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# Determination of Antimony (III) and (V) in Natural Water by Cathodic Stripping Voltammetry with *in-situ* Plated Bismuth Film Electrode

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**Abstract**   A method is described for the sequential determination of Sb(III) and Sb(V) using Osteryoung square wave cathodic stripping voltammetry. It employs an *in-situ* plated bismuth-film on edge-plane graphite substrate as the working electrode. Selective electro-deposition of Sb(III)/Sb(V) is accomplished by applying a potential of $-500$ mV vs Ag/AgCl, this followed by reduction to stibine at a more negative potential in the stripping step. Stripping was carried out by applying a square wave waveform between $-500$ and $-1400$ mV to the antimony deposited. The stripping peak current at $-1150$ mV is proportional to the concentration of Sb(III)/Sb(V). The calibration plots for Sb(III) were linear up to 12.0 µg $L^{-1}$ depending on the time of deposition. The calibration plots for Sb(V) were linear up to 7.0 µg $L^{-1}$, also depending on the time of deposition. The relative standard deviation in the determination of 0.1 µg $L^{-1}$ of Sb(III)  is 4.0% ($n = 5$), and the limit of detection is as low as 2 ng $L^{-1}$. In case of 0.1 µg $L^{-1}$ Sb(V), the relative standard deviation is 3.0% ($n = 5$) and the detection limit also is 2 ng $L^{-1}$. The method was applied to the analysis of river water and of sea water samples.

# Introduction

Antimony is present as the oxidation states (III) and (V) in environmental, biological and geological samples [1-4]. Antimony(III) is generally accepted to be more toxic than antimony(V). Since the toxicity depends on its chemical form and oxidation state, the speciation technique for antimony is required for a risk assessment to be performed. Until now, a variety of methods that meet these requirements have been developed and well established for the speciation of antimony(III) and antimony(V) at trace levels in natural waters. They include fluorometry [5], spectrophotometry [6], atomic absorption spectrometry [7-12], inductively coupled plasma optical emission spectrometry [13, 14], atomic fluorescence spectrometry [15, 16] and neutron activation analysis [17]. Among them, the spectroscopic techniques combined with volatile hydride generation ($SbH_3$) have extensively been utilized for this purpose, being detection limits of 0.1 or lower μg/L [7, 13, 15]. A variety of electrochemical methods have been reported for the determination of antimony by differential pulse anodic stripping voltammetry [18-22], differential pulse adsorptive stripping voltammetry [22, 23], anodic stripping voltammetry [24, 25], cathodic stripping voltammetry [26], constant-current stripping analysis [27], and coulometry [28]. The anodic or cathodic stripping voltammetry for antimony analysis was conducted on carbon screen-printed electrodes [24], gold film electrode [25], gold fiber electrode [28] as well as mercury-based electrodes [29-31]. Due to its high toxicity, use of mercury electrodes must be avoided because the increased risks in the environment and human health are associated. As an alternative to mercury electrodes, bismuth electrodes received much attention in electrochemical analysis [32], being used in anodic stripping, adsorptive stripping, and cathodic stripping

voltammetry [33-36]. To date, however, there is no report about antimony speciation by using bismuth related electrodes.

This paper describes a highly sensitive and simple method for the determination/speciation of Sb(III) and Sb(V) using *in-situ* bismuth film electrode by Osteryoung squre wave cathodic stripping voltammetry (OSWCSV). This method is based on the discrimination of Sb(III)/Sb(V) at different oxidation states to be performed by adjusting the acidity of test solution. Experimental parameters, calibration curves, detection limits, reproducibility, interferences from foreign ions, and sample analyses are investigated and discussed from the analytical point of view.

## Experimental

*Reagent and Chemicals*

All chemicals used were of analytical reagent grade, and all solutions were prepared with deionized and distilled water. The stock Bi(III) solution was prepared by dissolving solid $BiCl_3$ in $0.5$ mol $L^{-1}$ hydrochloric acid. The stock 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 stock Sb(V) solution ($1000$ mg $L^{-1}$) was prepared by dissolving a definite amount of $SbCl_5$ in $6$ M hydrochloric acid. The other metal ion solutions were prepared by diluting their standard solutions ($1000$ mg $L^{-1}$, Wako Pure Chemical Industries, Japan, http://www.wako-chem.co.jp) with $0.1$ mol $L^{-1}$ hydrochloric acid. All stock solutions were stored in refrigerator at $2$ °C.

