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Determination of trace arsenic(III) by differential-pulse anodic stripping voltammetry with *in-situ* plated bismuth-film electrode

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A sensitive and precise method is presented for the determination of As(III) by differential-pulse anodic stripping voltammetry (DPASV). This method is based on the co-deposition of As(III) with Bi(III) onto a basal-plane type of pyrolytic graphite substrate at an accumulation step. DPASV studies indicate that the As was oxidized with anodic scans to give an enhanced anodic peak at about 500 mV vs. Ag/AgCl. Addition of L-cysteine to test solutions was found to be highly effective to obtain reproducible oxidation responses due to $\text{As(0)} \rightarrow \text{As(III)}$. A linear relationship between the anodic stripping peak-current ratio ($I_{\text{As}}/I_{\text{Bi}}$) and As(III) concentration was observed over the concentration range from $0.0200 \mu\text{g L}^{-1}$ to $18.0 \mu\text{g L}^{-1}$. The detection limit of As(III) was $0.012 \mu\text{g L}^{-1}$ at a deposition time of 180 s. The relative standard deviation was 2.85% ($n=8$) at a concentration of $10.0 \mu\text{g L}^{-1}$ As(III). Analytical results demonstrate that the determination of As(III) in real water samples is possible by the proposed method.

Keywords: As(III) determination; *In-situ* plating; Bismuth; Basal-plane pyrolytic graphite; DPASV

1. Introduction

Arsenic is known to be one of the most toxic elements and has serious effects on human health, plants, and animals [1–4]. In particular, As(III) is considered to be more toxic than arsenic(V) species [1, 3–5]. Analytical methods for highly sensitive and reliable determination of As(III) in water samples such as drinking-water, groundwater, wastewater, food and biological tissue, etc., are therefore required for studies on geological survey, human health, environmental protection, as well as water preservation [4–7]. To date, a considerable number of analytical methods have been developed for As(III) determination in the concentration range of ppb or ppt levels, which include atomic adsorption spectrometry (HG-AAS, GFAAS), inductively coupled plasma (ICP), electrochemical methods like polarography, anodic stripping

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voltammetry (ASV), cathodic stripping voltammetry (CSV), and differential-pulse anodic stripping voltammetry (DPASV) [4–7].

Among the electroanalytical techniques, ASV and CSV modes have been proved to be powerful approaches for trace arsenic speciation of natural waters because of a high sensitivity, ease of operation, and low cost of instrumentations [4, 7]. Many kinds of working electrode materials have been reported for their applications and successful operation, which include mercury, platinum, gold, carbon substrates, and boron-doped diamond for electroanalysis of arsenic species [4, 8–12]. Mercury, mercury-film electrodes, and hanging mercury-drop electrodes have widely employed for arsenic species determination by various stripping modes. Recently, much more care has been needed for the analytical use of mercury due to toxicity and environmental pollution. To date, numerous gold electrodes have been used as the most suitable for arsenic determination based on ASV and CSV measurements. However, gold electrodes often give irregular responses for analytes arising from past history, pretreatment, and oxide film formations [4, 11, 13]. Compton *et al.* compared several types of carbon substrate modified by gold particles for As(III) detection [14]. Their studies showed that micron gold arrays in carbon-paste electrodes produced satisfactory results, except for a relatively poor detection limit of about $5(\pm 2) \times 10^{-9} \text{ mol L}^{-1}$ ($0.375 \pm 0.15 \mu\text{g L}^{-1}$ As(III)).

In the last few years, a novel bismuth film electrode has been recognized as an alternative to mercury electrodes; a bismuth electrode is environmentally friendly and has partial insensitivity to dissolved oxygen [15, 16]. DPASV methods using a bismuth film electrode have been reported for the determination of Pb(II), Cd(II), and Zn(II) which are oxidized at relatively negative potential regions [17]. Due to the limitations of available positive potential regions, generally, the bismuth electrode has not been applied to the DPASV determination of metal ions whose redox potentials are more positive than that of bismuth itself. Interestingly, Wang *et al.* used an internal standard method to obtain a reliable response for the detection of Pb(II) by DPASV combined with a bismuth film electrode [18].

