Speciation of Inorganic Antimony in Natural Waters by Electrothermal Atomic Absorption Spectrometry after Selective Separation and Preconcentration of Antimony(III) with Cloud Point Extraction

Ingrid Hagarová*, Jana Kubová,
Peter Matúš and Marek Bujdoš

Comenius University in Bratislava, Faculty of Natural Sciences, Geological Institute, Mlynská dolina G,
842 15 Bratislava 4, Slovak Republic

* Corresponding author: E-mail: hagarova @fns.uniba.sk

Received: 07-03-2008

Abstract

In this work, cloud point extraction (CPE) was applied as a separation/preconcentration step for electrothermal atomic absorption spectrometric (ETAAS) determination of ultratrace Sb(III) in natural water samples. After complexation with ammonium pyrrolidine dithiocarbamate (APDC) in mildly acidic medium, the analyte was quantitatively extracted to the phase rich in the non-ionic surfactant octyl phenoxy polyethoxy ethanol (Triton X-114) after centrifugation. Then the surfactant-rich phase was diluted by 0.20 mol L^{-1} HNO_3 in methanol and the concentrated analyte was introduced into ETAAS. Potential factors affecting the CPE separation/preconcentration of Sb(III) were investigated in detail. Under optimal conditions, the relative standard deviation (RSD) for ten replicate measurements at 0.40 µg L^{-1} Sb(III) level was 6.5% and the enrichment factor for this determination was 28. The linear concentration range was from 0.10 to 3.50 µg L^{-1} Sb(III). The detection limit of 0.03 µg L^{-1} Sb(III) was achieved. The optimized method was applied to the determination of Sb(III) in well and lake water samples.

Keywords: Antimony, speciation analysis, cloud point extraction, electrothermal atomic absorption spectrometry, water analysis

1. Introduction

Antimony is a cumulative toxic element with no known biological function and its physicochemical and toxic properties depend on its binding form and oxidation state.[1–5] All this information emphasizes the importance of identifying and quantifying the chemical forms of antimony to provide comprehensive information about its toxicity and environmental relevance.

In the aqueous environment, inorganic antimony mainly appears in the oxidation states +V and +III. Because of the extremely low concentrations of these inorganic forms of antimony in waters, the direct speciation is practically impossible.[6] So, many of the procedures for the selective separation/preconcentration and detection of antimony species in waters are based on the coupling of a selective separation technique with a sensitive detection method. Most of the analytical procedures for the specia-

tion of antimony in waters is based on the coupling of high-performance liquid chromatography (HPLC) to hydride generation atomic absorption spectrometry (HGAAS), inductively coupled plasma optical emission spectrometry (ICP-OES), or inductively coupled plasma mass spectrometry (ICP-MS).[7–11] However, methods above mentioned are often complicated, time consuming and require high operation costs. Thus, a simple and efficient separation/preconcentration technique for antimony species can be more essential for using in common labs.

During the past years, separations and preconcentrations based on cloud point extraction (CPE) are becoming an important and practical application of the use of surfactants in analytical chemistry. The technique is based on the property of most non-ionic surfactants in aqueous solutions to form micelles and become turbid when heated to the cloud point temperature. The theory and relevant applications of this impressive separation methodology are dis-

cussed in various interesting reviews.[12–22] Briefly, above the cloud point temperature the micellar solution separates in a surfactant-rich phase of a small volume and in a diluted aqueous phase, in which the surfactant concentration is close to the critical micellar concentration. Any analyte solubilized in the hydrophobic core of the micelles, will separate and become concentrated in the small volume of the surfactant-rich phase. Metallic elements can be extracted to the surfactant-rich phase, trapped in the hydrophobic micellar core, in the form of hydrophobic complexes that are formed between the metal ion and an appropriate chelating agent under adequate conditions.

