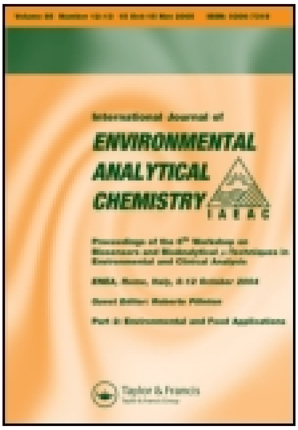

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Determination of total antimony(III,V) by square-wave anodic stripping voltammetry with *in situ* plated bismuth-film electrode

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A sensitive and reliable method is described for the determination of total Sb(III, V) at traces levels by Osteryoung square-wave anodic stripping voltammery (OSWASV). This method is based on the co-deposition of Sb(III, V) with Bi(III) onto an edge-plane pyrolytic graphite substrate at an accumulation step. OSWASV studies indicated that the co-deposited antimony was oxidised with anodic scans to give an enhanced anodic peak at about 450 mV vs. Ag/AgCl (sat. KCl). The anodic stripping peak current was directly proportional to the total concentration of antimony in the ranges of 0.01–0.10 $\mu g\,L^{-1}$, 0.10–1.0 $\mu g\,L^{-1}$ and 1.0–18.0 $\mu g\,L^{-1}$ with correlation coefficient higher than 0.995 when 2.0 $mol\,L^{-1}$ hydrochloric acid was used. The detection limits calculated as $S/N = 3$ was 5.0 $ng\,L^{-1}$ in 2.0 $mol\,L^{-1}$ hydrochloric acid at 180 s deposition time. The relative standard deviation was 5% ($n = 6$) at 0.10 $\mu g\,L^{-1}$ level of antimony. The analytical results demonstrate that the proposed method is applicable to analyses of real water samples.

Keywords: antimony determination; *in situ* plating; bismuth film electrode; edge-plane pyrolytic graphite; OSWASV

1. Introduction

Antimony and its compounds have been used in the manufacturing of polyester (as the catalyst), glass and ceramics. Due to human health and environmental preservation, they are listed as pollutants of priority interest by the Environmental Protection Agency of the United States (USEPA) [1] and the Council of the European Communities [2]. In fact, trace levels of antimony are found as antimony(III) and antimony(V) in environmental, biological and geochemical samples [1–5].

To date, various methodologies and techniques have been developed for antimony detection and determination in a variety of samples [6]: spectrophotometry [7], neutron activation analysis [8], microwave induced emission spectrometry, hydride generation atomic absorption spectrometry [9], inductively coupled plasma-atomic emission spectrometry and inductively coupled plasma-mass spectrometry [10]. These spectrometric methods are very simple in operation and obtain reproducible results, but the instruments are so costly that we cannot obtain them very often. The electroanalytical methods, further, have also been reported for the determination of trace or ultra-trace amount of antimony with high sensitivity, ease of operation and low-cost of instrumentations.

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They include differential pulse anodic stripping voltammetry [5,11–22], anodic adsorptive stripping voltammetry [23], cathodic adsorptive stripping voltammetry [4,24], anodic stripping potentiometric analysis [25] and constant-current stripping analysis [26] using mercury-based (HMDE, SMDE or MFE), graphite [13], gold [17,18,26] and silver nanoparticle modified carbon [20] as the working electrodes.

As an alternative to mercury, *in situ* or *ex situ* bismuth-film electrodes have been studied on such substrates as glassy carbon, pyrolytic graphite carbon and carbon paste, being less toxic and excellent in analytical performances [27–35]. Bismuth, however, was oxidised at more negative potentials than copper, arsenic, antimony, mercury and silver. It therefore has been considered that bismuth-based electrodes have some limitation for use of anodic stripping voltammetry for the determination of such metals that were oxidised at more positive potentials than bismuth. The available potential range (window) is relatively narrow. In the previous paper, we demonstrated that traces of arsenic(III) could be determined by differential-pulse anodic-stripping voltammetry with an *in situ* bismuth-film electrode, in which case the ratio of Bi(III)/As(III) peak current was taken for calibration [34]. In this research, an anodic peak due to Sb(III, V) peak appears at a potential more positive than the Bi(III) to be added in excess. This paper provides a new idea or a concept in the field of voltammetric analysis, and hopefully widens further developments of metal determination at trace levels. It is shown that a useful and reliable method was developed for antimony detection and determination without taking account of the anodic peak current due to bismuth. Experimental parameters, dynamic range of calibration curves, detection limit, reproducibility, interferences from foreign ions and sample analyses are investigated.

