Investigation of Copper(II) Interference on the Anodic Stripping Voltammetry of Lead(II) and Cadmium(II) at Bismuth Film Electrode

5 AUTHORS, INCLUDING:

Liang Wang
University of Newcastle
13 PUBLICATIONS   30 CITATIONS

SEE PROFILE

Zuliang Chen
University of South Australia
218 PUBLICATIONS   3,479 CITATIONS

SEE PROFILE

Megharaj Mallavarapu
University of Newcastle
324 PUBLICATIONS   4,509 CITATIONS

SEE PROFILE

Ravi Naidu
University of South Australia
595 PUBLICATIONS   11,437 CITATIONS

SEE PROFILE

Investigation of Copper(II) Interference on the Anodic Stripping Voltammetry of Lead(II) and Cadmium(II) at Bismuth Film Electrode

Die Yang,[*][a] *Liang Wang,*[a] *Zuliang Chen,*[a] *Mallavarapu Megharaj,*[a, b] *Ravi Naidu*[a, b]

[a] Centre for Environmental Risk Assessment and Remediation, University of South Australia, Mawson Lakes, SA 5095, Australia
[b] CRC for Contamination Assessment and Remediation of Environment, Mawson Lakes Boulevard, Mawson Lakes, SA 5095, Australia
*e-mail: Daisy.Yang@unisa.edu.au

Abstract
The bismuth-coated electrode is known to be prone to errors caused by copper(II). This study investigates copper(II) interference at bismuth film electrode for the detection of lead(II) and cadmium(II). It was conducted using glassy carbon electrode, while the bismuth film was plated in situ simultaneously with the target metal ions at −1200 mV. Copper(II) presented in solution significantly reduced the sensitivity of the electrode, for example there was an approximately 70% and 90% decrease in peak signals for lead(II) and cadmium(II), respectively, at a 10-fold molar excess of copper(II). The decrease in sensitivity was ascribed to the competition between copper and bismuth or the metal ions for surface active sites. Scanning electron microscopy (SEM) and energy dispersive X-ray (EDX) analysis suggested a large decrease in the amount of bismuth nanoparticles formed on the electrode surface in the presence of copper(II) occurred, validating the competition between copper and bismuth ions for surface active sites. Recovery of the stripping signal of lead(II) and cadmium(II) was obtained by adding ferrocyanide ion to the solution. Finally, the proposed method was successfully applied to determine lead(II) and cadmium(II) in water samples and the method was validated by ICP-MS technique.

Keywords: Bismuth film electrode, Copper interference, Ferrocyanide

1 Introduction

Anodic stripping voltammetry (ASV) has emerged as a favored method for detecting heavy metal ions at trace level, due to its low cost, high sensitivity and simple operation. Conventionally mercury, in the forms of hanging mercury-drop electrode and mercury-film electrode, has been used to measure heavy metal ions [1–5]. However, the toxicity of mercury and mercury salt and the risks associated with disposal have become a major concern when using this method [6]. In the search for more environmentally friendly electrodes, bismuth film electrodes (BiFEs) have received much attention during the last 10 years and studies have indicated that, in many cases, bismuth can replace mercury in ASV as a new material with less toxicity [7–13]. The attractive properties of bismuth electrode also include simple preparation, high sensitivity, well-defined and separated stripping signals, and insensitivity to dissolved oxygen (which is an essential property for on-site monitoring) [13,14]. The advantageous stripping performance of bismuth is based on its ability to form a "fused" alloy with other metals [15], in a way comparable to the ability of mercury to form amalgams [16].

Most of the earlier work on bismuth film electrodes was concerned with insights into their fundamental studies [7,10,14,15]. However, its application to the environment, food, and clinical analysis has proven to be limited [9]. A limitation of bismuth film electrodes for most samples routinely analysed is the interference caused by copper(II) [15,17]. As copper(II) is reduced at more positive potential than bismuth(III), it causes a severe decrease in the deposited bismuth on the electrode surface and thus infuences the deposition of trace metal ions at the bismuth film. On the other hand, copper is commonly found in enviromental samples and it poses problem for enviromental analysis of heavy metals.

The potential interferences from copper(II) could largely be eliminated by using a masking reagent [18–22]. Various masking reagents have been studied in order to effectively eliminate copper(II) interference without having an impact on metal responses. Of the different masking reagents, ferrocyanide was the most effective for removing copper(II) without affecting the target ions [20,21]. A sub-millimolar concentration of ferrocyanide

masked relatively high concentration of copper(II) effectively. The remarkable masking effect of ferrocyanide was attributed to the formation of the less soluble copper complex in the solution. The addition of ferrocyanide in the sample solution has been used previously with mercury-film [19] and bismuth-film electrodes [18] for releasing copper interference. Many other strategies have been proposed to remove copper(II) interference, including adding a third element (e.g. Ga(III)) [23,24], or hydrogen peroxide [25], or the selective removal of copper by ion-exchange [26]. However, most of these studies are focused on eliminating copper(II) interference at bismuth film electrodes, while the voltammetric behaviour of copper(II) and the competitive relationship between copper and bismuth or metal ions have seldom been studied [15,18]. An initial attempt has been reported in Wang's work [15] where overlapping Cu(II) and Bi(III) stripping peaks were observed and as the Cu(II) concentration increased, the magnitude of the Bi(III) stripping peaks decreased. This finding was postulated to result from the competition between the deposited copper and bismuth for the electrode substrate (glassy carbon). Accordingly, this caused the sensitivity of bismuth film electrode to decrease with reference to heavy metals detection [15]. Another possible contribution to the decrease in this sensitivity may result from the possible formation of an intermetallic compound between copper and metal ions (e.g. Zn or Pb) [15,18,21]. From these initial studies, it is clear that copper interference at bismuth film electrode is still obscure and a systematic study is required.