*Apparatus*

A BAS Model CV-50W voltammetric analyzer (Bioanalytical system, USA) was employed for measurements of cyclic voltammetry (CV) and OSWCSV. Unless otherwise stated, the settings for OSWCSV measurements were as follows: 4 mV step potential; 25 mV square wave amplitude; 15 Hz frequency; 10 s equilibrium time prior to cathodic scan. An edge-plane pyrolytic graphite disk (3.0 mm diameter, BAS) was used as the working electrode substrate. A platinum wire counter electrode and a Ag/AgCl (sat. KCl) reference electrodes from BAS were also used.

*Procedures*

The edge-plane graphite electrode surface was initially polished with aluminum oxide (Al$_2$O$_3$, Wako Pure Chemical industries, Japan) slurry and next with a piece of filter paper. The treated electrode was then immersed in 1.0 mol L$^{-1}$ hydrochloric acid for 1 min, and rinsed with distilled water. After voltammetric measurements, the working electrode was treated again and reactivated each time by keeping the electrode potential at 800 mV for 30 s.

   The established procedures for the determination of Sb(III)/Sb(V) by OSWCSV were carried out as follows: an aliquot (5.0 mL) of standard Sb(III)/Sb(V) solution was placed into a 10.0-mL electrochemical cell; the reagent solutions were then added to the standard solution, and the total volume of the test solution was finally made up to 10.0 mL with water; the equilibrium concentrations were adjusted to 0.1/0.6 mol L$^{-1}$ hydrochloric acid, 10 g L$^{-1}$ potassium chloride, and 100 μg L$^{-1}$ Bi(III) concentration. Nitrogen was then purged into the test solution for 5 min.

The Sb(III)/Sb(V) was initially reduced on the working electrode at a potential of –500 mV for 30 s in a stirred solution. After 10 s equilibrium time, the electrode potential was scanned from –500 mV to -1400 mV in the negative direction.

The real samples of seawater (Mikuni, Fukui, Japan) and river water (Kuzuryu, Fukui, Japan) for speciation analysis of Sb(III)/Sb(V) were filtered through a piece of 0.45-µm Nuclepore filter and acidified by 0.1/0.6 mol L$^{-1}$ hydrochloric acid. An aliquot of sample solution (5.0 mL) was introduced into 5.0 ml of blank solution for analysis at the final concentrations of 100 µg L$^{-1}$ Bi(III) and 10 g L$^{-1}$ potassium chloride. All water samples were analyzed by standard addition and background subtraction method.

## Results and Discussion

*Electrochemical Behavior of Antimony(III,V) on the Bismuth Film Modified Graphite Electrode*

The electrochemical nature of a catalytic hydrogen wave due to Sb(III,V) was investigated by CV. Fig. 1 shows typical CV curves obtained for 0.1 mol L$^{-1}$ hydrochloric acid (1) and the blank solution containing 100 µg L$^{-1}$ Bi(III) in the same acid solution (2), respectively. When the potential was scanned to a negative direction after 30 s pre-concentration at –400 mV, a small cathodic response due to Bi(III) was observed at about –1150 mV *vs*. Ag/AgCl before the final rise of hydrogen reduction wave. With the addition of 1.0 µg L$^{-1}$ Sb(III) to the blank solution, the hydrogen catalytic peak increased obviously, as shown in Fig.1(3). Our preliminary studies showed that there was no cathodic response due to Sb(III,V) observed at about –1150 mV without

Bi(III).