When CPE technique was used for the extraction of metal chelates, flame atomic absorption spectrometry (FAAS) was by far, the most frequently used technique for analyte detection. Although FAAS has certain advantages, especially concerning the time required for the final determination, techniques of higher sensitivity would improve considerably detection limits for several analytes (including antimony). In this sense, electrothermal atomic absorption spectrometry (ETAAS) is an efficient alternative, particularly because the matrix, consisting of the surfactant can be eliminated at least in part during the gradual increase in temperature prior to the atomization of the analyte.[23] Besides of excellent detection limits which can be achieved by ETAAS, the need of a very small sample injection volume is another advantage of this method. In this sense, ETAAS is suitable for analysis of small volumes of the surfactant-rich phase obtained in CPE schemes.

Until now, CPE has been used for the extraction and preconcentration of many metal ions including antimony prior to FAAS determination[24] and electrothermal vaporization ICP-OES determination.[25] To the best of our knowledge, the use of CPE as a separation/preconcentration of trace Sb(III) prior to ETAAS determination has not been reported before.

The aim of the present work was to use an optimized CPE procedure for the selective separation/preconcentration of Sb(III) prior to its determination by ETAAS. In this procedure, ammonium pyrrolidine dithiocarbamate (APDC) was used as the chelating agent and Triton X-114 (TX-114) as the extracting one. Potential factors affecting the CPE separation/preconcentration of Sb(III) were investigated in detail. A certified reference material for trace elements in riverine water SLRS-4 was used for checking the accuracy of the method for the total antimony determi-

nation after reduction of Sb(V) to Sb(III). This method was applied to the speciation of inorganic antimony in natural waters (well and lake waters).

2. Experimental

2. 1. Instrumentation

All measurements were carried out using a Perkin-Elmer 3030 atomic absorption spectrometer (Norwalk, CT, USA) equipped with an HGA 600 graphite furnace and an AS-60 autosampler. The spectrometer was provided with a Zeeman-based background corrector. All measurements were performed in the peak height mode. Pyrolytic graphite tubes (Perkin-Elmer) were used exclusively. Argon was used as the purge gas at a flow rate of 250 ml min^{-1}. Electrodeless discharge lamp for Sb (Perkin-Elmer) was operated at 8 W with a spectral bandwith of 0.7 nm. The selected wavelength was 217.6 nm. Injection of the sample solution (20 µl) was followed by modifier solution (10 µl of palladium nitrate). The graphite furnace temperature program is shown in Table 1.

The pH values were measured using an Ionometer MS-31 (Praque, Czech republic) pH-meter, equipped with a glass-combination electrode. A thermostated water bath maintained at the desired temperatures (Kavalier, Sazava, Czech republic) was used for cloud point temperature experiments and the phase separation was assisted with a centrifuge (Mechanika precyzyjna, Warsaw, Poland).

2. 2. Reagents

All reagents used were of analytical grade and all solutions were prepared in doubly deionized water (DDW). The non-ionic surfactant solutions were prepared by dissolving suitable amounts of Triton X-114 (Sigma-Aldrich, Steinheim, Germany) in DDW. The complexing agent solutions were prepared by dissolving suitable amounts of ammonium pyrrolidine dithiocarbamate (Sigma-Aldrich) in DDW. Stock standard antimony(III) and antimony(V) solutions (1000 mg L^{-1}) were prepared by dissolving appropriate amounts of potassium antimony tartrate (Sigma-Aldrich) and potassium hexahydroxyantimonate (Sigma-Aldrich) in DDW, respectively. Working antimony standard solutions were prepared by stepwise dilution of the stock solutions in DDW just before use.

Table 1. Graphite furnace temperature program for the determination of Sb in water samples submitted to the cloud point extraction.

Stage	Temperature (°C)	Ramp time (s)	Hold time (s)	Ar flow rate (ml min^{-1})
Drying	110	10	20	250
Pyrolysis	1200	10	20	250
Atomization	2500	0	30	
Cleaning	2550	1	1	250

Hydrochloric acid (Merck, Darmstadt, Germany) and sodium hydroxide (Merck) were employed to adjust the final pH of the standard and sample solutions. All stock solutions were stored in polyethylene bottles in a refrigerator held at 4 °C. All glassware was kept in 10% (v/v) nitric acid (Lachema, Brno, Czech republic) for at least 24 h and washed three times with DDW before use. A chemical modifier solution was prepared by diluting palladium nitrate stock solution (10 g L^{-1} of Pd) (Merck) in DDW. Solutions with studied concentrations of potentially interfering elements were prepared by stepwise dilution of their stock solutions (1000 mg L^{-1}) (Merck) in DDW just before use. Methanol (Merck) was used for the preparation of a dilution agent for the surfactant-rich phase. Certified reference material for trace elements in riverine water SLRS-4 (National Research Council of Canada, Ottawa, Canada) was used for checking the accuracy of the optimized method for the total antimony determination.

