Talanta 84 (2011) 696–701

Contents lists available at ScienceDirect

Talanta

journal homepage: www.elsevier.com/locate/talanta

Disposable Nafion-modified micro-fabricated bismuth-film sensors for voltammetric stripping analysis of trace metals in the presence of surfactants

Christos Kokkinos, Anastasios Economou*

Laboratory of Analytical Chemistry, Department of Chemistry, University of Athens, 157 71 Athens, Greece

ARTICLE INFO

Article history:
Received 18 October 2010
Received in revised form 25 January 2011
Accepted 30 January 2011
Available online 4 February 2011

Keywords:
Nafion-coated bismuth-film electrodes
Stripping voltammetry
Photolithography
Sputtering
Trace metal analysis

ABSTRACT

This work is a study of the analytical utility of Nafion-modified microfabricated bismuth film electrodes (BiFEs) for the determination of Pb(II) and Cd(II) by anodic stripping voltammetry (ASV) in the presence of surfactants. Micro-fabricated BiFEs were prepared by depositing a thin film of bismuth on the surface of a silicon substrate by sputtering while the two-dimensional geometry of the final sensors was defined by photolithography. The BiFEs were further drop-coated with a Nafion film. These devices were applied to the determination of Pb(II) and Cd(II) by square wave ASV (SWASV) in the presence of Triton X-100 (a non-ionic surfactant), cetyltrimethylammonium bromide (CTAB) (a cationic surfactant) and sodium dodecyl sulphate (SDS) (an anionic surfactant). It was found that the presence of Nafion afforded an increase in sensitivity and the tolerance against surfactants but these properties were severely influenced by both the thickness of the Nafion film and the nature of the interfering surfactant. Using a Nafion of 0.4 μm thickness and 120 s of preconcentration, the repeatability (expressed as the % relative standard deviation on the same sensor ($n = 8$)) at the 20 μg l^{-1} level was 3.8% for Pb(II) and 3.1% for Cd(II) and the limits of detection were 0.5 μg l^{-1} for Cd(II) and Pb(II). The sensors were applied to Cd(II) and Pb(II) determination in a certified lake-water sample.

1. Introduction

Bismuth has been shown to be the most promising alternative to mercury for electroanalysis in the negative potential region. Over the last decade, the utility of bismuth electrodes in stripping analysis has been the object of a large body of experimental work [1–4]. It has been demonstrated that bismuth electrodes exhibit electroanalytical properties similar to that of their mercury counterparts with the exception of a narrower anodic polarisation range [1–4]. The main attraction of bismuth as an electrode material is its low toxicity which allows the fabrication of environmentally friendly trace metal sensors. The methods of fabrication of bismuth and bismuth-modified sensors have been previously reviewed [1–4]. The most popular and widely applied type of bismuth electrodes are the bismuth-film electrodes (BiFEs), normally fabricated by electrodepositing a thin film of bismuth on a conductive substrate. Recently, microelectronic thin-film technologies have also been utilized for the formation of the bismuth film [5–7]. This novel method for the fabrication of sputtered BiFEs offers significant advantages over electroplating since no Bi(III) salts are required, a conductive substrate is not necessary and there is increased scope for the fabrication of inexpensive, reproducible and disposable devices at a large scale.

One of the most serious interferences in ASV on BiFEs arise from the presence of various surface-active compounds in many samples that can adsorb on, and deactivate, the electrode surface. Various (usually polymeric) materials have been utilised to form a protective film on the electrode surface. The basis of such protective modification schemes is that bulky surfactant species are not allowed to diffuse through the permselective membrane and, thus, fouling of the electrode surface is avoided. Among the different membranes applied on BiFEs, overoxidized poly-1-naphtylamine [8], poly(sodium 4-styrenesulfonate) [9] and polyaniline [10] have been reported but by far the most widespread coating films are composed of Nafion [11–21]. Nafion is chemically and thermally inert, non-electroactive, conductive and insoluble in water and is, therefore, particularly suitable for the modification of electrodes. In addition to its protective properties, Nafion acts as an ion-exchanger facilitating the preconcentration of cationic target analytes, helps to mechanically stabilise the underlying bismuth layer and, under certain circumstances, can improve the detection sensitivity [15]. So far, in all the reported applications using Nafion in conjunction with electroplated BiFEs, the electrode surface was initially covered with the polymeric membrane followed by electroplating of the bismuth film, usually *in situ*.