In this present article, a DPASV method is described for the determination of traces As(III) in aqueous medium with *in-situ* deposited bismuth on the basal plane graphite electrode. The sensitivity and precision of analysis have been greatly improved by taking into account of the As/Bi peak ratio for calibration. Results of bismuth-film electrode preparation and properties, dynamic range of the calibration curve, detection limit, reproducibility, interferences from foreign ions, and sample analyses are discussed.

2. Experimental

All electrochemical measurements were carried out using a BAS CV-50W voltammetric analyser (Bioanalytical Systems, West Lafayette, In). Unless specified otherwise, the settings for DPASV measurements were as follows: 50 mV pulse amplitude; 17 ms sample width; 50 ms pulse width; 200 ms pulse period; -200 mV initial potential; 600 mV final potential. A basal-plane pyrolytic graphite disk electrode (3.0 mm diameter, BAS) as a working electrode substrate, a platinum wire counter electrode and Ag/AgCl (3 M KCl) as a reference electrode from BAS were used.

All solutions were prepared with deionized and distilled water. The As(III) stock solutions were prepared by diluting the standard solution (1000 mg L^{-1} , Wako Pure Chemical Industries, Tokyo) with 5.0 mol L^{-1} of HCl and were stored in a refrigerator at 4°C . Fresh solutions of L-cysteine as a reducing agent to avoid As(III) oxidation were prepared daily just before the experiments.

The recommended procedures for the DPASV determination of As(III) were established as follows. An aliquot of the standard As(III) solution was placed into a 10-mL electrochemical glass cell. Fixed amounts of 5.0 mol L^{-1} HCl, L-cysteine and Bi(III) were successively added to the test solution, and the equilibrium concentrations were made up to 5.0 mol L^{-1} , 10 mg L^{-1} , and 0.1 g L^{-1} , respectively. Before DPASV measurements, the sample solution was purged by nitrogen for 600 s. In a stirred solution, As(III) was initially reduced to the As onto the bismuth film electrode at a deposition potential of -400 mV and a deposition time of 180 s. After a quiet time of 10 s, the As was oxidized anodically at a scan rate of 20 mV s^{-1} .

After each anodic scan, a special cleaning and reactivation procedure for the working electrode substrate was conducted by applying a potential of 600 mV for 180 s in another cell containing 3.0 mol L^{-1} HCl prior to subsequent experiments. In this study, the peak current ratio of As/Bi ($I_{\text{As}}/I_{\text{Bi}}$) was calculated as the arsenic response for enhancing the precision of analysis [18].

Model samples were prepared from the standard solutions. For analysis of As(III) in natural water, sea water, and river water, samples were taken at Mikuni and Kuzuryu (Fukui, Japan), respectively. The samples were filtered and then acidified with 0.1 mol L^{-1} of HCl just after samplings. Sample analyses were carried out by the standard addition method ($\mu\text{g L}^{-1}$ concentration levels of As(III) solution were successively added to the sample solution). All data were estimated by the background-subtraction method.

3. Results and discussion

3.1 Electrochemical behaviour of arsenic on the bismuth-film graphite electrode

In the absence of As(III) and Bi(III), no peak was observed on the DPASV curve shown in figure 1a (curve 1) as a blank test. Figure 1a (curve 2) illustrates a typical DPASV curve obtained for As(III) by scanning the potential to a positive direction at $20\text{ mV}^{-1}\text{s}^{-1}$, after the As(III) was deposited beforehand at -400 mV onto a bare pyrolytic graphite electrode for 3 min. The anodic peak due to $\text{As}(0) \rightarrow \text{As}(\text{III})$ at 492 mV was greatly enhanced by addition of 2.5 and 10 mg L^{-1} Bi(III), as shown in figure 1a (curves 3 and 4, respectively). The addition of 10 mg L^{-1} of Bi(III) gave a very high and distorted peak at 336 mV (figure 1a, curve 4). It is clear that at the deposition step, Bi(III) assists the arsenic co-deposition with the metal followed by anodic dissolution. The addition of excess amounts of Bi(III), however, partially restricts the arsenic oxidation, which is probably because some 'fusing' alloys or intermetallic compounds between As and Bi was formed on the electrode surface. When L-cysteine was added as a reducing agent, as shown in figure 1a (curve 5), the two anodic peaks appeared at -110 mV and 208 mV , corresponding to bismuth and arsenic oxidation, respectively. Figure 1b shows DPASV curves obtained for $\mu\text{g L}^{-1}$