2.3 Samples

Synthetic water (SW) was prepared by dissolving of $CaCl_2.2H_2O$ (0.2942 g), NaCl (0.2160 g), $MgSO_4.7H_2O$ (0.0862 g), KCl (0.0097 g), and $(NH_4)_2HPO_4$ (0.0073 g) in 1000 ml of DDW. Lake water (LW) from Lubietova (Slovakia) was collected from the site situated in the NE part of Slovenske Stredohorie Mts., which include the northern part of the neovolcanic massive Polana and the northern part of Ciertaz Mts. (Verporske Vrchy Mts.). Contaminated well water (WW) was collected from a domestic well situated in Komarno (south part of Slovakia). Natural waters were filtered through a 0.45 μm pore size membrane filter immediately after sampling and stored at 4 °C in polyethylene bottles. The samples were used for the speciation studies on the next day after sampling.

2. 4. Procedures

For the cloud point extraction, aliquots of 10.0 ml of a sample solution (pH 5.5 ± 0.1) containing 0.02% (m/v) APDC and 0.08% (m/v) TX-114 were heated in a thermostated water bath at 45 °C for 5 min. The mixture was centrifuged at 4000 rpm for 5 min to accelerate the separation, and then cooled in an ice-bath for 10 min to increase the viscosity of the surfactant-rich phase. The bulk aqueous phase was easily decanted by simply inverting the tube. Two hundred microliters of a solution containing 0.2 mol L^{-1} HNO_3 in methanol was added to the surfactant-rich phase to reduce its viscosity before ETAAS determination.

3. Results and Discussion

3. 1. Optimization of the Furnace Conditions

To reduce interferences and to increase accuracy in ETAAS determination of relatively volatile elements, the use of a chemical modifier has become indispensable. Since, antimony can be lost from the graphite tube at relatively low pyrolysis temperatures, different chemical modifiers (mainly noble elements) have been utilized to stabilize antimony to the higher temperatures. Among them, palladium has been extensively studied and utilized during the past years. In this work, measurements with no chemical modifier and measurements with palladium nitrate (1 g L^{-1} of Pd) were compared. Pyrolysis and atomization curves were established using Sb(III) standard solution, submitted to the CPE procedure. Aliquots containing 20 μl of the final extract in methanolic 0.2 mol L^{-1} HNO_3 were used for ETAAS analysis. The pyrolysis and atomization temperatures were investigated in the range of 500–1800 °C and 1400–2600 °C, respectively (Fig. 1). The analysis of the extracts from the CPE procedure resulted in a maximum loss-free pyrolysis temperature of 900 °C in the absence of any modifier and 1300 °C in the presence of palladium. The absorbance reached the maximum increasing the atomization temperature to 1800 °C in the absence of any modifier and 2400 °C in the presence of palladium. Usually pyrolysis temperatures above 600 °C are sufficient to eliminate quantitatively organic matrix that results from CPE but higher sensitivity and precision were achieved in the presence of palladium nitrate. Based on these observations, palladium nitrate was used in all measurements and the pyrolysis temperature of 1200 °C and atomization temperature of 2500 °C were selected and used in the temperature program for the determination of antimony after CPE separation/preconcentration (see Table 1).
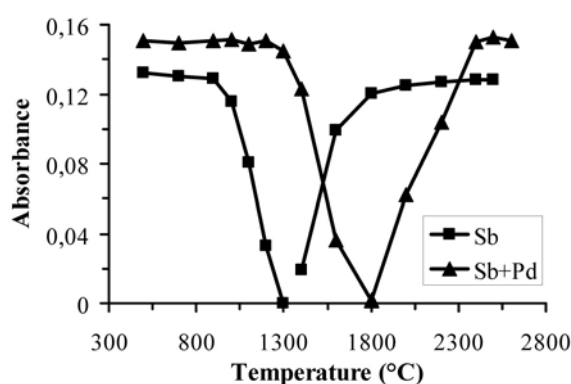

Figure 1. Pyrolysis and atomization curves for Sb(III) standard solution submitted to the cloud point extraction. Applied conditions: 1.6 μg L^{-1} Sb(III), 0.1% (m/v) APDC, 0.2% (m/v) TX-114.