In order to clarify the electrode process of a cathodic hydrogen wave, the effect of scan rate ($v$) on the peak current ($I_p$) was investigated. The results showed that there was a linear relationship between $|I_p|$ and $v^{1/2}$ and no zero intercept ($|I_p| = 2.7636\ v^{1/2} + 11.839$, $R^2 = 0.9968$), suggesting a typical irreversible and catalytic behavior of antimony. The dependence of ($|I_p| / v^{1/2}$) on the scan rate is used as a diagnostic test for catalytic reactions. The value of $|I_p| / v^{1/2}$ decreased with increasing scan rate in the range of 25─600 mV s$^{-1}$. The enhanced cathodic peak due to Sb(III) at −1150 mV, therefore, is considered to have a nature of catalytic electrode process.

In this study, OSWCSV was employed for the determination of Sb(III)/Sb(V) at sub-ppb levels in aqueous media at ppt concentration levels. It can be seen from Fig. 2 that the catalytic stripping peak current  is directly proportional to Sb(III)/Sb(V) concentration initially taken. This indicates that the proposed OSWCSV method enables determination of traces of Sb(III)/Sb(V) in natural waters.

*Effect of Hydrochloric Acid and Potassium Chloride Concentration*

A supporting electrolyte mostly used for the voltammetric determination of antimony is hydrochloric acid solution or a mixture of hydrochloric acid and potassium chloride. The Effect of hydrochloric acid concentration on the catalytic peak currents due to Sb(III) and Sb(V) was investigated. The results shown in Fig. 3 indicate that the stripping signal for Sb(III) reached a maximum at 0.1 mol L$^{-1}$ hydrochloric acid, and then decreased with increasing the acid concentration. Sb(III) gave no stripping peak in the range of 0.4─0.8 mol L$^{-1}$ hydrochloric acid.

The peak current for Sb(V), on the other hand, was negligibly small at 0.1 mol L$^{-1}$ hydrochloric acid and gradually increased with the acid concentration up to 0.3 mol L$^{-1}$. A constant Sb(V) peak current was obtained at acidities ranging form 0.3 to 0.8 mol L$^{-1}$. The difference in peak current between Sb(III) and Sb(V) was observed, and the speciation analysis of both species was performed at 0.1 and 0.6 mol L$^{-1}$ hydrochloric acid, respectively. The addition of potassium chloride enhanced stripping responses for Sb(III) and Sb(V) in the range of 0─30 g L$^{-1}$. In the subsequent experiments, a potassium chloride concentration of 10 g L$^{-1}$ was chosen as the optimum.

*Effect of Bi (III) Concentration*

The effect of Bi(III) concentration on the OSWCSV peak currents was investigated for 1.0 µg L$^{-1}$ Sb(III) / Sb(V) at 0.1/0.6 mol L$^{-1}$ hydrochloric acid, respectively. It can be seen from Fig. 4 that the peak currents decreased exponentially as Bi(III) concentration increased from 10.0 to 500 µg L$^{-1}$. The addition of Bi(III) at higher concentrations interfered with co-deposition antimony species on the electrode surface, which resulted in decrease of the antimony stripping signals. Furthermore, our preliminary studies showed that no OSWCSV response was observed in the absence of Bi(III). All subsequent experiments were conducted using a Bi(III) concentration of 100 µg L$^{-1}$.

*Effect of Deposition Potential and Time*

The effect of deposition potential on OSWCSV peak currents was investigated in the range of −100 to −800 mV vs. Ag/AgCl. The results shown in Fig. 5 indicate that the antimony peak currents reached maxima at −500 mV and then decreased sharply at more negative potentials up to −800 mV as hydrogen was evolved on the working electrode. The effect of deposition time on the antimony peak currents was investigated in the range of 10–60 s. The antimony peak current ($I_p$, -μA) increased linearly as the deposition time ($t$, s) increased (for Sb(III) $I_p = 1.66t$ - 10.2, $R^2$ = 0.9940; for Sb(V) $I_p = 1.62t$ - 17.5, $R^2$ = 0.9896). A longer deposition time may improve the sensitivity of OSWCSV method but produce a poor reproducibility. In order to achieve antimony determination at ultra-trace concentrations, a deposition potential of −500 mV and a deposition time of 30 s were chosen in this study.