concentration levels of As(III). No response was observed at about 200 mV for the blank test, as shown in figure 1b (curve 1). With the *in-situ* bismuth film electrode, it was found that the anodic peak current for arsenic was directly proportional to the metal ion concentration at around $\mu\text{g L}^{-1}$ concentration levels, as shown in figure 1b (curves 2, 3, and 4). This indicates that the proposed DPASV method enables determination of traces of As(III) in natural water.

3.2 Experimental parameters

The experimental parameters for the DPASV determination of As(III) were studied under the conditions described in section 2. A standard solution of As(III) was taken to investigate such experimental conditions as HCl concentration, and L-cysteine, deposition potential, and deposition time. Hydrochloric acid was chosen as the best supporting electrolyte because it can provide a well-defined peak for arsenic on the DPASV curve and high sensitivity for the determination of As(III). The effect of HCl concentration on the arsenic peak current was therefore investigated in the range from 2.0 to 6.0 mol L^{-1} , as shown in figure 2. The maximum peak current could be obtained with 5.0 mol L^{-1} HCl. The peak potential shifted to negative directions as HCl concentration increased.

Addition of L-cysteine as a reducing agent was found to make a composite peak split into the two peaks due to oxidation of arsenic and bismuth. The effect of L-cysteine concentration on the arsenic peak current was investigated in the range of 0–0.2 g L^{-1} against 0.50 $\mu\text{g L}^{-1}$ As(III), as shown in figure 3. As L-cysteine concentration was increased, the peak current gradually increased, and the peak potential shifted to negative directions. Furthermore, we observed that the presence of L-cysteine in excess

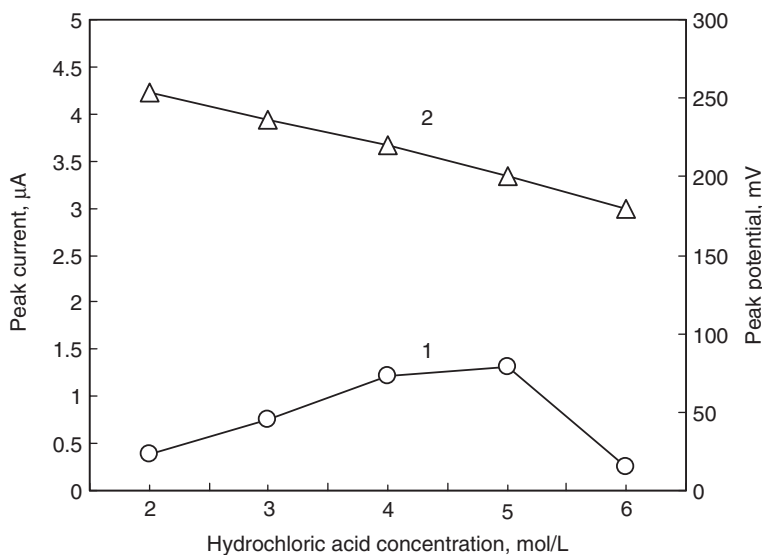


Figure 2. Effect of hydrochloric acid concentration. (1) peak current; (2) peak potential; sample solution: 0.125 mg L^{-1} of As(III) + 5.0 mg L^{-1} of Bi(III) + 0.1 g L^{-1} L-cysteine; deposition potential: -300 mV ; scan rate: 20 mV s^{-1} ; deposition time: 120 s.