2. Experimental

A BAS Model CV-50 W voltammetric analyser (Bioanalytical Systems, USA) was employed for measurements of cyclic voltammetry (CV) and OSWASV. Unless otherwise stated, the settings for OSWASV measurements were as follows: 4 mV step potential, 25 mV square wave amplitude, 15 Hz frequency, 10 s rest period prior to anodic scan. The three electrode system consisted of an edge-plane pyrolytic graphite disk (3.0 mm diameter, BAS) working electrode, a platinum wire counter electrode, and Ag/AgCl (sat. KCl) reference electrode.

All solutions were prepared with deionised or distilled water. The reagents used in this study were from Wako Pure Chemical Industries Co. (Tokyo, Japan). The Sb(III) solution was prepared by diluting a 1000 mg L^{-1} standard for atomic spectroscopy with 0.1 mol L^{-1} hydrochloric acid. The Sb(V) solution was prepared by dissolving a definite amount of $SbCl_5$ in 6 M hydrochloric acid. The stock Bi(III) solution was prepared by dissolving $BiCl_3$ in 0.5 mol L^{-1} hydrochloric acid. The foreign metal ion solutions were prepared by diluting their standard solutions (1000 mg L^{-1}) with 0.1 mol L^{-1} hydrochloric acid. The chemical forms were $AlCl_3$, $Ca(NO_3)_2$, $MgCl_2$, NaCl, $Cd(NO_3)_2$, $Co(NO_3)_2$, $NiCl_2$, $MnCl_2$, $Zn(NO_3)_2$, $Na_2WO_4 \cdot 2H_2O$, NH_4VO_3, $SnCl_2$, $(NH_4)_6Mo_7O_{24}$, Na_2SeO_3, $Cu(NO_3)_2$, $HgCl_2$, $Pb(NO_3)_2$, As_2O_3, $Fe(NO_3)_3$, KH_2PO_4, $(NH_4)_2SO_4$, and KNO_3. All stock solutions were stored in a refrigerator at 2°C.

Synthetic water samples (model samples) were prepared from the standard Sb(III) or Sb(V) solution at different concentrations. After a coastal sea water sample (Mikuni, Fukui, Japan) was taken up, the samples were filtered with a 0.45 μm membrane filter and then acidified to 2.0 mol L^{-1} hydrochloric acid. All samples were analysed by the standard addition and background subtraction method.

Prior to the electrochemical measurement, the edge-plane graphite electrode was cleaned daily by polishing with aluminium oxide slurry and next with a piece of Nuclepore filter paper. The treated electrode was then immersed in 1.0 mol L^{-1} hydrochloric acid for 1 min, and rinsed with water. After voltammetric measurements, the working electrode was treated as described above and reactivated each time by keeping the electrode potential at 800 mV for 30 s.

The established procedures for the determination of total antimony by OSWASV were set as follows: an aliquot (5.0 mL) of standard or sample solutions containing Sb(III)/Sb(V) was placed into a 20.0 mL electrolytic glass cell. The reagent solutions were then added to the standard or sample solution, and the total volume of the test solution was finally made up to 10.0 mL with water. The equilibrium concentrations of added reagents except Sb(III) and Sb(V) were adjusted to 2.0 mol L^{-1} hydrochloric acid, 500 µg L^{-1} Bi(III), 30 g L^{-1} potassium chloride solution, and 1.0 g L^{-1} L-cysteine. Before OSWASV and CV measurement, the sample solution was purged by nitrogen for 600 s. Both Sb(III) and Sb(V) were initially reduced at a potential of −400 mV for 180 s in a stirred solution. After 10 s rest period, OSWASV and CV measurements were carried out by scanning the electrode potential from −400 to 800 mV in the positive direction. The scan rates were set at 60 and 100 mV s^{-1} for OSWASV and CV measurement, respectively.