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* Corresponding author. Tel.: +30 210 7274298; fax: +30 210 7274750.
E-mail addresses: aeconomo@chem.uoa.gr, aeconomo@chem.chem.auth.gr (A. Economou).

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doi:10.1016/j.talanta.2011.01.077

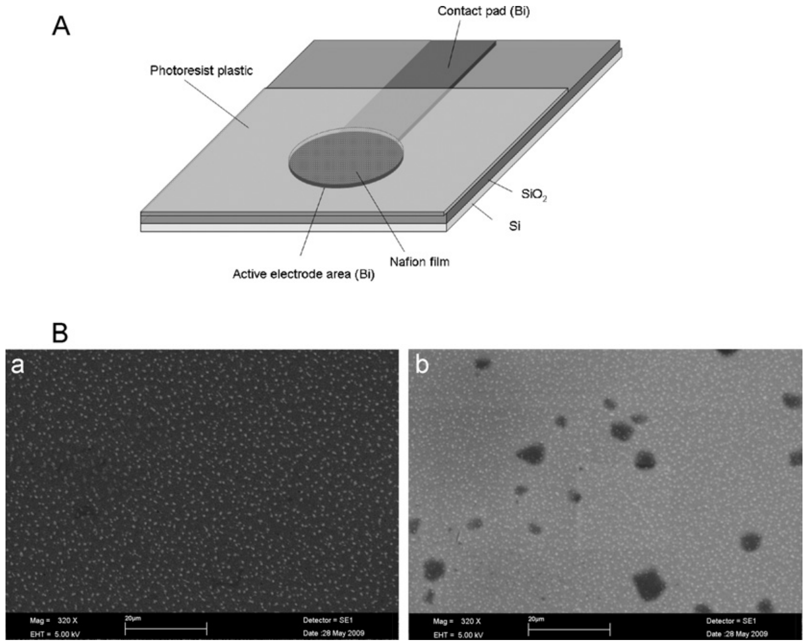

Fig. 1. (A) Schematic diagram of a Nafion-modified sputtered BiFE. (B) SEM images of: (a) a sputtered BiFE and (b) a Nafion-modified sputtered BiFE with thickness 0.8 μm.

This work extends our original work with micro-fabricated BiFEs [5,6] to Nafion-modified sensors. In contrast to electroplated BiFEs, the proposed polymer-modified micro-fabricated BiFEs were prepared by applying a drop of a Nafion solution on the pre-plated bismuth film. The modification of the BiFE surface was studied in terms of the Nafion film thickness, the detection sensitivity and the electrode selectivity in the presence of "model" surfactants. Finally, these sensors were successfully applied to the determination of Cd(II) and Pb(II) in a certified lake water sample.

2. Experimental

2.1. Chemicals and reagents

All the chemicals were of analytical grade. Nafion (5% (w/v) solution in a mixture of water and lower alcohols) was purchased from Aldrich (St. Louis, MO); more dilute Nafion solutions were prepared after dilution with absolute ethanol. Working metal ion solutions were prepared from 1000 mg l^{-1} atomic absorption standard solutions after appropriate dilution with water. The stock supporting electrolyte solution was 0.1 mol l^{-1} acetate buffer (pH 4.5). A 0.01 mol^{-1} solution of $K_4[Fe(CN)_6]$ and 1000 mg l^{-1} solutions of Triton X-100, cetyltrimethylammonium bromide (CTAB) and sodium dodecyl sulphate (SDS) were prepared in water.