3. 2. Optimization of the CPE Conditions

3. 2. 1. Effect of pH

The separation of metal ions by CPE involves the formation of a metal-chelate complex with sufficient hydrophobicity to be extracted to the small volume of sur-

factant-rich phase. The extraction efficiency depends on the pH at which the complex formation occurs, thus the pH was the first critical parameter evaluated for its effect on the extraction of Sb(III). The pH of Sb(V) complex formation was also examined in order to avoid Sb(V) interferences. The examined pH of the solutions of the both antimony oxidation forms ranged from 1.0 to 8.0. The results showed that Sb(III) was completely extracted at the pH 1.0–6.0, while Sb(V) was quantitatively extracted at pH < 1.5. At pH > 4.0, Sb(V) does not form a dithiocarbamate complex and is not extracted to the surfactant-rich phase (Fig. 2). Based on these observations, selective separation of Sb(III) and Sb(V) can be achieved at pH 5.0–6.0, so subsequent experiments were made with pH adjustment to 5.5 ± 0.1. These results are in agreement with results published by Li et al.[25]
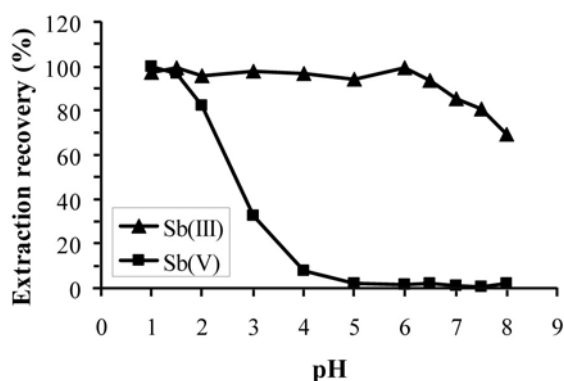

Figure 2. Effect of pH on the cloud point extraction of Sb(III) and Sb(V). Applied conditions: 0.4 µg L^{-1} Sb(III), 0.4 µg L^{-1} Sb(V), 0.1% (m/v) APDC, 0.2% (m/v) TX-114.

3. 2. 2. Effect of Ammonium Pyrrolidine Dithiocarbamate Concentration

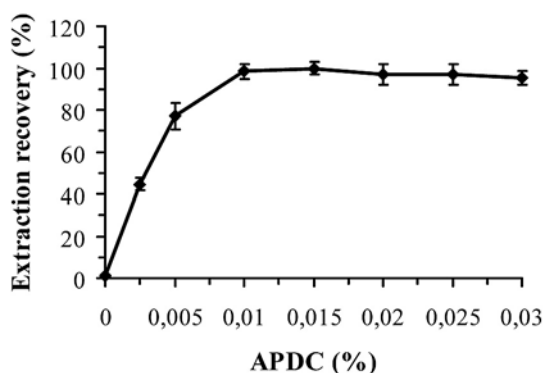A chelating agent, such as APDC forms very stable complexes with the elements that have a vacant d orbital,

Figure 3. Effect of APDC concentration on the extraction recovery of Sb(III). Applied conditions: 0.4 µg L^{-1} Sb(III), 0.10% (m/v) TX-114.

or a filled d orbital with low charge such as in case of transition and semi-metals.[26] It does not form complexes with alkali and alkali earth metals. Hence, it has been extensively used in extraction of trace metals from water samples. In this work, we used APDC as the chelating agent for Sb(III). The extraction recovery as a function of APDC concentration is shown in Fig. 3. For this study, 10 ml of a solution containing 0.4 µg L^{-1} Sb(III) in 0.10% (m/v) TX-114 with various amounts of APDC was subjected to the CPE preconcentration procedure. At this stated concentration of Sb(III), quantitative extraction was achieved for an APDC concentration of 0.01% (m/v). Finally the concentration of 0.02% (m/v) APDC was chosen for subsequent experiments.

