0% (v/v) Triton X-114, pH 5.0, equilibrium temperature 50 °C and incubation time 15 min.

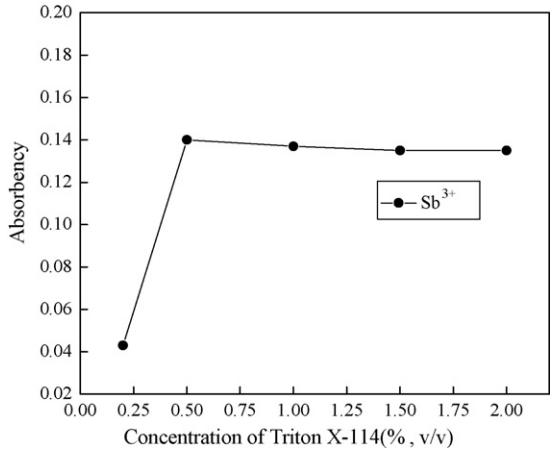

Fig. 3. Effect of Triton X-114 concentration on the analytical signal intensity of antimony(III). Condition: Sb(III) standard solutions (1.0 ng mL^{-1}, 6.00 mL), 0.5 mL 2.5% (w/v) APDC, 1.0 mL 0.2–1.0% (v/v) Triton X-114, pH 5.0, equilibrium temperature 50 °C and incubation time 15 min.

3.5. Effects of equilibrium temperature and incubation time

The effect of equilibrium temperature was investigated from room temperature to 70 °C. It was found that the solutions became turbid as soon as the solutions were put into the water bath with temperature higher than 40 °C, and the temperature had no considerable effect upon the extraction efficiency and the analytical signal kept constant at temperature range of 40–70 °C. Thus, 50 °C was chosen as the equilibrium temperature. Keeping the equilibrium temperature of 50 °C, the influence of incubation time on CPE was studied within range of 5–30 min. It was observed that, 15 min was sufficient to achieve a quantitative extraction of analyte. Then, 15 min incubation time was employed for CPE procedure.

3.6. Effect of sample volume

In order to obtain a higher enrichment factor, a large volume of sample solution is required. For this purpose, 4.00, 5.00, 6.00, 7.00 mL of sample solutions containing 6.0 ng of Sb(III) were extracted according to the procedure of CPE. It was shown that quantitative extraction of the analyte was obtained with the sample volumes no more than 6.00 mL. For further studies, 6.00 mL of sample volume was selected.

3.7. Interferences of coexisting ions

The effect of potential interference of some metal ions on the preconcentration and determination of Sb(III) was examined. In these experiments, solutions containing Sb(III) (1.0 ng mL^{-1}) and the added interfering ions were treated according to the recommended procedure under the optimum conditions, and the results obtained were given in Table 2. As could be seen, the developed method is fairly selective.

3.8. Analytical performance

Under the optimum conditions described above, the proposed method provided a linear calibration range from 0.1 to 3.0 ng mL^{-1} for Sb(III) and the detection limit (3σ) was 0.02 ng mL^{-1}, and the relative standard deviation (R.S.D.) were 7.8% (c = 1.0 ng mL^{-1}, n = 7).

Table 4
Speciation of antimony(III) and antimony(V) in the leaching solutions of food packaging materials ($n = 3$, mean ± SD, ng mL^{-1}).

Samples	Sb(III)	Total Sb	Sb(V)[a]
Plastic pipes (PP)	0.57 ± 0.05	1.97 ± 0.05	1.40 ± 0.04
Ceramic container II	0.93 ± 0.06	1.89 ± 0.14	0.96 ± 0.08
Drinking cup (PC)	1.78 ± 0.09	2.34 ± 0.15	0.56 ± 0.05

All the concentration values were normalized by the same sample volume 400 mL.
[a] The content of antimony(V) calculated by subtraction antimony(III) from the total antimony.

3.9. Analysis of real samples

The proposed method was applied for the speciation of Sb(III) and Sb(V) in leaching solutions of different food packaging materials. The leaching solutions were obtained from the ceramic containers for food, plastic drinking cups (AS and PC materials) and plastic drinking-water pipes (PP materials). In order to validate the proposed method, recovery experiments were also carried out by spiking the samples with different amounts of Sb(III) or Sb(V) before treatment, and the obtained results were listed in Table 3. As could be seen, the recoveries for the spiked samples were in the acceptable range (91.0–118.0%). The analytical results of Sb(III) and Sb(V) by CPE-ETAAS for another three kinds of food packaging materials were showed in Table 4. From all the analytical results obtained, it could be found that the leaching quantity of Sb(III) and Sb(V) was quite different for the kinds of ceramic materials. For the ceramic container II, the leaching quantity of Sb(III) and Sb(V) was nearly the same. However, for the ceramic container I, the leaching quantity of Sb(III) was much larger than that of Sb(V). And for plastic pipes (PP) and drinking cups (AS), the leaching quantity of Sb(III) and Sb(V) were nearly at the same level, and the quantity of Sb(V) was more than two times than that of Sb(III). But, for drinking cups (PC), the leaching quantity of Sb(V) was much smaller than that of Sb(III). These may explain by the fact that different food packaging products were produced by different raw materials, process and additives.

4. Conclusions

A simple, sensitive method for the speciation of inorganic antimony by cloud point extraction combined with electrothermal atomic absorption spectrometry (ETAAS) was proposed in this paper. The advantages of the proposed method are summarized as follows: (1) simplicity, selectivity, safety and low cost; (2) by combination cloud point extraction with ETAAS, lower detection limit could be achieved. The proposed method was successfully applied to the speciation of Sb(III) and Sb(V) in leaching solution of food packaging materials.

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