In this paper, we investigated the effect of copper interference on lead(II) and cadmium(II) at a bismuth film electrode by probing the copper-bismuth and copper-metal ions relationships, which may affect the electrode's voltammetric performance to achieve high sensitivity and stability. SEM and EDX analysis were performed to reveal the growth of bismuth over the surface of the substrate electrode in the presence of copper ions. The bismuth(III) concentration which may influence the voltammetric performance of electrode in the presence of copper(II) was investigated. An effective complexing reagent – ferrocyanide – was used to circumvent the detrimental effect of copper(II) on the stripping response of lead(II) and cadmium(II) at the bismuth film electrode. The proposed method was tested to analyse standard reference materials and water samples.

2 Experimental

2.1 Chemicals and Solutions

All chemicals were of analytical grade, obtained from Sigma-Aldrich and used without further purification unless stated otherwise. Ultra-pure water of pH of 5.6 ± 0.1, with a resistivity of $18.2\ M\Omega\ cm$, obtained from Milli-Q Elga System, was used in all experiments. The bismuth, copper, lead and cadmium solutions were prepared from 1000 mg/L atomic absorption standard solutions after ap-

propriate dilution with 1 % (Pb and Cd) or 5 % (Bi) nitric acid (w/v). Potassium ferrocyanide was obtained from BDH Ltd. 0.1 M acetate buffer (pH 4.5) was used as supporting electrolyte. All glassware was soaked in 2 % nitric acid for at least 24 h, rinsed with copious amounts of deionised water and then rinsed twice with Milli-Q water before use.

2.2 Apparatus

All voltammetric measurements were performed with an electrochemical analyzer (Model BAS-100B), in connection with a personal computer. A glassy carbon electrode (GCE) (disc diameter of 3 mm, BAS) was used as the working electrode, with the Ag/AgCl (3 M NaCl) and Pt wire as the reference electrode and counter electrode, respectively. Stirring was carried out using a magnetic stirrer. No deaeration of the solutions was employed at any stage of this study. To validate the stripping voltammetric method, ICP-MS technique was employed, using Bruker 820-MS instrument. Scanning electron micrographs were obtained with a FEI Quanta 450 FEG ESEM with an EDAX Apollo X SDD EDX detector, using an accelerating voltage of 20 kV.

2.3 Voltammetric Procedure

Unless otherwise indicated the general procedure for the voltammetric measurement was as follows. The three electrodes were immersed into an electrochemical cell, containing 0.1 M acetate buffer (pH 4.5) and appropriate bismuth(III). Standard solution of lead(II) and cadmium(II) was added into the cell and the mixed solution was stirred at the potential of $-1200\ mV$ for 2 min. Following the preconcentration step, the stirring was stopped. After 10 s of quiet time, square wave anodic stripping voltammetry (SWASV) was performed by potential scan from $-1200\ mV$ to $+300\ mV$ with frequency 25 Hz, potential amplitude 40 mV and potential step of 4 mV. To obtain reproducible results the electrode was regenerated by holding the electrode at $+300\ mV$ for 40 s prior to the next cycle.

2.4 Sample Preparation

Tap water was obtained in our laboratory and other water samples were collected from the River Torrens (site 1) and Barossa Valley (site 2) (South Australia), respectively. These samples were filtered through a 0.45 μm filter and stored after acidification to pH 2–3 with conc. nitric acid. Generally, 10 cm^3 of the water sample was mixed with an equal volume of 0.2 M acetate buffer (pH 4.5) and then analysed using the optimized SWASV method.