3. 2. 3. Effect of Triton X-114 Concentration

In this study a non-ionic surfactant Triton X-114 (octyl phenoxy polyethoxy ethanol; TX-114), was chosen for the formation of the surfactant-rich phase due to its excellent physicochemical characteristics: low cloud point temperature, high density of a surfactant-rich phase (which facilitates phase separation by centrifugation), commercial availability, relatively low price, and low toxicity.[27] The effect of the surfactant concentration on the extraction recovery is shown on Fig. 4. TX-114 was found to quantitatively extract the Sb(III)-PDC complex from the aqueous sample at surfactant concentrations above 0.05% (m/v). Using more than 0.15% (m/v) of surfactant, the extraction recovery decreased due to dilution of the sample by additional surfactant solution. For further studies, a TX-114 concentration of 0.08% (m/v) was selected.
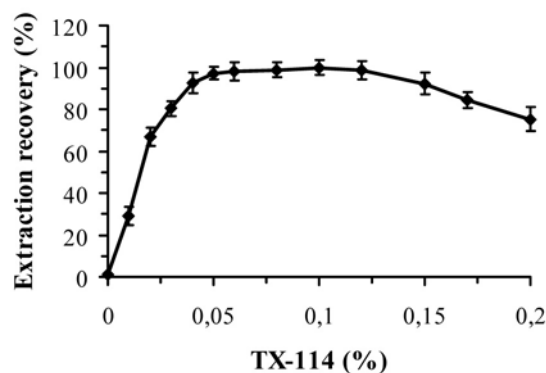

Figure 4. Effect of TX-114 concentration on the extraction recovery of Sb(III). Applied conditions: 0.4 µg L^{-1} Sb(III), 0.02% (m/v) APDC.

3. 2. 4. Effect of Different HNO₃ Concentrations in Methanol

To reduce high viscosity of the surfactant-rich phase before ETAAS determination, pure methanol and methanol with different concentrations of HNO_3 were tested

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(see Fig. 5). The obtained results showed that using pure methanol, extraction recovery around 85% was achieved, while using 0.2 mol L^{-1} HNO$_3$ in methanol, extraction recovery near 100% was achieved. Higher concentration of HNO$_3$ in methanol led to the similar extraction recovery (~ 100%). It seems that presence of HNO$_3$ is essential to prevent from analyte losses (e.g. by adsorption on tube walls). Thus, 0.2 mol L^{-1} HNO$_3$ in methanol was chosen and used to reduce the viscosity of the surfactant-rich phase in all experiments.
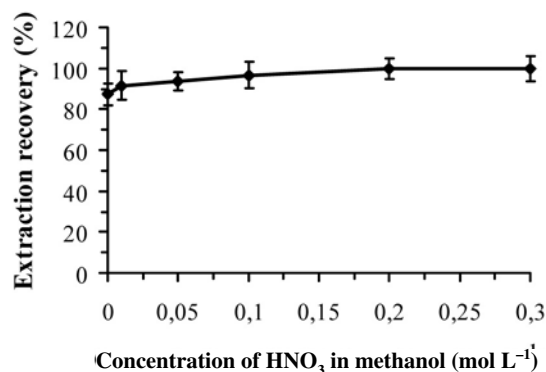

Figure 5. Effect of different concentrations of HNO$_3$ in methanol on the extraction recovery of Sb(III). Applied conditions: 0.4 µg L^{-1} Sb(III), 0.02% (m/v) APDC, 0.08% (m/v) TX-114.