2.2. Fabrication of the electrodes

The fabrication of the sputtered BiFE sensor has been described previously [6]. A silicon wafer (3″ in diameter, 500 μm in thickness) was covered with a layer of SiO_2 1080 nm thick by means of wet thermal oxidation. The wafer was spin-coated with a layer of photoresist (1 μm thickness) and the shape of the electrodes was defined by photolithography. Then, bismuth was sputtered on the wafer at a nominal thickness of 400 nm from a Bi target (99.9% purity, Williams Advanced Materials, Buffalo, NY) at a constant current of 7 mA using a thin film deposition system (CV401, Cooke VacuumProducts, South Norwalk, CT). The electrode was patterned by a lift-off process of the polymer. A second photolothographic step allowed to define the sensing area and to isolated it from the grip area. The diameter of the sensing area is 5 mm and the dimensions of the grip area are 5 mm × 4 mm. Electrical contact of the sensor to the potentiostat was made with a crocodile clip.

A 5.0 μl drop of the Nafion solution was placed on the electrode surface and the solvent were left to evaporate at room temperature for 10 min. Then, the polymer membrane was cured with a hot air stream from a heat-gun for 1 min and left to cool to room temperature before being used. A schematic diagram of the Nafion-modified sensor is illustrated in Fig. 1(A).

2.3. Apparatus

A home-made potentiostat was interfaced to a Pentium PC through a multi-function interface card (6025 E PCI, National Instruments, TX). SWASV was carried out by purpose-developed application programmes developed in LabVIEW 7.1. Experiments were carried out in a standard electrochemical cell equipped with a Ag/AgCl reference electrode and a Pt counter electrode.

The surface morphology of the sensors was observed with a scanning electron microscope (SEM) (Leo 440, Carl Zeiss, Germany).

2.4. Experimental procedure

2.4.1. Sample preparation

10.0 ml of the certified lake water sample (TM-23.3, NWRI, Canada) was buffered to pH 4.5 using ammonia solution; this pH was selected for reasons discussed previously [6]. The solution was spiked with ferrocyanide ions to a final concentration of 0.02 mmol l^{-1} and subjected to analysis with no further treatment.

2.4.2. Measurement procedure

The sensor was immersed in the sample solution and electrolytic preconcentration of Pb(II) and Cd(II) was carried out at −1.2 V for a predefined time period in stirred solution. After the accumulation, the stirring was stopped, the solution was allowed to settle for 10 s and the voltammogram was recorded in the square wave (SW) mode (frequency, 50 Hz; step increment, 4 mV; pulse height, 40 mV) from −1.2 to −0.3 V. Then, the electrode was cleaned from traces of remaining target metals for 20 s at −0.3 V.

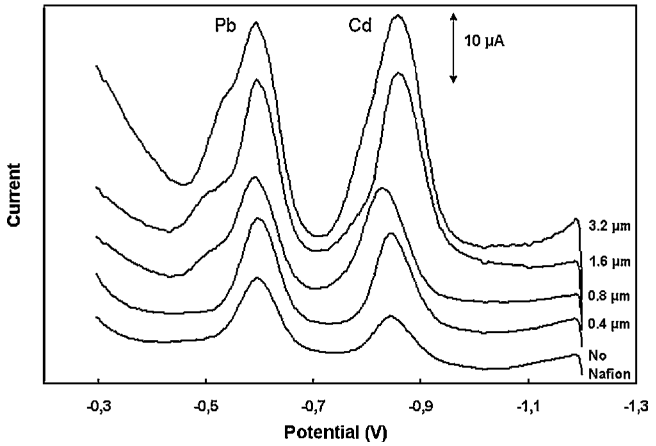

Fig. 2. SWASV responses in a solution containing 20 μg l^{-1} of Pb(II) and Cd(II) on a sputtered BiFE without Nafion modification and Nafion-modified sputtered BiFEs (the thickness of the Nafion film is indicated in the figure). Electrolyte 0.1 mol l^{-1} acetate buffer (pH 4.5); preconcentration potential −1.20 V; preconcentration time 120 s; SW frequency 50 Hz; pulse height 40 mV; step increment 4 mV.