3. Results and discussion

3.1 *Electrochemical behaviour of antimony on the bismuth-film graphite electrode*

The electrochemical behaviour of electroactive Sb(III) and Sb(V) in hydrochloric acid on the *in situ* bismuth-film modified edge plane graphite electrode was investigated by cyclic voltammetry and OSWASV, as shown in Figure 1. After Sb(III) and Sb(V) were reduced to the antimony with Bi(III) at −400 mV vs. Ag/AgCl, a well-defined bismuth stripping peak was obtained at about −150 mV and an antimony stripping response at 450 mV when the potential was scanned to the positive direction. In the absence of Bi(III), a very small stripping peak appeared due to Sb(III) and Sb(V). It, therefore, is evident that Bi-Sb alloy was formed on the edge plane graphite substrate at the deposition step. The stripping peak current observed at 450 mV was directly proportional to the initial concentration of total antimony taken at around µg L^{-1} concentration levels or below. The proposed OSWASV enables determination of total Sb(III,V) at trace levels in natural waters. It was also found that the addition of potassium chloride as an electrolyte and L-cysteine as a complexing agent helped to get a higher and reproducible peak current due to Sb(III) and Sb(V).

3.2 *Experimental parameters*

The effect of hydrochloric acid concentration on the OSWASV peak currents of 10.0 µg L^{-1} Sb(III) or Sb(V) was investigated. The results shown in Figure 2 indicate that the peak currents gradually increased from 0.10 to 2.0 mol L^{-1} hydrochloric acid and remained constant at hydrochloric acid concentrations between 2.0 and 3.0 mol L^{-1}. It was found that the peak currents for Sb(III) and Sb(V) were the same at 2.0 mol L^{-1} hydrochloric acid. In the subsequent experiments, 2.0 mol L^{-1} hydrochloric acid was chosen as the most optimum concentration. Further, the addition of potassium chloride