*Calibration Curve and Detection Limit*

Under the optimized experimental conditions, the calibration curves for Sb(III)/Sb(V) determination were constructed by this OSWCSV at different deposition times. Although an S-shaped calibration curve for Sb(III) was obtained with 30 s deposition time, the linear relationships between cathodic peak current and Sb(III) concentration held over the concentration ranges of 0.01–0.10 μg L$^{-1}$ ($I_p = 360C$ + 13.6, $R^2$ = 0.9961, where $I_p$ is peak current in -μA and $C$ is antimony concentration in μg L$^{-1}$) and 0.10–1.0 μg L$^{-1}$ ($I_p = 61.7C$ + 45.8, $R^2$ = 0.9922). The relative standard deviation was 4.0% ($n$ = 5) for a 0.1 μg L$^{-1}$ Sb(III) solution. The detection limit calculated as 3σ from a calibration point at 10 ng L$^{-1}$ of Sb(III) was 2 ng L$^{-1}$ with a deposition time of 30 s. The calibration curve obtained with a shorter deposition time of 10 s was linear over

the concentration range of 1.0─12.0 µg L$^{-1}$ ($I_p$ = 6.53$C$ + 9.95, R$^2$ = 0.9974), and the 3σ detection limit was 0.08 µg L$^{-1}$.

For the OSWCSV determination of Sb(V), the linear calibration curves were obtained over the concentration ranges of 0.01─0.20 µg L$^{-1}$ ($I_p$ = 309$C$ + 9.47, R$^2$ = 0.9911) and 0.20─0.80 µg L$^{-1}$ ($I_p$ = 66.0$C$ + 57.1, R$^2$ = 0.9968) with 30 s deposition time. The relative standard deviation was 3.0% ($n$ = 5) for a 0.1 µg L$^{-1}$ Sb(V) solution, and the detection limit was 2 ng L$^{-1}$ for a deposition time of 30 s. The calibration curve obtained with a shorter deposition time of 10 s was linear over the concentration of 1.0─7.0 µg L$^{-1}$ ($I_p$ = 10.4$C$ - 6.30, R$^2$ = 0.9938), and the 3σ detection limit was 0.018 µg L$^{-1}$.

*Interference*

The effect of foreign ions on the OSWCSV determination of 1.0 µg L$^{-1}$ Sb(III)/Sb(V) by the proposed method was investigated at a range of concentrations. The tolerance levels to be determined within ±10% error were 0.5 µg L$^{-1}$ for Cu(II) and 1.0 µg L$^{-1}$ for Fe(III), respectively. The following metal ions were tolerable up to 10-fold amounts excess over Sb(III) or Sb(V) for Pb(II) and Cd(II), 20-fold amounts for Hg(II) and Sn(II), 50-fold amounts for Mn(II), Se(IV) and As(III), and a 70-fold amount for V(V), respectively. No interference was also observed for Na(I), Mg(II), Al(III), Ca(II), Zn(II), Co(II), Ni(II), Mo(VI), and W(VI) at 1000-fold amounts. Such anions as NO$_3^-$ and SO$_4^{2-}$ up to 1.0 mg L$^{-1}$, H$_2$PO$_4^-$ 0.5 mg L$^{-1}$ and NH$_4^+$ 0.1 mg L$^{-1}$ had no influence. Organic compounds such as L-cysteine, sodium dodecylbenzene sulfonate, polyethyleneglycol mono-*p*-nonylpheny ether, and EDTA were tolerable at 0.1 mg L$^{-1}$, 0.3 mg L$^{-1}$,

1 mg L$^{-1}$, and 10 mg L$^{-1}$, respectively. The presence of most organic compounds should be minimized as much as possible for real sample analysis. The determination of Sb(III)/Sb(V) up to 10.0 μg L$^{-1}$ showed no interference from each other at any concentration ratios between 10 and 0.1.