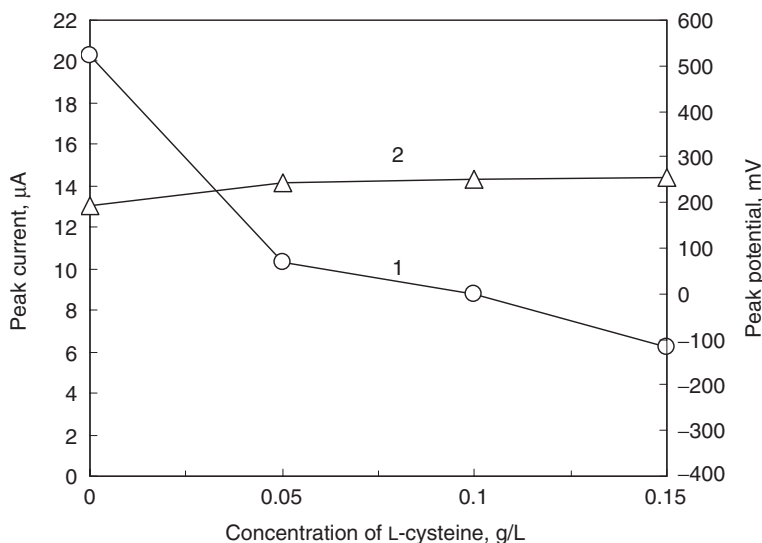


Figure 3. Effect of L-cysteine concentration. (1) peak current; (2) peak potential; sample solution: $0.5 \mu\text{g L}^{-1}$ As(III) + 5.0 mg L^{-1} Bi(III) + 5.0 mol L^{-1} HCl; deposition potential: -300 mV ; deposition time: 300 s; scan rate: 20 mV s^{-1} .

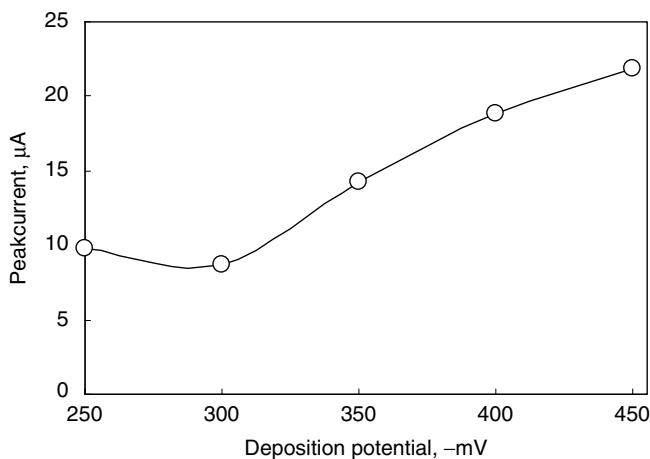


Figure 4. Effect of deposition potential. Sample solution: $10 \mu\text{g L}^{-1}$ of As(III) + 5.0 mg L^{-1} of Bi(III) + 0.1 g L^{-1} of L-cysteine + 5.0 mol L^{-1} of HCl; deposition time: 300 s.

over As(III) should be avoided because the arsenic peak was negligibly small. The addition of 0.1 g L^{-1} of L-cysteine was the most adequate to obtain the reproducible and accurate peak current due to As(III).

The effect of deposition potential on the arsenic peak current for arsenic was investigated in the range of -250 to -450 mV . The results shown in figure 4 indicate that the arsenic peak current gradually increased with decreasing deposition potentials below -300 mV . At potentials lower than -450 mV , the arsenic peak current remained almost constant. The effect of deposition time on the peak current was also investigated in the range of 20–300 s. The results shown in figure 5 indicate that the arsenic peak