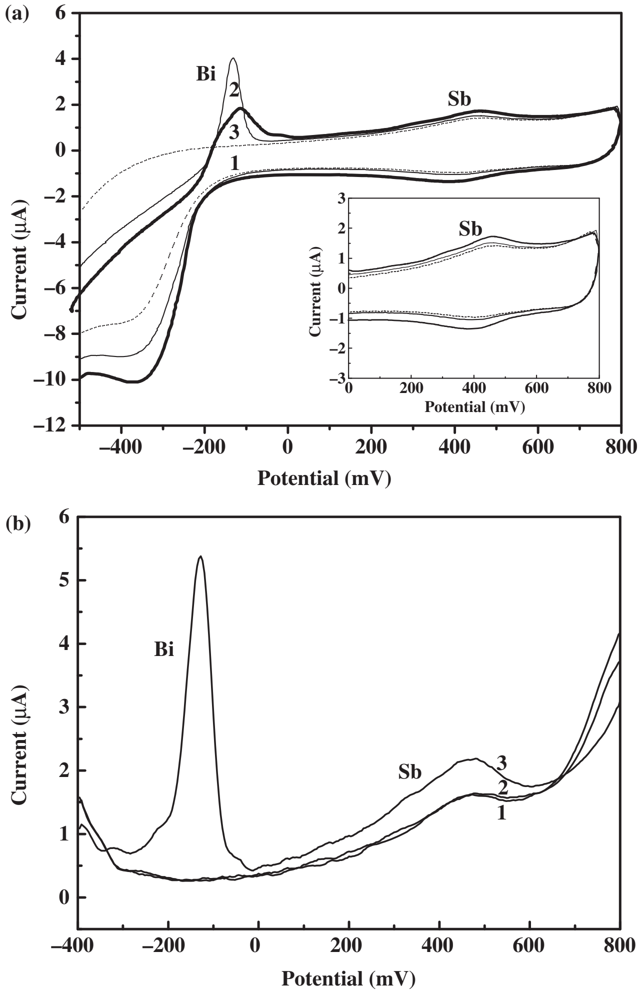

Figure 1. Cyclic voltammograms (a) and OSWASV curves (b) for Sb determination. (a) (1) blank test (2.0 mol L^{-1} HCl + 5 g L^{-1} KCl); (2) (1) + 500 μg L^{-1} Bi (III); (3) (2) + 10 μg L^{-1} Sb(V). Measurement parameters: −400 mV deposition potential, 60 s deposition time and 100 mV s^{-1} scan rate. (b) (1) blank test (2.0 mol L^{-1} HCl + 5 g L^{-1} KCl); (2) (1) + 10 μg L^{-1} Sb(V); (3) (2) + 500 μg L^{-1} Bi (III). Measurement parameters: −400 mV deposition potential and 60 s deposition time.

from 0 to 30.0 g L^{-1} concentration levels as another electrolyte gradually enhanced the peak currents for both Sb(III) and Sb(V), and the reproducibility was greatly improved as well. In this study, 30 g L^{-1} of potassium chloride was added.

The effect of Bi(III) concentration on the OSWASV peak currents of 10.0 μg L^{-1} Sb(V) was investigated at 2.0 mol L^{-1} hydrochloric acid. As seen from Figure 3, the peak current was found to sharply increase with Bi(III) concentration from 0 to 100 μg L^{-1} above which concentrations it gradually increased up to 900 μg L^{-1}. The addition of Bi(III) seems to assist the formation of antimony metal on the carbon electrode surface, resulting in increase of OSWASV response. In this study, 500 μg L^{-1} Bi(III) was added to test solutions. Addition of L-cysteine as a complexing agent was found to split a composite

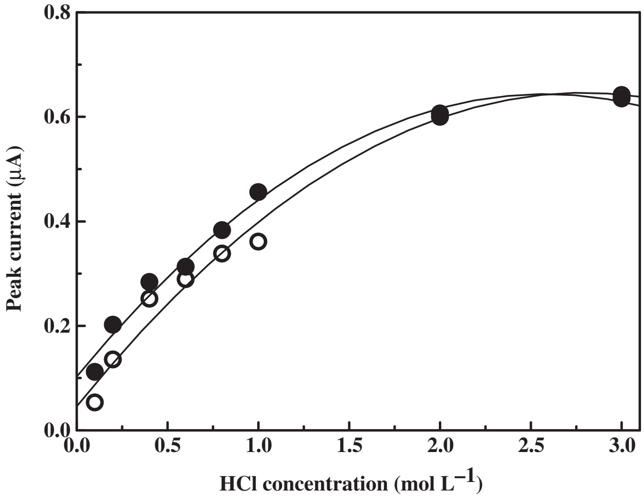

Figure 2. Effect of hydrochloric acid concentration on anodic stripping peak-current. ● 10 μg L^{-1} Sb(III); ○ 10 μg L^{-1} Sb(V). Measurement parameters: 500 μg L^{-1} Bi(III), 5 g L^{-1} KCl, −400 mV deposition potential and 180 s deposition time.

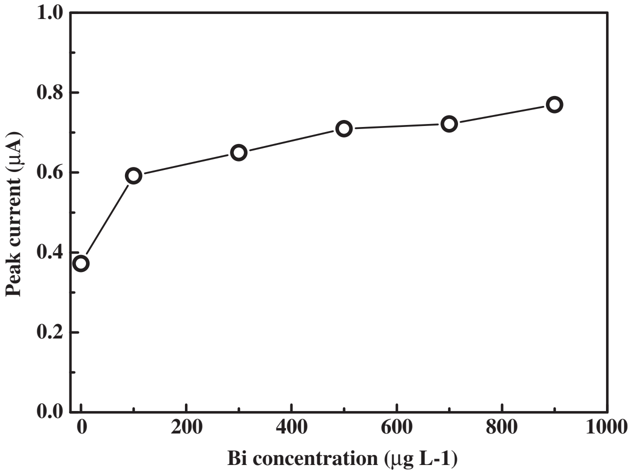

Figure 3. Effect of Bi(III) concentration on anodic stripping peak-current. ○ 10 μg L^{-1} Sb(III) or Sb(V) in 2.0 mol L^{-1} HCl; 10 g L^{-1} KCl; 1.0 g L^{-1} L-cysteine. Deposition potential, −400 mV; deposition time, 180 s.