*Sample Analysis*

At established experimental parameters, the proposed OSWCSV method was adapted for real sample analyses by using standard addition and background subtraction method. The accuracy of this proposed method was assessed by recovery tests. The spiked river water samples (Kuzuryu, Fukui, Japan) were analyzed because antimony was not found in the investigated real samples. Good recovery (96─103%) was observed when compared with spiked concentration (see Table 1). Fig. 6 shows typical OSWCSV curves obtained for the determination of Sb(V) in a coastal sea water sample (Mikuni, Fukui, Japan). Table 1 also summarizes the experimental results for speciation analysis of Sb(III) and Sb(V) in the sea water on four replicate analyses, which were calculated to be 0.049±0.001 μg L$^{-1}$ and 0.199±0.003 μg L$^{-1}$, respectively. The speciation analysis of natural water samples was achieved with satisfactory results.

## Conclusions

The proposed OSWCSV method enables antimony speciation at the trace levels by utilizing the co-deposition of Bi(III) and Sb(III)/Sb(V) onto the edge-plane pyrolytic graphite substrate. The

detection limit was estimated to be 2 ng $L^{-1}$ Sb(III)/Sb(V) based on the $3\sigma$ method with 30 s deposition time. The coastal seawater and river water samples could be analyzed with good results.

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Table 1 Results for recovery test and speciation analysis of Sb(III) and Sb(V) in real water samples

| Samples | Spiked Sb(III) in samples ($\mu$g L$^{-1}$) | Sb(III) found ($\mu$g L$^{-1}$) | Spiked Sb(V) in samples ($\mu$g L$^{-1}$) | Sb(V) found ($\mu$g L$^{-1}$) |
|---|---|---|---|---|
| River water | 4.000 | 4.037±0.008[b] | 4.000 | 4.095±0.004[b] |
| | 4.000 | 4.033±0.006[b] | 0.400 | 0.492±0.005[a] |
| | 0.400 | 0.432±0.01[a] | 4.000 | 4.089±0.004[b] |
| Seawater | 0.400 | 0.449 ± 0.001[a] | -- | -- |
| | -- | -- | 0 | 0.199 ± 0.003[a] |
| | -- | -- | 4.000 | 4.201 ± 0.02[b] |

[a] 30 s deposition time.

[b] 10 s deposition time.

**Figure captions**

**Fig. 1.** Cyclic voltammograms. (1) 0.1 mol L$^{-1}$ HCl; (2) (1) + 100 μg L$^{-1}$ Bi(III); (3) (2) +1.0 μg L$^{-1}$ Sb(III); deposition potential: −400 mV; deposition time: 30 s; scan rate: 100 mV s$^{-1}$.

**Fig. 2.** OSWCSV curves. (1) 0.1 mol L$^{-1}$ HCl + 10 g L$^{-1}$ KCl; (2) (1) + 100 μg L$^{-1}$ Bi(III); (3) (2) +10 ng L$^{-1}$ Sb(III); (4) (2) +50 ng L$^{-1}$ Sb(III); (5) (2) +0.1 μg L$^{-1}$ Sb(III); deposition potential: −500 mV; deposition time: 30 s.

**Fig. 3.** Effect of hydrochloric acid concentration on OSWCSV peak current. Sb(III): 0.1 mol L$^{-1}$ HCl + 100 μg L$^{-1}$ Bi(III) + 1.0 μg L$^{-1}$ Sb(III); Sb(V): 0.6 mol L$^{-1}$ HCl + 100 μg L$^{-1}$ Bi(III) + 1.0 μg L$^{-1}$ Sb(V). Deposition potential: −400 mV; deposition time: 30 s.

**Fig. 4.** Effect of Bi(III) concentration on OSWCSV peak current. Sb(III): 0.1 mol L$^{-1}$ HCl + 10 g L$^{-1}$ KCl + 1.0 μg L$^{-1}$ Sb(III); Sb(V): 0.6 mol L$^{-1}$ HCl + 10 g L$^{-1}$ KCl + 1.0 μg L$^{-1}$ Sb(V). Deposition potential: -400 mV; deposition time: 30 s.

**Fig.5.** Effect of deposition potential on OSWCSV peak current. Sb(III): 0.1 mol L$^{-1}$ HCl + 10 g L$^{-1}$ KCl + 100 μg L$^{-1}$ Bi(III) + 1.0 μg L$^{-1}$ Sb(III); Sb(V): 0.6 mol L$^{-1}$ HCl + 10 g L$^{-1}$ KCl + 100 μg L$^{-1}$ Bi(III) + 1.0 μg L$^{-1}$ Sb(V). Deposition time: 30 s.