3 Results and Discussion

3.1 Response of the Bismuth Film Electrode in the Presence of Copper(II)

As Figure 1A shows, copper(II) has a significant influence on the stripping response of lead(II) and cadmium(II) at bismuth film electrode. In the absence of copper, well-defined lead(II) and cadmium(II) peaks were observed (as shown in Figure 1A, curve a). However, the presence of copper(II) (10-fold molar excess) severely reduced the stripping signals of lead(II) and cadmium(II) on bismuth film electrode (Figure 1A, curve b). At 10-fold molar excess of copper(II), the peak of lead(II) was still measurable, but the voltammetric response of cadmium(II) was
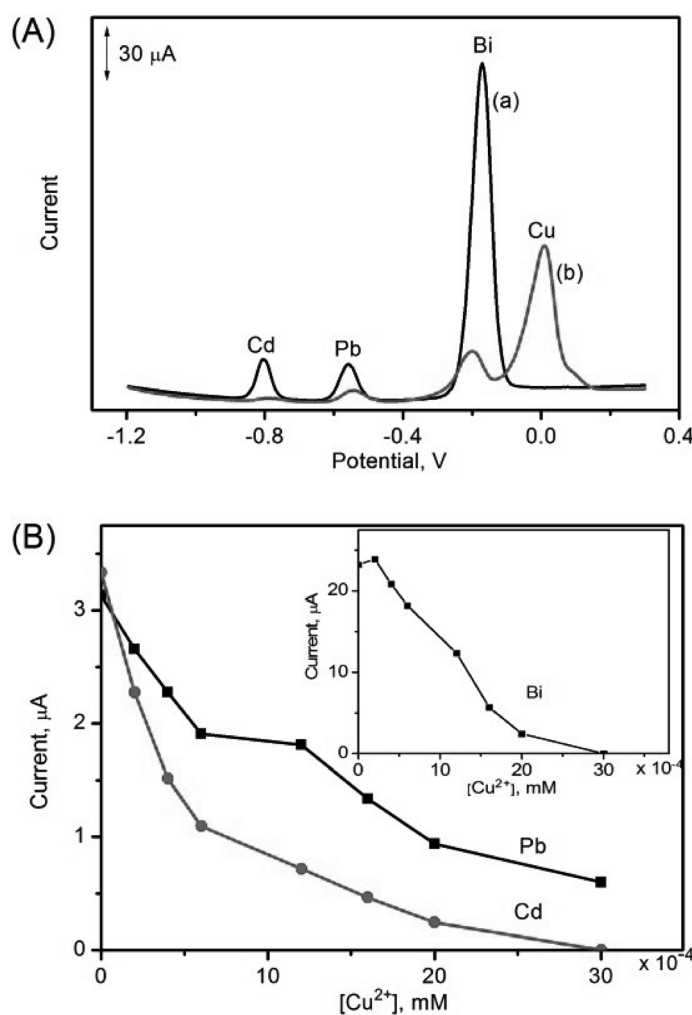

Fig. 1. (A) Stripping voltammograms of 2×10^{-4} mM lead(II) and cadmium(II) at bismuth-coated glassy carbon electrode (a) in the absence of copper(II), (b) in the presence of 10-fold molar excess copper(II). (B) Variation of 2×10^{-4} mM lead(II) and cadmium(II) responses in the presence of different concentrations of copper(II). Supporting electrolyte: 0.1 M acetate buffer (pH 4.5); deposition potential: -1.2 V; deposition time: 120 s; quiet time; 10 s; frequency: 25 Hz; potential amplitude: 40 mV; potential step: 4 mV; Bi(III) concentration: 2.4×10^{-3} mM.

hardly observed. It is also important to note that the bismuth(III) peak decreased significantly. Such effects have been previously observed on bismuth film electrodes [15,27].

Figure 1B shows the effect of copper(II) on the stripping response of lead(II) and cadmium(II) at bismuth film electrode when copper(II) concentrations increased. The interference of copper ions appeared at even low concentration (equal amount to lead(II) and cadmium(II) concentration) and the stripping responses of both lead(II) and cadmium(II) decreased very rapidly as the concentration of copper(II) increased, especially for cadmium. Furthermore, there was a rapid decrease of the bismuth peak (Figure 1B, Inset). At 15-fold molar excess of copper(II) (30×10^{-4} mM), cadmium(II) and bismuth(III) were not detectable, while lead(II) was still measurable.

It is known that lead(II) and cadmium(II) do not compete with bismuth(III) for the active surface sites on the electrode. Instead they form binary alloys with bismuth, which is responsible for the high sensitivity of the bismuth film electrode [15,27]. The decrease of bismuth(III) peak was obviously caused by the existence of copper(II). Since copper(II) is reduced at a more positive potential than bismuth(III), the suppression of the bismuth(III) peak is most probably due to the competition between electrodeposited bismuth and copper for surface active sites on the electrode. Accordingly, this results in the decrease of the lead(II) and cadmium(II) stripping peaks. Other potential contributions to the decrease in the lead(II) and cadmium(II) stripping responses by copper(II) include: firstly, lead, cadmium and copper ions competing for active bismuth sites; and secondly, the formation of an intermetallic compound between copper and metal ions [15,21].