peak due to oxidation of antimony and bismuth into the two and separate peaks. The effect of L-cysteine concentration on the antimony peak current was investigated in the range of 0.05 to 2.0 g L^{-1} against 10.0 μg L^{-1} Sb(III) or Sb(V). When the L-cysteine concentration increased, the peak current exponentially decreased and the peak potential shifted more positively. The addition of 1.0 g L^{-1} L-cysteine was the most adequate to obtain the reproducible and accurate peak current due to Sb(III) and Sb(V).

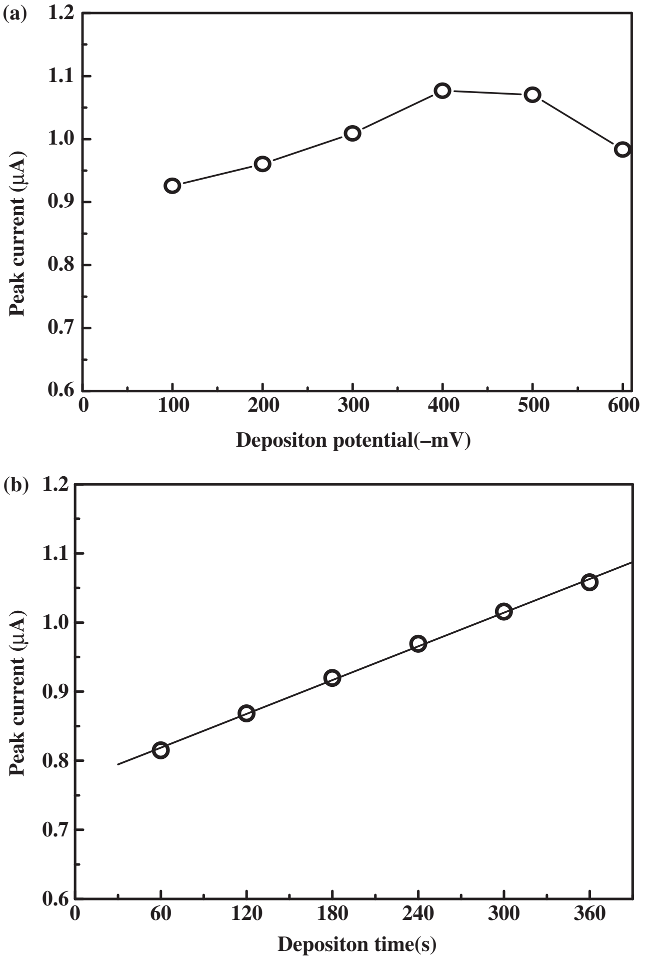

Figure 4. Effect of deposition potential (a) and deposition time (b). ○ 10 μg L^{-1} Sb(III) or Sb(V) in 2.0 mol L^{-1} HCl; 30 g L^{-1} KCl; 1.0 g L^{-1} L-cysteine; 500 μg L^{-1} Bi(III). (a) Deposition time, 180 s; (b) Deposition potential, −400 mV.

The effect of deposition potential on the antimony peak currents was investigated in the range of −100 mV to −600 mV. The results shown in Figure 4(a) indicate that the antimony peak current gradually increased with decreasing deposition potentials below −400 mV. At potentials between −400 and −500 mV, the antimony peak current remained almost a constant. The effect of deposition time on the peak current was also investigated in the range of 60 to 360 s. The results shown in Figure 4(b) indicate that the antimony peak current increased linearly as the deposition time increased. In this study, we chose a deposition potential of −400 mV and a deposition time of 180 s, respectively.