**Fig. 6.** OSWCSV curves for the determination of Sb(V) in a sea water sample. (1) 0.6 mol L$^{-1}$ HCl + 10 g L$^{-1}$ KCl; (2) (1) + 100 μg L$^{-1}$ Bi(III); (3) (2) + seawater; (4-6) (3) + successive addition of 40 ng L$^{-1}$ Sb(V). Deposition potential: −500 mV; deposition time: 30 s.
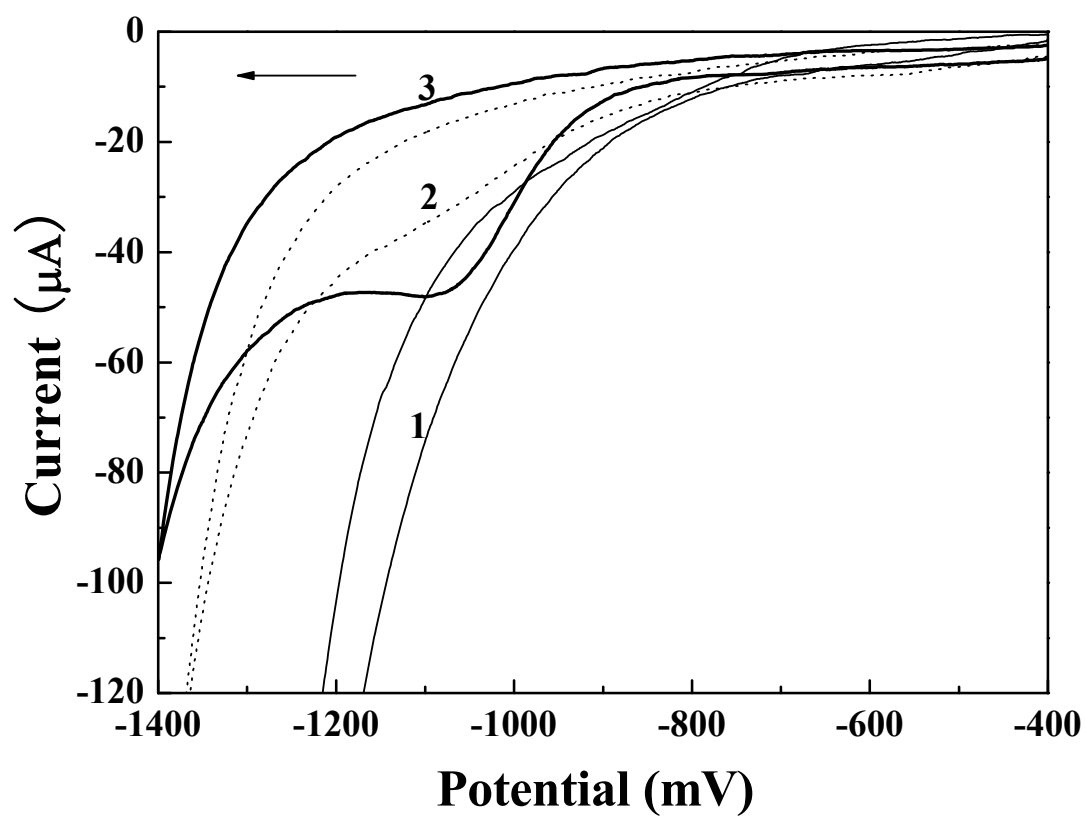