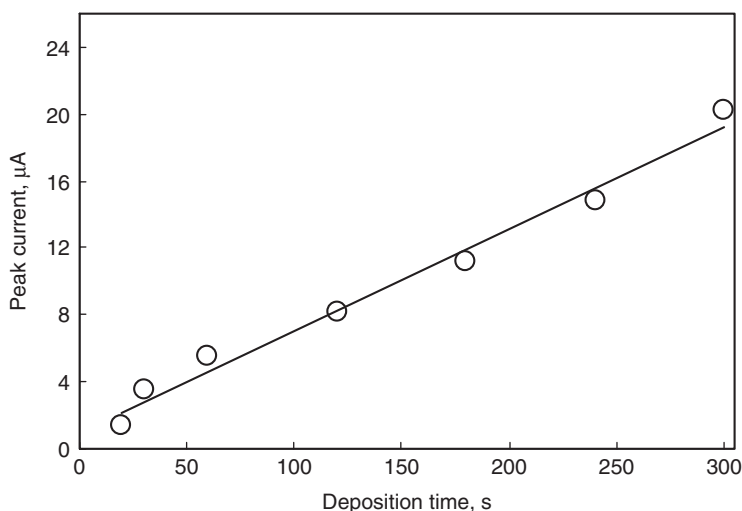


Figure 5. Effect of deposition time. Sample solution: $10\ \mu\text{g L}^{-1}$ of As(III) + $5.0\ \text{mg L}^{-1}$ of Bi(III) + $0.1\ \text{g L}^{-1}$ of L-cysteine + $5.0\ \text{mol L}^{-1}$ of HCl; deposition time: 300 s.

current increased linearly as the deposition time increased. In this study, we chose a deposition potential of $-400\ \text{mV}$ and a deposition time of 180 s, respectively.

3.3 Reproducibility

The reproducibility of arsenic peak current was tested for the DPASV determination at $10.0\ \mu\text{g L}^{-1}$ of As(III). Figure 6 shows the arsenic stripping currents plotted against the number of successive measurements, and a relative standard deviation (RSD, %) of 15.5% ($n=8$) was obtained. Since the bismuth anodic peak appears at around $-250\ \text{mV}$, the so-called internal standard method was used for the DPASV determination of As(III) in this study. The ratio of arsenic/bismuth stripping currents ($I_{\text{As}}/I_{\text{Bi}}$) was adopted as the arsenic response, and the RSD value was greatly lowered to 2.85% ($n=8$). Obviously, the internal standard method was very convenient to reduce and compensate the variations and interferences from physical parameters, solution changes, and operation effects. This is mainly because both arsenic and bismuth stripping currents are subject to the same effect under the experimental conditions.

3.4 Calibration curve and detection limit

The calibration curve for the determination of As(III) by the proposed DPASV method was constructed under the recommended conditions. The linear relationship between the ratio of two anodic peak currents and As(III) concentration was obtained over the concentration range from 0.0200 to $18.0\ \mu\text{g L}^{-1}$ with correlation coefficients of $0.994 \sim 0.980$. A limit of detection (LOD) was calculated as 3σ : $\text{LOD} = 3\sigma/b$ where σ is the standard deviation of the y -coordinates from the calibration curve and b the slope of the curve. The detection limit based on the 3σ method was $0.012\ \mu\text{g L}^{-1}$ at