3. Results and discussion

3.1. Effect on the Nafion film thickness on the stripping response of Cd(II) and Pb(II)

The Nafion film was deposited on the electrode surface by the spread-coating method from Nafion solution containing 0.25, 0.5, 1 and 2% (w/v) of Nafion. Applying a 5.0 μl drop of the Nafion solution on the sensing area of the sensor and assuming complete coverage, the average thickness of the Nafion film was calculated as 0.4, 0.8, 1.6 and 3.2 μm, respectively [15]. Examination of the electrode surface by SEM before and after application of Nafion (Fig. 1B(a) and B(b), respectively) indicated that extensive coverage of the electrode surface was achieved with only a few scattered uncovered regions. Macroscopic inspection revealed that the appearance of the Nafion-coated electrode was dull in comparison with the silver, mirror-like surface of the bare sputterd BiFE.

Comparison between the SWASV responses on a microfabricated BiFE and Nafion-covered microfabricated BiFEs with different Nafion film thickness indicated that the sensitivity was always higher on the Nafion-covered micro-fabricated BiFEs (Fig. 2). This phenomenon has also been observed in the case of pulsed stripping techniques on electroplated Nafion-coated BiFEs [15] and has been attributed to the fact that the polymer film confines the stripped species close to the electrode surface where repetitive replating–stripping cycling occur resulting in signal amplification. Another observation was that, as the Nafion films became thicker, the sensitivity, especially in the case of Cd(II), increased. This could be explained by the fact that at pH 4.5–5.0 the sulfonate groups in the Nafion film were negatively charged and, as a result, the polymeric membrane acted as an effective cation-exchanger facilitating the non-faradaic preconcentration of metal cations. So, the thicker the Nafion films, the more effective their cation-exchanging activity (due to the larger surface area exposed in the solutions) and the most effective the non-faradaic preconcentration of Cd(II) and Pb(II).

This explanation of Nafion serving as a cation-exchanger was corroborated by the appearance of a double stripping peak for Pb and a wider peak for Cd when the thicker Nafion films were used (Fig. 2). In particular, as the thickness of the Nafion film increased, a second stripping peak progressively began to appear at more positive potential than the main peak. The gradual evolution of the more anodic peak at the thicker Nafion films could be accounted for by assuming that the metals are pre-concentrated both on the bismuth film and on the Nafion membrane. Metals deposited on the polymer electrostatically (i.e. via a cation-exchange mechanism) possess a slightly more anodic oxidation potential than the metals preconcentrated electrolytically on the Bi film (given that the formation of bismuth alloys renders the oxidation of the respective metals more reversible); this gives rise to a noticeable double peak for Pb and a wide peak for Cd on the thicker Nafion films at which a larger amount of metals is accumulated by electrostatic forces.

3.2. Effect of the preconcentration time and the deposition potential

In order to access the possibility of mass-transfer limitations of the target analytes due to the presence of the Nafion film, the electrolytic preconcentration time was studied in the range 15–240 s for a solution containing 15 μg l^{-1} of Pb(II) and 30 μg l^{-1} Cd(II) in 0.1 mol l^{-1} acetate buffer (pH 4.5). The stripping currents for the two metals increased rectilinearly with the deposition time on both the sputtered BiFEs and the Nafion-coated sputtered BiFEs with the stripping currents increasing rapidly at short deposition times and more slowly at higher deposition times before eventual levelling off. Saturation of the surface was achieved in the same time-scale on both the sputtered BiFEs and the Nafion-coated sputtered BiFEs suggesting that the mass transport was not influenced neither from the presence of Nafion nor from the thickness of the polymer films.

The effect of the deposition potential was studied in the range −0.50 to −1.5 V for a solution containing 15 μg l^{-1} of Pb(II) and 30 μg l^{-1} Cd(II) in 0.1 mol l^{-1} acetate buffer (pH 4.5). The stripping currents increased as the deposition potential became more negative up to −1.1 V and leveled off in the range −1.1 to −1.4 V. At deposition potentials more negative than −1.4 V the stripping currents started to decrease probably due to disruption of the deposition process by hydrogen evolution. Therefore, a deposition potential of −1.2 V was selected for further work.