To further validate the above hypothesis, the copper-bismuth and copper-lead and/or cadmium competition relationship for surface active sites was investigated. The competition between bismuth and copper ions for surface active sites (glassy carbon) was investigated at increasing concentrations of copper(II) with bismuth concentration fixed at 2.4×10^{-3} mM (the figure is not shown here). The results showed that as the copper(II) concentration increased, the stripping peaks of bismuth declined, indicating competition between the two species for surface sites. This is consistent with previous studies [15]. Figure 2A shows the voltammetric response of lead(II) and cadmium(II) on an ex situ formed bismuth film electrode with the presence and absence of copper(II), respectively. In the absence of copper(II), well defined and sharp peaks were observed for lead(II) and cadmium(II) (Figure 2A, curve a) while the presence of two-fold molar excess of copper(II) severely decreased the metals' stripping peaks (Figure 2A, curve b). This confirmed the competition between copper, lead and cadmium for active bismuth sites. Figure 2B and 2C depict the voltammetric response of lead(II) or cadmium(II) in the absence (curve a) and the presence (curve b) of the same level of copper(II) at
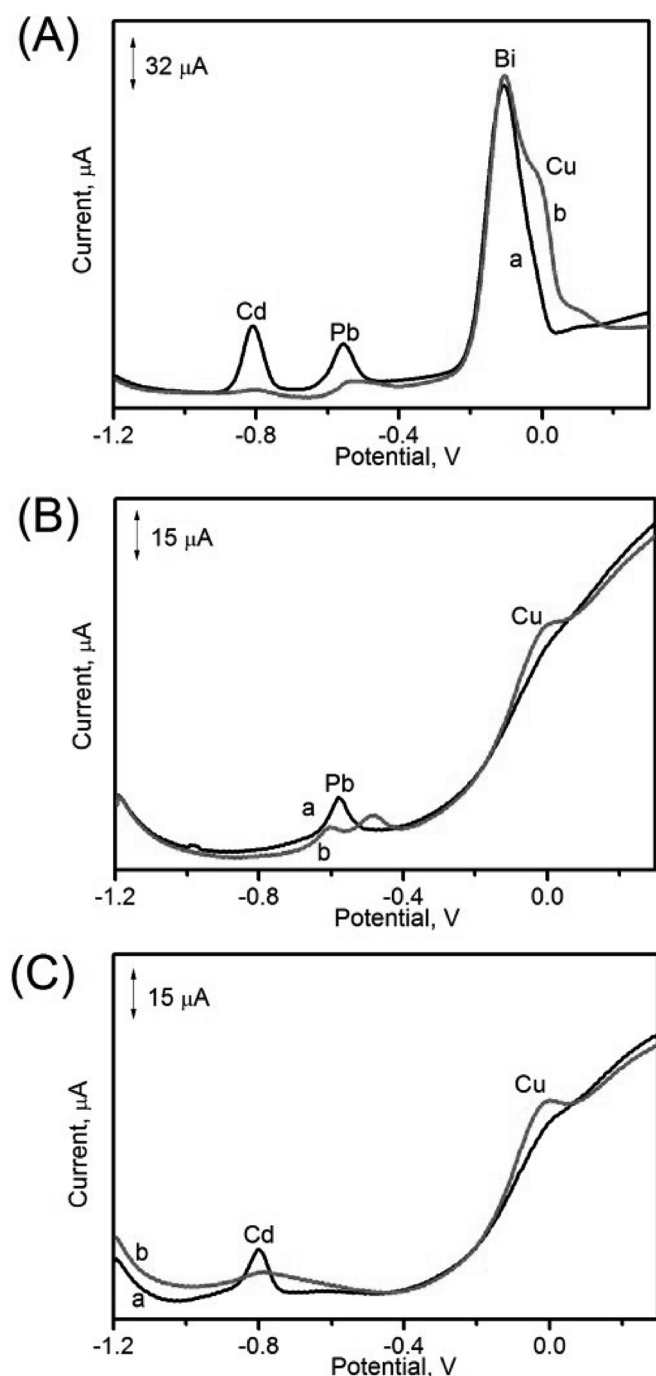
Fig. 2. (A) Effect of copper(II) on the stripping response of 2×10^{-4} mM lead(II) and cadmium(II) at an ex situ formed bismuth film electrode: (a) in the absence of copper(II), (b) in the presence of 2-fold molar excess copper(II). (Ex situ BiFE was prepared by electrodeposition from a buffer solution containing 0.05 mM bismuth(III) for 5 min.) (B) and (C) Effect of copper(II) on the stripping response of 2×10^{-4} mM lead(II) or cadmium(II) at bare glassy carbon electrode (a) in the absence of copper(II) and (b) in the presence of the same level of copper(II), respectively. Other experimental conditions are the same as those in Figure 1.

a bare glassy carbon electrode, respectively. It is clearly evident that the presence of copper ions significantly de-

creased the peaks of both lead(II) and cadmium(II), suggesting the competition between copper and metal ions for the surface sites (glassy carbon) (the high background observed around Cu(II) signal at glassy carbon electrode in Figure 2B and 2C was most likely due to the oxidation reaction of the surface functional groups induced by the electrode's surface pretreatment [28]). Furthermore, a split (dual) lead peak at more positive potential (see Figure 2B) occurred. The double peak appears to reflect the stripping of lead in different forms (probably due to the formation of an intermetallic compound between copper and lead) as suggested by previous studies [18,21]. However, this was not observed at bismuth film electrodes.

SEM can take useful insights into the growth patterns of the bismuth film on the glassy carbon electrode with or without the existence of copper(II). Different surface morphologies were observed at the glassy carbon electrodes. The SEM image of the bismuth film coated glassy carbon electrode (Figure 3A, left) indicated a highly porous, three-dimensional dendritic-like network with bismuth unevenly distributed on the electrode surface (isolated locations with higher thickness of bismuth appeared as brighter patches). A closer look revealed that the bismuth nanoparticles were highly agglomerated (see Figure 3A, right). After being co-deposited with copper, the bismuth-coated glassy carbon electrode revealed a very different surface which is relatively homogeneous and smooth with no obvious structures observed (Figure 3B, left). This suggests a large decrease in the number of the bismuth nanoparticles that had formed on the electrode surface. A higher magnification of the image revealed that the surface was not entirely smooth but instead consisted of some small brighter particles randomly grown onto the grey particles composited matrix (as shown in Figure 3B, right). Apparently, copper has a profound effect upon the nucleation and growth of the bismuth deposit and, hence, upon its structural features. EDX elemental analysis of the images indicated a considerable amount of Cu (relative to Bi) co-existed with Bi on the bismuth/copper co-deposited glassy carbon electrode (as listed in Table 1). The findings strengthened the argument that competition for surface sites occurs when bismuth and copper are co-deposited on the electrode surface.