3.3 *Calibration curve and detection limit*

The calibration curves for the determination of total Sb(III, V) were obtained with 2.0 mol L^{-1} hydrochloric acid. As can be seen from Figure 5, the linear relationships held

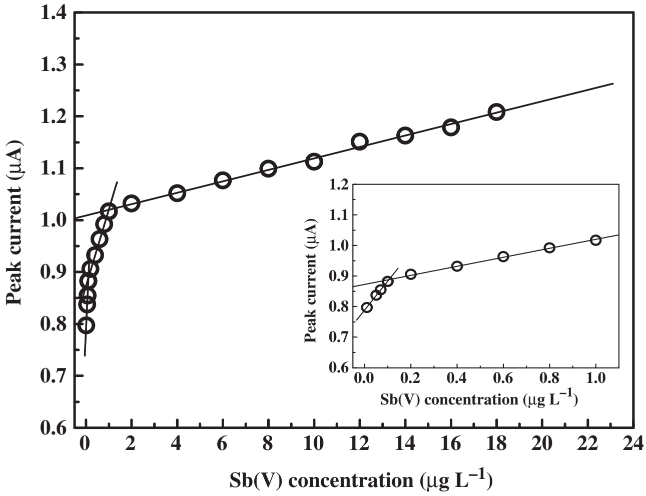

Figure 5. Relationship between peak current and Sb(V) concentration. Measurement parameters: 2.0 mol L^{-1} HCl; 30 g L^{-1} KCl; 1.0 g L^{-1} L-cysteine; 500 μg L^{-1} Bi(III); deposition potential, −400 mV; deposition time, 180 s.

over the concentration ranges of 0.01–0.10 μg L^{-1}, 0.10–1.0 μg L^{-1} and 1.0–18.0 μg L^{-1} with correlation coefficients higher than 0.995. When Sb(III, V) concentration increased, the slope of calibration curve is decreased. We, therefore, should choose the calibration curve depending on the concentration orders. The relative standard deviation was 5.0% ($n = 6$) for 0.10 μg L^{-1} Sb(III) or Sb(V) solution in 2.0 mol L^{-1} hydrochloric acid. The limits of detection calculated as $S/N = 3$ was 5.0 ng L^{-1} Sb(III, V) in 2.0 mol L^{-1} hydrochloric acid at 180 s deposition time. This value is lower than those obtained by using gold-based electrodes [17,18,26] and comparable with that obtained by mercury-based electrodes [15], revealing the superior characteristics of the bismuth film electrode for the determination of total antimony.

3.4 *Interference*

The effect of foreign ions on the OSWASV determination of 1.0 μg L^{-1} Sb(III) or Sb(V) by the proposed method was investigated at a range of concentrations. The tolerance amounts of 1.0 μg L^{-1} Sb(III) or Sb(V) (determined within ±10% relative errors) were 2.0 μg L^{-1} for Se(IV), 30 μg L^{-1} for As(III), 100 μg L^{-1} for Cu(II), 200 μg L^{-1} for Pb(II), and 500 μg L^{-1} for Hg(II), V(V), Mo(VI), respectively. Se(IV) gave a small OSWASV peak at the same Sb potential. When Sb, As and Cu coexist in natural waters, and the conventional ASV methods can hardly applied to the metal determinations because their redox potentials are very close to each other. The proposed method gives less interference from such closely related metals than the usual ASV methods. There was no interference from Na(I), K(I), Mg(II), Al(III), Ca(II), Ni(II), Cd(II), Co(II), Mn(II), Zn(II), Sn(II), W(VI), Fe(III) at 1000-fold amounts excess over Sb(III) or Sb(V). Except for Se(IV), the proposed method was relatively free from the interference of common metal ions. Such anions as NO_3^-, PO_4^{3-}, and SO_4^{2-} had no effect at 1.0 mg L^{-1}, 3.0 mg L^{-1}, and 5.0 mg L^{-1}, respectively.