3. 2. 5. Effect of Incubation Temperature and Time

To achieve easy phase separation and preconcentration as efficient as possible, optimal incubation temperature and time are necessary to complete reactions. The effect of incubation temperature was investigated in the range of 25–65 °C. The results (illustrated in Fig. 6) show excellent recoveries for incubation temperature from 30 to 55 °C. Lower and higher temperatures lead to the 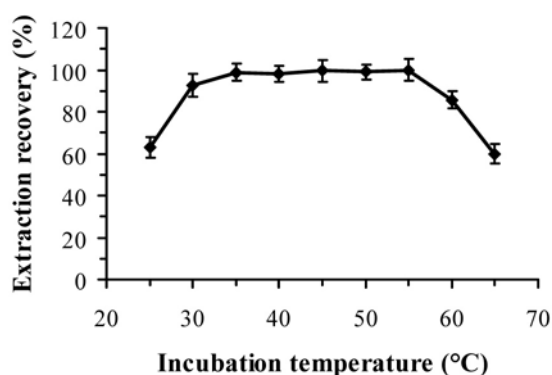reduction of the extraction yield. Using TX-114, clouding occurs in the range of 23–25 °C,[15] so temperatures lower than 30 °C are not sufficient for this procedure. Reduction of the extraction yield at higher temperatures than 60 °C can be probably caused by thermal degradation of Sb(III)-PDC complex. Therefore temperature of 45 °C was chosen and used in all subsequent experiments. Keeping the incubation temperature of 45 °C, the effect of incubation time on the CPE procedure was investigated. This dependence was studied in the range of 1–10 min. An incubation time of 1 min was already sufficient for quantitative extraction but finally the incubation time of 5 min was chosen and used in the optimized procedure because a better reproducibility of the procedure was achieved.

3. 2. 6. Effect of Ionic Strength and Centrifugation Time

The influence of ionic strength on the extraction recovery of Sb(III) was examined in the presence of known concentration of NaCl. It was proved that the overall process remained unaffected for NaCl concentration varying in 0–3% (m/v). Thus, the subsequent experiments were made with no NaCl addition.

The effect of centrifugation time on the extraction recovery was studied in the range of 5–20 min. The complete phase separation was already achieved after a 5 min of centrifugal time. This time was chosen and used in subsequent experiments.

3. 3. Interference Studies

In the view of the high selectivity provided by ETAAS determination, the main interferences studied were those related to the preconcentration step. Metal ions that may react with APDC and may be co-extracted with Sb(III) to the surfactant-rich phase were studied. To perform this study, 10 ml of a solution containing 0.4 µg L^{-1} Sb(III) and an interferent ion in different analyte-to-interferent ratios was subjected to the CPE procedure. The ratios of 1:5, 1:10, and 1:100 were tested for Ag(I), Cd(II), Co(II), Cu(II), Mn(II), Ni(II), Pb(II), and Se(IV); the ratio of 1:500 was tested for Fe(III) and Zn(II); and the ratio of 1:1000 was tested for Al(III) and As(III) with satisfactory results (extraction recovery in the range of 90–110%).

Figure 6. Effect of incubation temperature on the extraction recovery of Sb(III). Applied conditions: 0.4 µg L^{-1} Sb(III), 0.02% (m/v) APDC, 0.08% (m/v) TX-114.

Table 2. Determination of Sb(III) in the synthetic water (SW) after CPE separation and preconcentration.

Sample	Sb(III) added (µg L^{-1})	Sb(III) determined (µg L^{-1})[a]	Extraction recovery (%)
SW	0.40	0.41 ± 0.02	102.5
SW	0.80	0.79 ± 0.03	97.5
SW	1.60	1.68 ± 0.02	105.0
SW	3.20	3.26 ± 0.01	101.9

[a] Mean of four experiments ± standard deviation.

To confirm that major matrix components of natural waters such as K(I), Na(I), Mg(II), and Ca(II) do not influence the CPE procedure of Sb(III), synthetic water (SW) spiked with different concentrations of Sb(III) was submitted to the optimized CPE procedure. The obtained results can be seen in Table 2.