3.2 Influence of Bismuth(III) Concentration

Figure 4 shows the dependence of the stripping currents on the concentration ratio of bismuth to copper ions in the solution. As the Bi(III) concentration increased from the standard level (2.4×10^{-3} mM) and the copper(II) concentration was fixed at 2×10^{-3} mM, the peak currents of lead(II) and cadmium(II) underwent a slight increase at low concentration ($\leq 3.8 \times 10^{-3}$ mM), while a further increase in the bismuth(III) concentration did not significantly alter the peak currents. Generally, the concentration of Bi(III) in the solution controls the thickness of the bismuth film. Increasing the concentration of Bi(III) en-
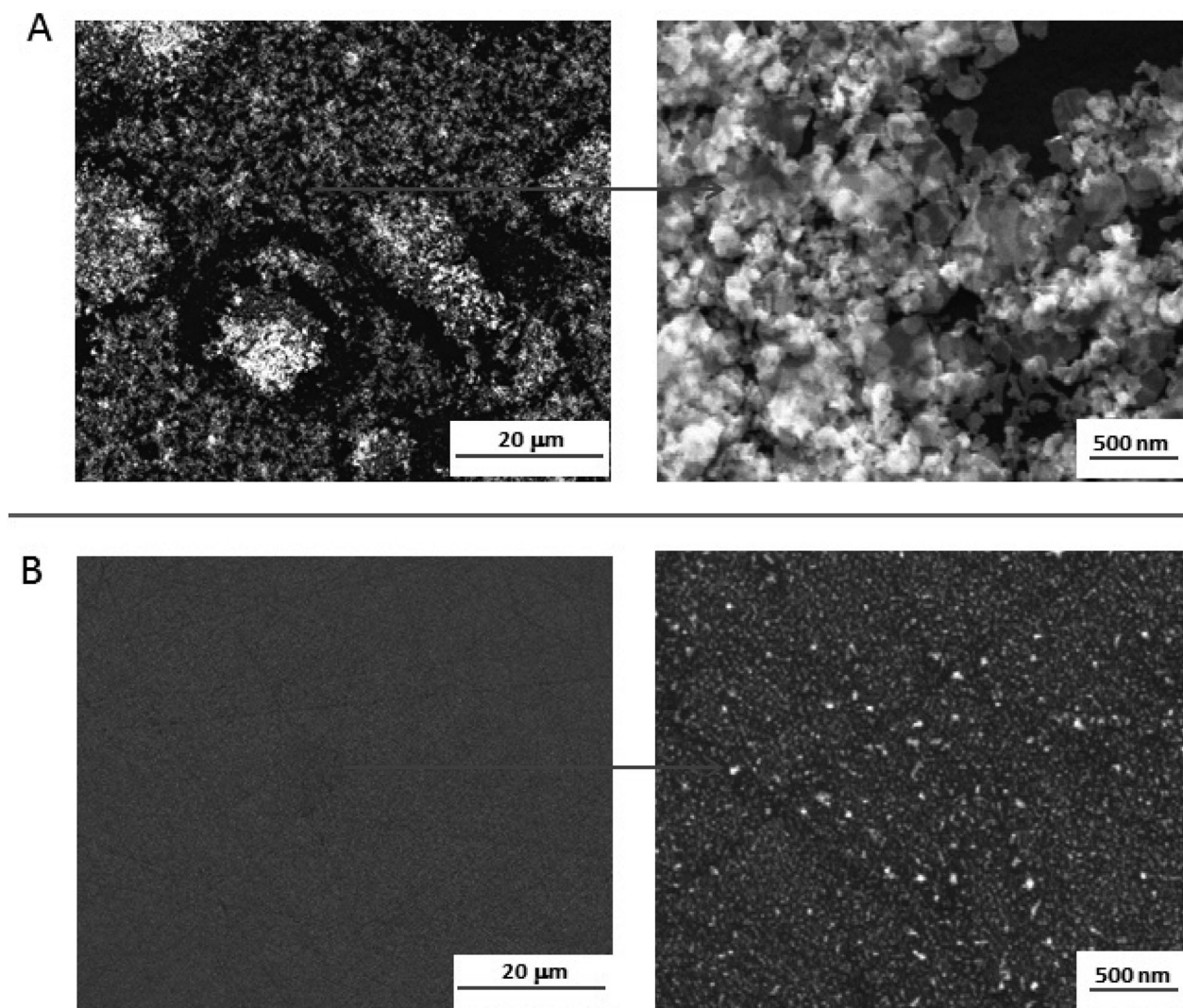
Fig. 3.   SEM images of (A) bismuth-coated glassy carbon electrode; and (B) bismuth/copper co-deposited glassy carbon electrode at lower (left) and higher (right) magnification. Deposition was carried out for 1000s at -1.2 V with stirring, from 0.1 M acetate buffer (pH 4.5). The concentration of bismuth(III) and copper(II) are 0.05 and 0.02 mM, respectively.

hances the competition ability of bismuth ion for unoccupied active surface sites and it is expected that with a large excess amount of Bi(III), the effect of copper(II) interference consequently diminishes. However, this effect was not observed on the BiFE. It is possible that the glassy carbon electrode surface was poisoned with copper(II) before significant deposition of bismuth(III), considering that copper(II) is oxidised at a more positive potential than bismuth(III). This can be verified on a bismuth(III) "pretreated" glassy carbon electrode surface. However, our results showed that for an ex situ BiFE where bismuth ions were deposited on the electrode surface before being immersed into the solution containing target metal ions and copper(II), the impact of interference from copper(II) prevailed due to the competition between copper and metal ions as discussed in Section 3.1 (see Figure 2A). Therefore, the increase in the bismuth(III) concentration had little effect on the strip-

ping response of lead(II) and cadmium(II) at BiFE in the presence of copper(II).