3.5 *Sample analyses*

The standard addition method was used for recovery test and real sample analyses. Good recovery percentages between 96–106% were obtained with synthetic samples (Models 1–5) including Sb(III) and/or Sb(V) at concentrations of 0.040 µg L^{-1} and 2.0 µg L^{-1}, as can be seen from Table 1. The presented data indicate that fresh water may be determined because major metal ions such as Na, K, Ca, Mg, Fe and Al showed no effect for the proposed OSWASV determination of total antimony. A coastal sea water (Mikuni, Fukui, Japan) was analysed on four replicate determinations to evaluate the present method. The typical OSWASV curves obtained for the determination of total antimony in the sea water are shown in Figure 6. The analytical result of total Sb(III, V)

Table 1. Analytical results of Sb(III, V) determination in synthetic and real water samples.

	Samples	Experimental results (µg L^{-1})	Spiked Sb(III) or Sb(V) in samples (µg L^{-1})	Recovery (%)	Correlation coefficient (r^2)
Sb(III)	Model 1	0.0496	0.050	99	0.9984
	Model 2	0.2125	0.200	106	0.996
	Model 3	0.3920	0.400	98	0.995
Sb(V)	Model 4	0.0406	0.040	102	0.9965
	Model 5	0.1926	0.200	96	0.9998
Sb(III, V)	Sea water	0.262 ± 0.02	–	–	0.9998
		0.625 ± 0.03	0.340[a]	–	0.9995

Note: [a]Concentration of Sb(V) spiked.

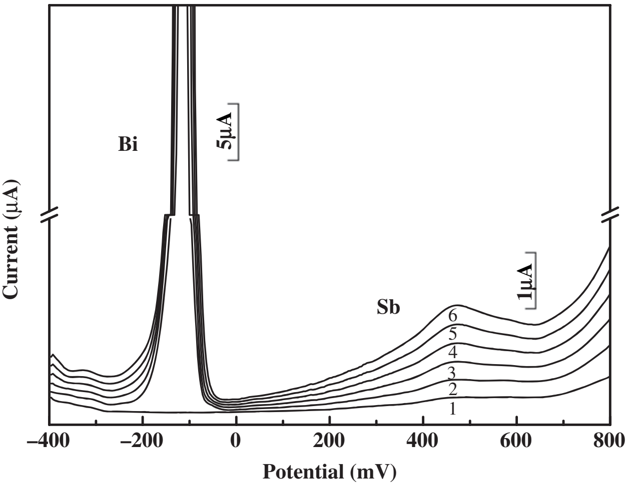

Figure 6. OSWASV curves obtained for total antimony determination in seawater. (1) 2.0 mol L^{-1} HCl, 30 g L^{-1} KCl, 1.0 g L^{-1} L-cysteine; (2) (1) + 500 µg L^{-1} Bi(III); (3) (2) + sea water (spiked 0.34 µg L^{-1} Sb(V)); (4–6) (3) + successive addition of 0.1 µg L^{-1} Sb(V). Deposition potential, −400 mV; deposition time, 180 s.

was $0.262 \pm 0.02\,\mu g\,L^{-1}$ for the sea water (see Table 1). The proposed method is so sensitive and reliable that traces of Sb(III, V) in natural samples can be determined with good results.

4. Conclusions

The total concentration of Sb(III, V) at trace levels could be determined by the proposed OSWASV method using the bismuth co-deposition onto an edge-plane pyrolytic graphite substrate. There is no difficulty in measuring the anodic peak current of Sb(III, V). Probably, square-wave voltammetry makes it possible to directly determine Sb(III, V), instead of taking a peak current ratio of Bi(III)/Sb(III, V) for calibration. In addition, the Sb(III, V) peak can be resolved well from Bi(III) and As(III) ones by adding L-cysteine as a complexing agent, although in general the two metal ions can hardly be separated by voltammetric analysis. The proposed method still holds high sensitivity and good selectivity by adding a definite amount of Bi(III). The anodic stripping response for antimony at 450 mV was enhanced significantly on bismuth film electrode, which enables the determination of antimony at ppt concentration levels. The synthetic samples and coastal sea water could be analysed with satisfactory results.

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