3.3. Calibration features-sensor stability

Calibration for Pb(II) and Cd(II) in the range 0–45 μg l^{-1} and 0–90 μg l^{-1}, respectively, was performed on bare sputtered BiFEs and the Nafion-coated sputtered BiFEs of different thicknesses. In all cases linear calibration plots with coefficients of variation, $R^2 > 0.99$ were obtained. The analytical sensitivities were 0.50, 0.60, 0.66, 1.04 and 1.05 μA μg^{-1} l for Pb(II) and 0.21, 0.31, 0.35, 0.56 and 0.66 μA μg^{-1} l for Cd(II) on the bare BiFE and the Nafion-coated BiFEs with thicknesses of 0.4, 0.8, 1.6 and 3.2 μm, respectively, at a deposition time of 120 s. Considering that Nafion films thicker than 0.4 μm produced a double stripping peak for Pb and a wide stripping peak for Cd, the 0.4 μm-thick Nafion membrane was selected for further work. The calibration graphs for Pb(II) (in the range 0–45 μg l^{-1}) and Cd(II) (in the range 0–05 μg l^{-1}) on this Nafion-coated BiFE are described by the equations:

$$\mathrm{I_{Pb}}\ (\mu\mathrm{A}) = (0.60 \pm 0.01)\ (\mu\mathrm{A}\ \ \mu\mathrm{g}^{-1}\ \ \mathrm{l})\ \mathrm{C_{Pb}}\ \ (\mu\mathrm{g}\ \ \mathrm{l}^{-1}) + (0.23 \pm 0.11)\ (\mu\mathrm{A})$$

$$\mathrm{I_{Cd}}\ (\mu\mathrm{A}) = (0.31 \pm 0.01)\ (\mu\mathrm{A}\ \ \mu\mathrm{g}^{-1}\ \ \mathrm{l})\ \mathrm{C_{Cd}}\ \ (\mu\mathrm{g}\ \ \mathrm{l}^{-1}) + (0.28 \pm 0.05)\ (\mu\mathrm{A})$$

The limits of detection (calculated as LOD = $3\sigma_\beta/S$, where σ_β is the standard deviation of the intercept of the calibration plot and S is the analytical sensitivity (i.e. the slope of the calibration plot)) were 0.5 μg l^{-1} for both Pb(II) and Cd(II) at a preconcentration time of 120 s. Using a longer preconcentration time of 240 s, the LODs