3.3 Reducing the Copper Interference

To successfully circumvent the detrimental impact of copper(II) on the voltammetric determination of lead(II) and cadmium(II) at bismuth film electrode, ferrocyanide was used. The result of adding ferrocyanide is demonstrated in Figure 5. As mentioned previously, the presence of copper(II) severely suppressed the stripping response of lead(II) and cadmium(II) at bismuth film electrode (see Figure 1). Figure 5A clearly shows that after adding 1×10^{-2} mM of ferrocyanide to the solution containing 2×10^{-4} mM of lead(II), cadmium(II) and 2×10^{-3} mM of copper(II), the suppressed stripping peaks almost returned to their original levels with no effect on the target metal ion peaks (Figure 5A, curve c). Also note is the
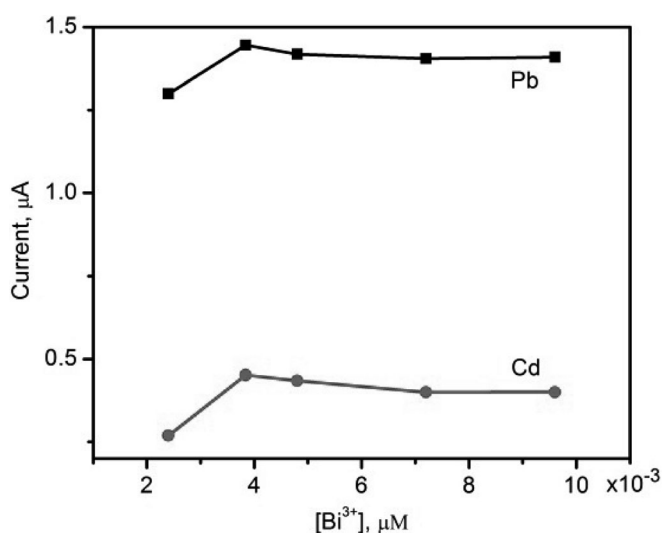
Fig. 4. Effects of the concentration of bismuth(III) on the stripping response of 2×10^{-4} mM lead(II) and cadmium(II) in the presence of 10-fold molar excess copper(II) at the bismuth-coated glassy carbon electrode. Other experimental conditions are the same as those in Figure 1.

suppression of copper peak and the recovery of bismuth peak after adding ferrocyanide to the solution, reflecting the effective masking effect of ferrocyanide ion on the copper(II). The concentration of added ferrocyanide ion was determined by studying the effect of copper(II) (2×10^{-3} mM) on 2×10^{-4} mM of lead(II) and cadmium(II), as shown in Figure 5B. Experiments shown that a concentration of 6×10^{-3} mM of ferrocyanide was proved to be sufficient in alleviating the interference of copper(II), with lead and cadmium peaks recovered at 100 % and 80 % of their original levels, respectively. Additionally, concentrations of ferrocyanide higher than 6×10^{-3} mM slightly reduced the stripping peaks of lead(II) and cadmium(II). Higher concentrations of ferrocyanide (concentrations at 1 mM and 10 mM) were added to the solution to examine their effect on the stripping peaks. Results show that a large excess amount of ferrocyanide has no further effect on the stripping peaks. This finding agrees with previous studies [19–20]. Note that ferrocyanide has to be added to the test solution prior to the accumulation step as copper reduced at a more positive potential than bismuth during this step [21].

The reproducibility of the proposed method for reducing copper interference was evaluated in this study, revealing a relative standard deviation (RSD) < 5 % ($n = 9$) for 2×10^{-4} mM lead(II) and cadmium(II) with a concentration of 6×10^{-3} mM of ferrocyanide added to the solution containing 2×10^{-3} mM copper(II).