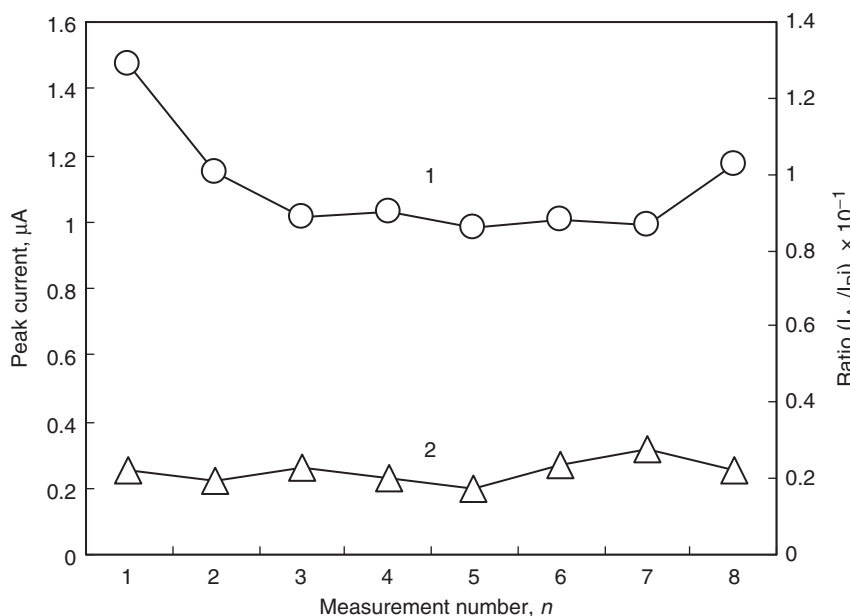


Figure 6. Reproducibility test. (1): I_{As} (μA); (2): current ratio (I_{As}/I_{Bi}); sample solution: $10.0 \mu g L^{-1}$ of As(III) + $5.0 mg L^{-1}$ of Bi(III) + $0.1 g L^{-1}$ of L-cysteine + $5.0 mol L^{-1}$ of HCl; deposition potential: $-400 mV$; deposition time: 180 s.

a deposition time of 180 s. This LOD value is apparently lower than or comparable with those obtained with similar methodologies ranging from 0.05 to $0.1 \mu g L^{-1}$ [12, 19–21].

3.5 Interference

The effect of foreign ions on the DPASV determination of $10.0 \mu g L^{-1}$ As(III) by the proposed method was investigated at a range of concentrations. Table 1 summarizes the tolerance amounts that $10 \mu g L^{-1}$ of As(III) could be determined within $\pm 5\%$ error. The tolerance levels were $2.5 \mu g L^{-1}$, $1.0 \mu g L^{-1}$, $0.5 \mu g L^{-1}$, $0.1 \mu g L^{-1}$, and $0.1 \mu g L^{-1}$ for Cu(II), Se(IV), Sb(III), Hg(II), and Pb(II), respectively. In particular, Cu(II), Hg(II), and Se(IV) are known to cause the formation of binary intermetallic compounds. The redox potentials of Sb(III) and Pb(II) are similar to that of Bi(III). Metal ions such as V(V) and Fe(III) were tolerable at amounts up to $10 \mu g L^{-1}$ and $1.0 mg L^{-1}$, respectively. There was no interference from Na(I), Mg(II), Ca(II), K(I), Al(III), Cd(II), Co(II), Ni(II), Mn(II), Zn(II), Sn(II), W(VI), or Mo(VI) at 1000-fold amounts relative to As(III). Anions such as NO_3^- , $H_3PO_4^-$, and SO_4^{2-} had no effect at $10 mg L^{-1}$, $7.0 mg L^{-1}$, and $40 mg L^{-1}$, respectively.

3.6 Sample analyses

The standard addition method was used for recovery test and real sample analyses. Good recovery percentages above 99% were obtained with model samples involving As(III) at concentrations of $0.02 \mu g L^{-1}$ and $0.08 \mu g L^{-1}$, as can be seen from table 2.

Table 1. Effect of foreign ions for determination of 10.0 µg L⁻¹ As(III).

Foreign inorganic ions	Tolerance level (µg L ⁻¹)
Cu(II)	2.5
Se(IV), Fe(III)	1.0
Sb(III)	0.5
Hg(II), Pb(II)	0.1
V(V)	10
Na(I), Mg(II), Ca(II), K(I)	10 ⁴
Al(III), Cd(II), Co(II), Ni(II), Mn(II), Zn(II), Sn(II), W(VI), Mo(VI)	1.6 × 10 ³
NH ₄ ⁺	10 ⁴
NO ₃ ⁻	7.0 × 10 ³
H ₂ PO ₄ ⁻	4.0 × 10 ⁴
SO ₄ ²⁻	

Table 2. Analytical results for water samples.