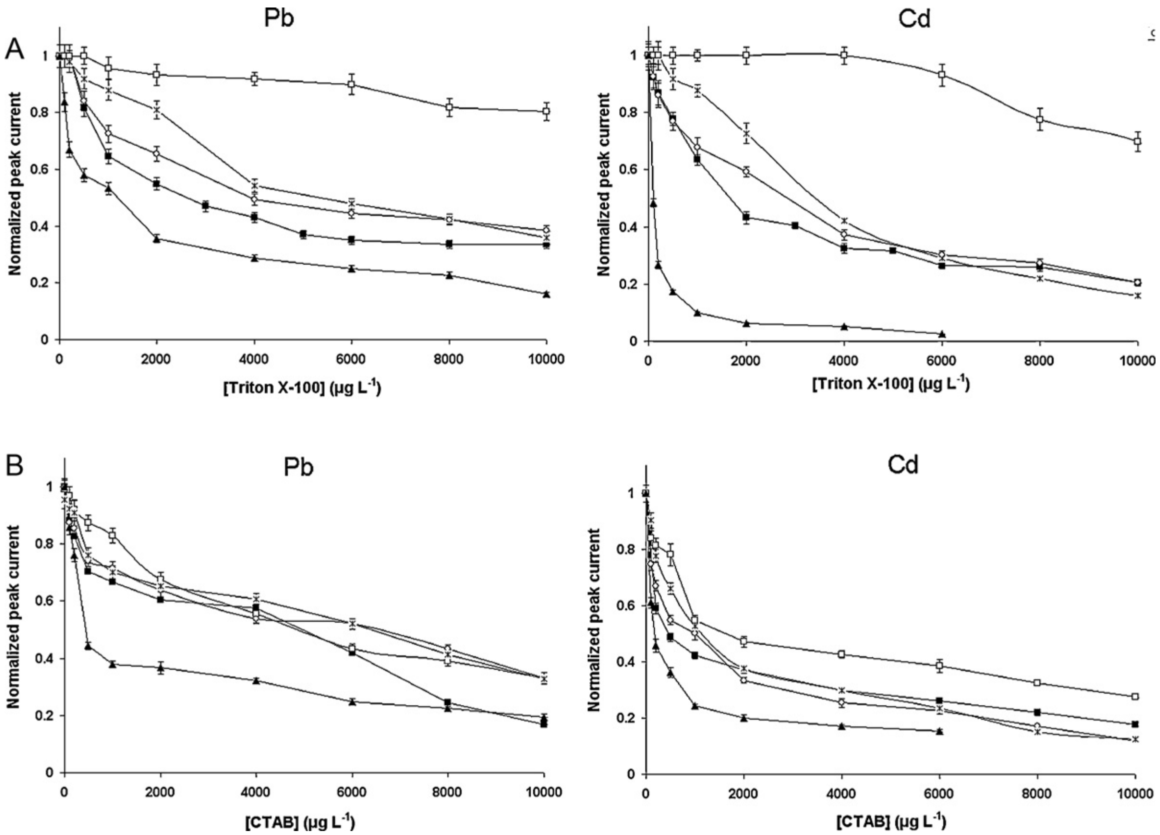

Fig. 3. Effect of different concentrations: (A) Triton X-100 and (B) CTAB on the normalized stripping peak currents of Pb and Cd in a solution containing 20 μg l^{-1} Pb(II) and Cd(II). Sputtered BiFEs: (▲) without Nafion, and with Nafion coating with thickness 0.4 μm (■), 0.8 μm (○), 1.6 μm (*) and 3.2 μm (□). Conditions as in Fig. 2.

were 0.4 μg l^{-1} for both Pb(II) and Cd(II). The modest decrease of the LODs after doubling the preconcentration time reflected the fact that the sensitivity increased only slightly by increasing the deposition time as a result of the rectilinear relationship between current and deposition time (as discussed in Section 3.2). Yet, the LODs on the Nafion-modified BiFE were better than on the an unmodified sputtered BiFE (at which the LODs were 0.5 μg l^{-1} for Pb(II) and 1 μg l^{-1} for Cd(II)) at a preconcentration time of 240 s [6]). For the rest of this work, 120 s of preconcentration was used because it provided a good compromise between sensitivity and short analysis time. Even lower LODs were calculated for thicker Nafion membranes (due to the increased sensitivity they provide) but these were obtained at the expense of wider peaks, as discussed previously. The repeatability, expressed as the % relative standard deviation of 8 consecutive measurements on the same sensor, was 3.8% for Pb(II) and 3.1% for Cd(II) at the 20 μg l^{-1} level at a preconcentration time of 120 s. The reproducibility, expressed as the % relative standard deviation obtained at 3 different sensors with 6 consecutive measurements on the same sensor (18 measurements), was 8.7% for Pb(II) and 9.1% for Cd(II) at the 20 μg l^{-1} level (n =) with a preconcentration time of 120 s.

The life-time of the sensors was dictated by the life-time of the bismuth film. Under continuous use was at least successive 20 preconcentration/stripping cycles (corresponding to life-times longer than 30 min) in acetate buffer provided that the electrode potential remained more positive than −0.3 V to avoid oxidation of the bismuth film. At longer operation times, microscopic examination revealed that the bismuth film eventually eroded and fractured, resulting initially in loss of sensitivity and then in complete loss of conductivity. The usual practice in this work was to utilise these sensors in the semi-disposable mode by carrying out a complete analysis cycle (e.g. measurement of sample with standard additions or of standards to plot a calibration curve) on a single electrode.