3. 4. Analytical Figures of Merit

The figures of merit for the optimized CPE procedure of Sb(III) prior to ETAAS determination were as follows. The relative standard deviation (RSD) obtained for 10 samples of 0.4 μg L^{-1} Sb(III) subjected to the CPE procedure was 6.5%. The enrichment factor (EF), calculated as the ratio between the slopes of a curve established using aqueous solutions submitted to the CPE procedure and a curve with aqueous standards not submitted to this procedure, was 28 (obtained by preconcentration a 10 ml of sample volume). The linear concentration range was from 0.10 to 3.5 μg L^{-1} for Sb(III). The calibration function with a slope 0.1882 (five standards, $n = 3$) and a correlation coefficient 0.998 was achieved. The detection limit, calculated according to $3s_0/s$, where s_0 was obtained from the standard deviation for 10 replicates of a blank solution, and s is the slope of the calibration graph obtained after CPE procedure, was 0.03 μg L^{-1}.

3. 5. Application to Real Samples

The optimized CPE procedure was applied for the selective determination of Sb(III) in two local water samples involving well and lake water. Lake water (LW) was collected from the northern part of the neovolcanic massive and well water (WW) from a contaminated domestic well. Higher concentrations of matrix ions were determined in the both samples. Analytical results are given in Table 3. As can be seen, recoveries in the range of 91–105% were obtained by analysis of the spiked real samples. A certified reference material for trace elements in riverine water SLRS-4 was used for checking the accuracy of the optimized method for the total antimony determination after reduction of Sb(V) to Sb(III) with L-cysteine.[24,28]

4. Conclusions

In the present work, the use of the optimized CPE procedure for the separation/preconcentration of ultratrace levels of Sb(III) in natural waters prior to ETAAS determination is described. The separation occurred efficiently, resulting in the good enrichment factor (28) and the low detection limit (0.03 μg L^{-1}). The obtained results showed that the CPE technique can effectively improve the analyte sensitivity. This methodology offers a relatively simple, rapid, safe, sensitive, inexpensive and environmental friendly alternative to other separation/preconcentration techniques.

5. Acknowledgement

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Table 3. Determination of Sb(III) and total Sb in real samples after CPE separation and preconcentration.

Sample	Added (μg L^{-1}) Sb(III)	Determined (μg L^{-1}) [a] Sb(III)	Sb(total)[b]	Extraction recovery (%) Sb(III)	Sb(total)
WW	–	0.35 ± 0.04	2.06 ± 0.05	–	
	0.40	0.72 ± 0.02	2.48 ± 0.06	92.5	105.0
LW	–	0.13 ± 0.02	2.25 ± 0.01	–	–
	0.40	0.51 ± 0.03	2.62 ± 0.05	95.0	92.5
SLRS-4[c]	–	–	0.21 ± 0.03	–	91.3
	0.40	0.41 ± 0.04	0.60 ± 0.01	102.5	97.5

[a] Mean of four experiments ± standard deviation. [b] Determined after reduction of Sb(V) to Sb(III) with L-cysteine. [c] Certified value for total antimony: 0.23 ± 0.04 μg L^{-1}.

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Povzetek

Za ločbo in predkoncentracijo pri določevanju ultra sledov Sb(III) v vzorcih naravnih vod z elektrotermično atomsko absorpcijsko spektrometrijo smo uporabili ekstrakcijo pri točki zmotnitve (cloud point extraction). Po kompleksiranju z amonijevim pirolidin ditiokarbamatom v rahlo kislem mediju, smo s centrifugiranjem izvedli ekstrakcijo v raztopino neionskega tenzida oktilfenoksipolietoksietanola (TRITON X-114). Fazo, ki je vsebovala TRITON X-114 smo razredčili z 0,20 M HNO$_3$ v metanolu in jo analizirali z ETAAS. Podrobno smo raziskali možne dejavnike, ki vplivajo na ločbo pri uporabljeni ekstrakciji in na predkoncentracijo Sb(III). Za raztopino Sb(III) s koncentracijo 0,40 µg L^{-1} smo pri desetih ponovitvah meritve ugotovili relativni standardni odmik 6,5 % in faktor obogatitve 28. Metoda daje linearen odziv v koncentracijskem območju 0,1 do 3,50 µg L^{-1} Sb(III), dosegli pa smo spodnjo mejo detekcije 0,03 µg L^{-1} Sb(III). Metodo smo uporabili za določevanje Sb(III) v vodi iz vodnjakov in jezer.