Samples			Experimental results (µg L ⁻¹)	Reference values (µg L ⁻¹)	Correlation coefficient (r ²)
As(III)	Recovery test	Model 1	0.0203	0.0200	0.9993
		Model 2	0.0785	0.0800	0.9913
	Sea water (Mikuni, Fukui, Japan)		0.0448 ± 0.010 ^a	0.02 ~ 0.05 [9]	0.9771
	River water (Kuzuryu, Fukui, Japan)		0.0730 ± 0.009 ^a	—	0.9906

^aAnalysed on four replicate determinations; blank value: 0.0178.

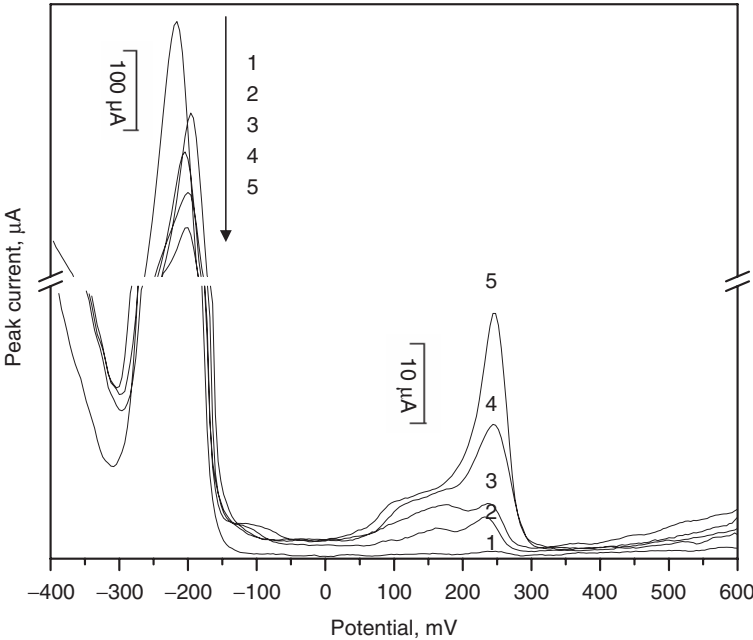


Figure 7. DPASV curves for the determination of As(III) in sea water. (1) Blank test (0.1 g L⁻¹ of L-cysteine + 5.0 mol L⁻¹ of HCl + 5.0 mg L⁻¹ of Bi(III)); (2) sea water; (3) sea water + 10 ng L⁻¹ of As(III); (4) sea water + 50 ng L⁻¹ of As(III); (5) sea water + 100 ng L⁻¹ of As(III); deposition potential: -400 mV; deposition time: 180 s.

Coastal sea water (Mikuni, Fukui, Japan) and river water (Kuzuryu, Fukui, Japan) samples were analysed on four replicate determinations to evaluate the present method. The typical DPASV curves obtained for As(III) determination are shown in figure 7. The analytical results were 0.0448 ± 0.010 and 0.0730 ± 0.009 for the sea water [8] and river water samples, respectively (see table 2). The proposed method is so sensitive and reliable that traces of As(III) in natural samples can be determined with good results.

4. Conclusions

Traces of As(III) can be determined by the proposed DPASV method using the bismuth co-deposition onto a basal-plane pyrolytic graphite substrate. The bismuth film electrode is formed *in situ* with arsenic, and its anodic peak gives enhanced sensitivity. The linear relationship between the ratio of the two peak currents and As(III) concentration holds in the range from 0.0200 to $18.0 \mu\text{g L}^{-1}$. The detection limit was estimated to be $0.012 \mu\text{g L}^{-1}$ As(III) based on the 3σ method. The results of interference studies indicate that the presence of Cu(II), Sb(III), Hg(II), and Se(IV) has positive effects on the arsenic stripping peak. Therefore, the four metal ions should be minimized below the tolerable concentrations on trace As(III) determination. Coastal sea-water and river-water samples can be analysed with satisfactory results.

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