3.4. Effect of surfactants on the stripping response for Cd(II) and Pb(II) on the bare and the Nafion-coated sputtered BiFEs

To study the effect of typical surfactants on the sputtered BiFEs and the Nafion-coated sputtered BiFEs, Triton X-100 (non-ionic), CTAB (cationic) and SDS (anionic) were selected as "model" compounds. The normalized peak currents, calculated as I_s/I_o (where I_s and I_o were the stripping peak currents in the presence and the absence of surfactant, respectively) were plotted *vs* the concentration of the surfactant (Fig. 3). In the presence of Triton X-100, it was clear that the Nafion-coated sputtered BiFEs were much more tolerant to the presence of the surface-active compound than the sputtered BiFE (Fig. 3A). This resistance to the presence of surfactant was attributed to the polymeric film that formed an effective barrier to the transport of macromolecules to the electrode surface. As expected, the electrode tolerance to Triton X-100 clearly increased in the order: 0.4 < 0.8 < 1.6 < 3.2 μm Nafion thickness. In this case, the molecules of Triton X-100 were not charged and so mass-transport took place exclusively by diffusion. So, the thicker Nafion membranes caused higher resistance to the transport of macromolecules of the surfactant to the electrode surface.

The effect of CTAB on the stripping response of Pb(II) and Cd(II) is illustrated in Fig. 3(B) and, in this case, a different behaviour was observed. Again, Nafion-coated sputtered BiFEs were more tolerant to the presence of the surfactant but, in this case, there was not clear trend related to the thickness of the Nafion film and the effect of the Nafion coating was less pronounced. This phenomenon could be explained by the fact that the CTAB particles were positively charged and were consequently strongly attracted to the