3.4 Application to Real Samples

Since interference from copper(II) can undermine the utility of bismuth film electrodes for analyzing lead(II) and cadmium(II) in certain matrices when copper is pres-
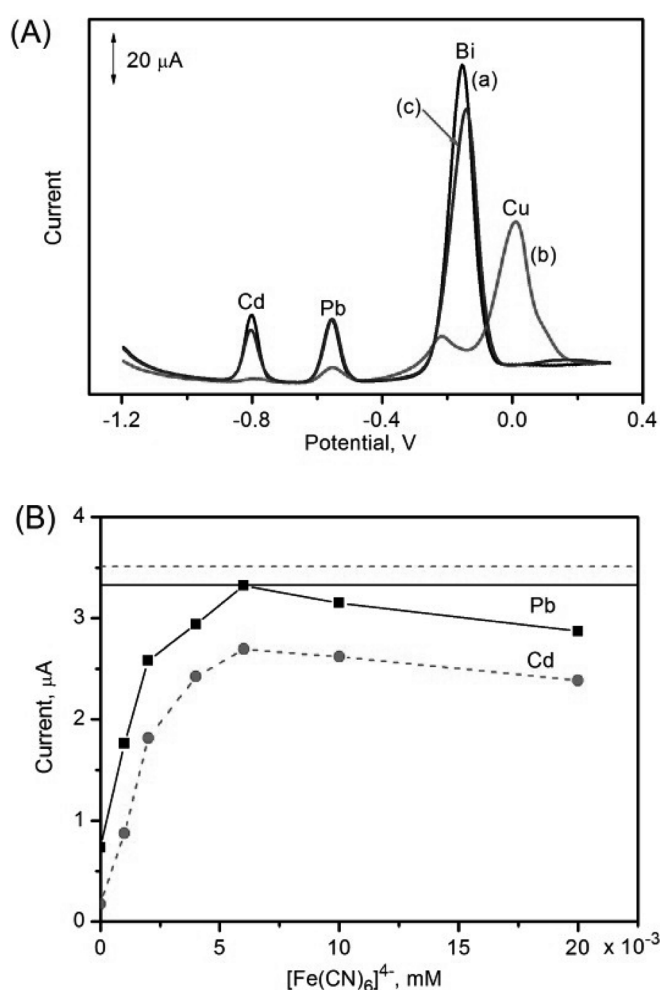

Fig. 5. (A) Effect of ferrocyanide on the stripping response of 2×10^{-4} mM lead(II) and cadmium(II) in the presence of copper(II): (a) in the absence of copper(II), (b) in the presence of 10-fold molar excess copper(II), and (c) 10-fold molar excess copper(II) + 1×10^{-2} mM ferrocyanide. (B) Variation of 2×10^{-4} mM lead(II) and cadmium(II) responses in the presence of copper(II) (2×10^{-3} mM) as a function of the ferrocyanide concentration. Straight lines represent the original levels of lead(II) (solid line) and cadmium(II) (dotted line) peaks, respectively, in the absence of copper(II). Other experimental conditions are the same as those in Figure 1.

ent at a significant level, the practicability of the method described above for alleviating this scenario was examined using water samples. Representative stripping voltammograms for the determination of lead(II) and cadmium(II) are illustrated in Figure 6 for tap water. As shown in Figure 6 (curve a), without the addition of ferrocyanide a large copper peak appeared that suppressed the bismuth peak and all other metal peaks, suggesting that copper exists in large excess amount in the solution. If 1×10^{-2} mM ferrocyanide was added to the solution before the voltammetry measurements, a prominent Bi peak appeared together with the appearance of an apparent Pb peak (Figure 6, curves b–d). A significant decrease in the copper peak occurred, reflecting the remarkable masking

Table 1. EDX results of SEM images in Figure 3.

Wt %	C	O	Bi	Cu
Bismuth-coated glassy carbon electrode	94.72	4.45	0.83	–
Bismuth/copper co-deposited glassy carbon electrode	95.87	3.25	0.65	0.23

Table 2. Results for the determination of lead(II) and cadmium(II) in real water samples by SWASV when adding ferrocyanide, and ICP-MS technique. N. D.: not detected; SWASV: square wave anodic stripping voltammetry.

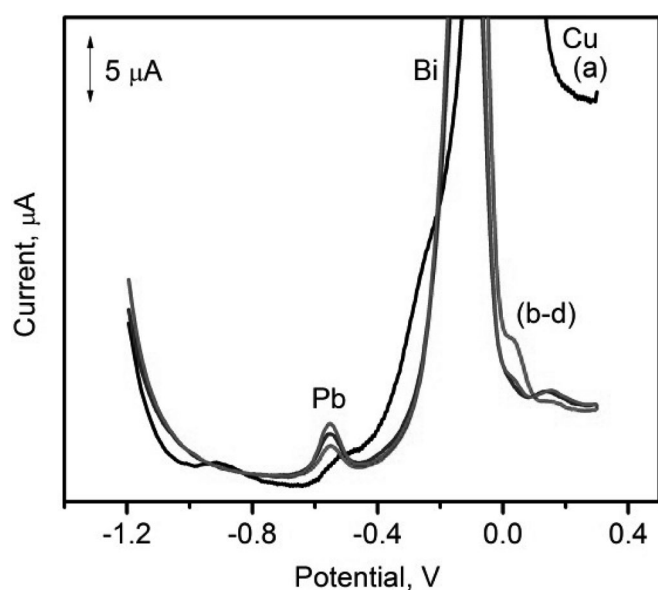| Sample	Lead(II) (µg/L)		Cadmium(II) (µg/L)		Copper(II) (µg/L)
	SWASV	ICP-MS	SWASV	ICP-MS	ICP-MS
Tap water	4.24 ± 0.36	5.54 ± 0.84	N. D.	0.068 ± 0.003	509 ± 17
Site 1	1.46 ± 0.07	1.58 ± 0.06	N. D.	0.022 ± 0.002	17.7 ± 0.2
Site 2	7.86 ± 0.08	8.55 ± 0.23	N. D.	0.059 ± 0.003	18.6 ± 0.2

Fig. 6. Stripping voltammograms showing the benefit of adding ferrocyanide for eliminating copper interference on the determination of lead(II) and cadmium(II) in tap water at bismuth-coated glassy carbon electrode, (a) no ferrocyanide added; and (b–d) ferrocyanide added, from below: no added Pb(II) and two standard additions of 1×10^{-5} mM Pb(II) each. Other experimental conditions are the same as those in Figure 1.

effect of ferrocyanide to copper interference. Table 2 show the results obtained for several water samples when using the proposed method. The concentration data obtained from this table, closer to the reference values obtained with ICP-MS methods, illustrate the benefits of using the copper-removal method for analyzing data on bismuth film electrodes.