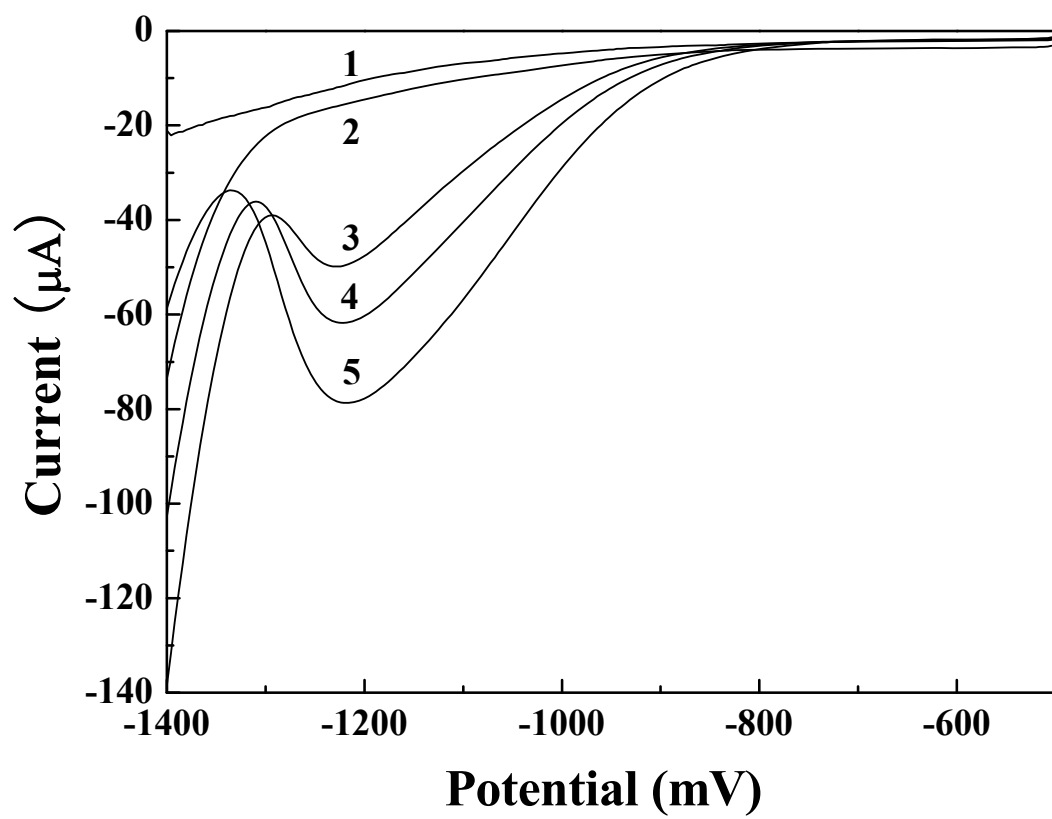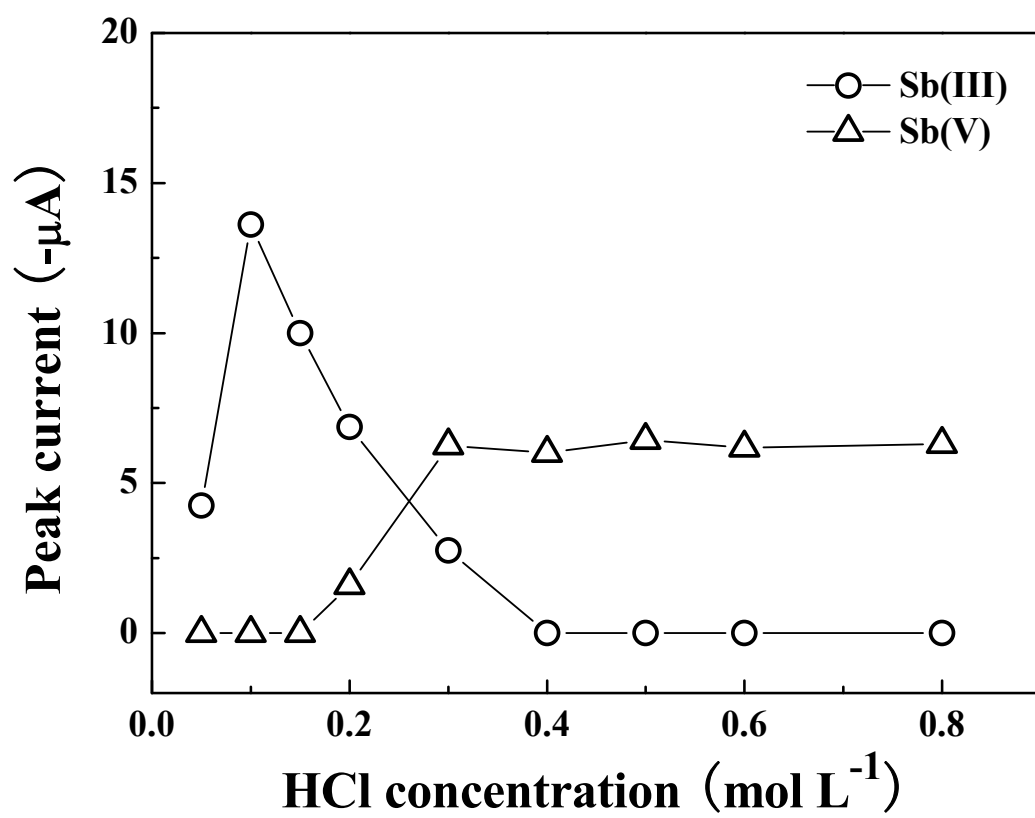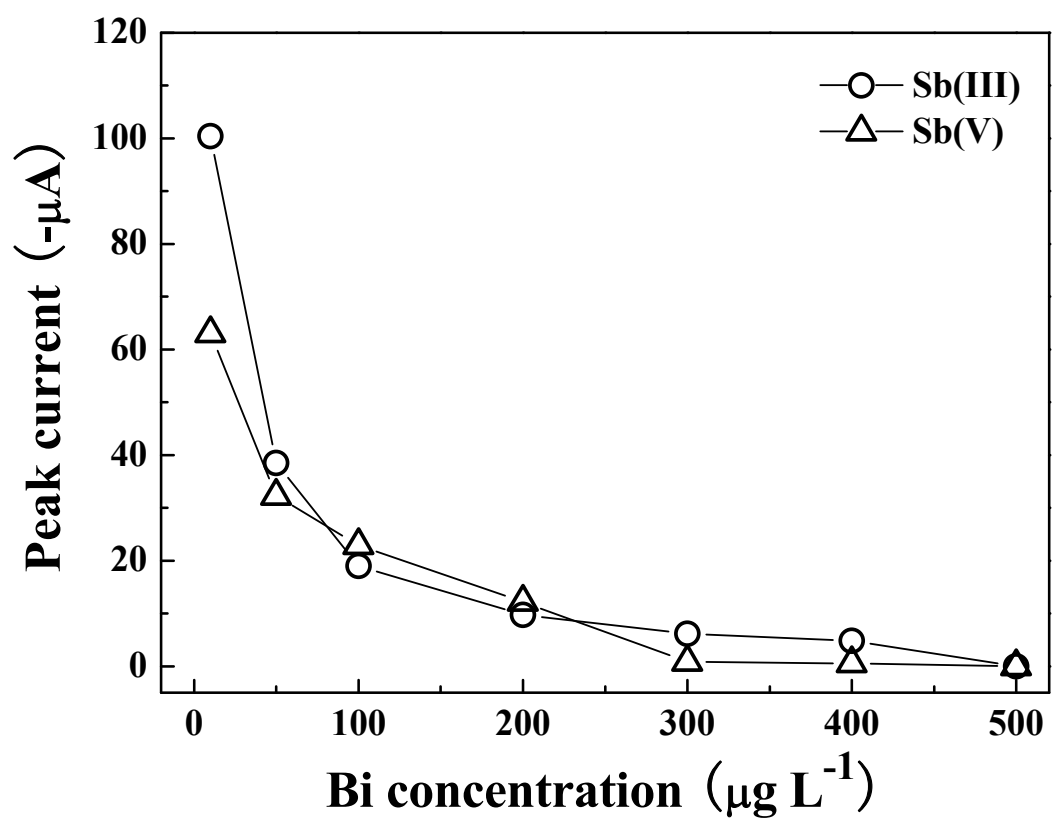
Fig. 1

Fig. 2

Fig. 3

Fig. 4

Fig. 5

Fig. 6