4 Conclusions

This study demonstrated that the presence of significant amounts of copper(II) in water samples severely suppressed the stripping responses of lead(II) and cadmium(II) at bismuth film electrodes. The suppression of the lead and cadmium peaks caused by copper is mainly due to competition between copper and bismuth or metal ions for surface active sites on the electrode. Since copper is widely abundant in the natural environment, the interference caused by copper may severely limit the application of bismuth film electrodes when analyzing water sample. Hence, a remarkable recovery of the lead(II) and cadmium(II) stripping signal in the large excess amount of copper was achieved by adding ferrocyanide ion into the test solutions. In addtion, the concentration data obtained was validated by ICP-MS results, illustrating the benefit of using the proposed method for sample analysis at bismuth film electrodes. These findings and our improved understanding of this scenario should facilitate the effective application of bismuth-based electrodes on the electroanalysis of trace heavy metals.

References

[1] W. Lund, M. Salberg, *Anal. Chim. Acta* **1975**, *76*, 131.
[2] M. J. Pinchin, J. Newham, *Anal. Chim. Acta* **1977**, *90*, 91.
[3] S. Daniele, M.-A. Baldo, P. Ugo, G.-A. Mazzocchin, *Anal. Chim. Acta* **1989**, *219*, 9.
[4] E. Fischer, C. M. G. van den Berg, *Anal. Chim. Acta* **1999**, *385*, 273.
[5] M. Oliveira, A. Saczk, L. Okumura, A. Fernandes, M. Moraes, N. Stradiotto, *Anal. Bioanal. Chem.* **2004**, *380*, 135.
[6] A. Economou, P. R. Fielden, *Analyst* **2003**, *128*, 205.
[7] S. B. Hočevar, B. Ogorevc, J. Wang, B. Pihlar, *Electroanalysis* **2002**, *14*, 1707.
[8] G. Kefala, A. Economou, A. Voulgaropoulos, M. Sofoniou, *Talanta* **2003**, *61*, 603.
[9] A. Economou, *TrAC – Trends Anal. Chem.* **2005**, *24*, 334.
[10] R. Pauliukaitė, C. M. A. Brett, *Electroanalysis* **2005**, *17*, 1354.
[11] J. Wang, *Electroanalysis* **2005**, *17*, 1341.
[12] S. Legeai, O. Vittori, *Anal. Chim. Acta* **2006**, *560*, 184.

[13] I. Švancara, C. Prior, S. B. Hočevar, J. Wang, *Electroanalysis* **2010**, *22*, 1405.

[14] J. Wang, J. Lu, S. B. Hocevar, P. A. M. Farias, B. Ogorevc, *Anal. Chem.* **2000**, *72*, 3218.

[15] J. Wang, J. Lu, Ü. A. Kirgöz, S. B. Hocevar, B. Ogorevc, *Anal. Chim. Acta* **2001**, *434*, 29.

[16] K. E. Toghill, G. G. Wildgoose, A. Moshar, C. Mulcahy, R. G. Compton, *Electroanalysis* **2008**, *20*, 1731.

[17] H. Xu, L. Zeng, D. Huang, Y. Xian, L. Jin, *Food Chem.* **2008**, *109*, 834.

[18] R. O. Kadara, I. E. Tothill, *Talanta* **2005**, *66*, 1089.

[19] K. Crowley, J. Cassidy, *Electroanalysis* **2002**, *14*, 1077.

[20] C. Kokkinos, A. Economou, I. Raptis, C. E. Efstathiou, *Electrochim. Acta* **2008**, *53*, 5294.

[21] B. Liu, L. Lu, M. Wang, Y. Zi, *Electroanalysis* **2008**, *20*, 2363.

[22] K. C. Honeychurch, J. P. Hart, D. C. Cowell, *Anal. Chim. Acta* **2001**, *431*, 89.

[23] C. Prior, C. E. Lenehan, G. S. Walker, *Anal. Chim. Acta* **2007**, *598*, 65.

[24] G. Kefala, A. Economou, *Anal. Chim. Acta* **2006**, *576*, 283.

[25] W. F. Pacheco, E. M. Miguel, G. V. Ramos, C. E. Cardoso, P. A. M. Farias, R. Q. Aucélio, *Anal. Chim. Acta* **2008**, *625*, 22.

[26] R. R. Dalangin, H. Gunasingham, *Analyst* **1994**, *119*, 2187.

[27] G. H. Hwang, W. K. Han, J. S. Park, S. G. Kang, *Talanta* **2008**, *76*, 301.

[28] G. Ilangovan, K. Chandrasekara Pillai, *J. Solid State Electrochem.* **1999**, *3*, 357.