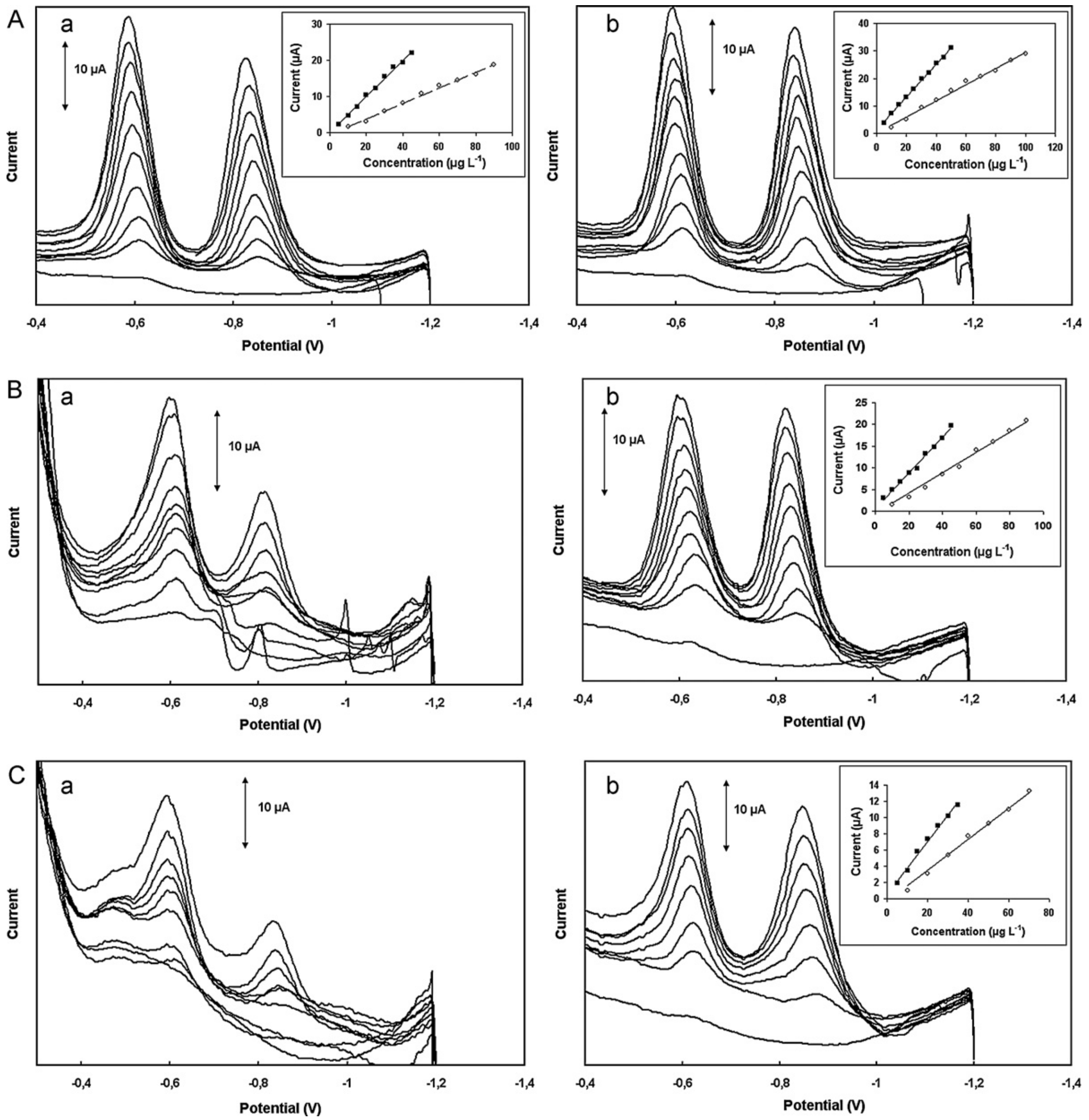

Fig. 4. SWASV responses at successively increasing concentrations of Pb(II) and Cd(II) in steps of 5 μg l^{-1} and 10 μg l^{-1}, respectively, (A) in the absence of surfactants and in the presence of 1 mg l^{-1} of: (B) Triton X-100, and; (C) CTAB on: (a) a sputtered BiFE without Nafion modification, and (b) sputtered BiFE modified with a 0.4 μm Nafion membrane. The calibration curves are shown as insets (Pb: —■—, Cd: —○—). Conditions as in Fig. 2.

negatively charged Nafion membranes. Therefore, strong accumulation of surfactant on the Nafion surface was favoured resulting in less effective action of the polymeric membrane.

The effect of the anionic surfactant SDS was negligible at low concentrations and was apparent only at concentrations higher than 4 mg l^{-1}. This behaviour was accounted for by considering that there was strong electrostatic repulsion between the negatively charged surfactant species and the electrode surface.

Typical comparative voltammograms for increasing concentrations of Pb(II) and Cd(II) on the sputtered BiFEs and the Nafion-coated sputtered BiFEs in the absence and the presence of surfactants are illustrated in Fig. 4. Fig. 4A(a) illustrates stripping voltammograms for increasing concentrations of Pb(II) and Cd(II) on an unmodified sputtered BiFE, showing good linearity and analytical sensitivities of 0.50 and 0.21 μA μg^{-1} l for Pb(II) and Cd(II), respectively. Fig. 4B(a) and C(a) illustrate voltammograms on an unmodified sputtered BiFE in the presence of 1 mg l^{-1} of Triton X-100 and 1 mg l^{-1} CTAB, respectively. The stripping peaks of the two metals were severely affected by the presence of surfactants to such an extend that the calibration plots were far from linear and determination of the metals was impossible. On the other hand, similar voltammograms on a Nafion-coated BiFE are illustrated in Fig. 4A(b) for increasing concentrations of Pb(II) and Cd(II) in the absence of surfactants and in Fig. 4B(b) and C(b) in the presence of 1 mg l^{-1} of Triton X-100 and 1 mg l^{-1} of CTAB, respectively. Linear calibration plots ($R^2 > 0.99$) were obtained in all cases with analytical sensitivities of 0.60, 0.41 and 0.33 μA μg^{-1} l for Pb(II), respectively, and 0.31, 0.23 and 0.19 μA μg^{-1} l for Cd(II), respectively. The presence of the surfactants did suppress the response to some extent (as indicated by the decrease in the analytical sensitivities, a trend which was more pronounced in the case of CTAB for the reasons discussed in the previous section). However, quantification of Pb(II) and Pb(II) was possible on the Nafion-modified BiFEs as opposed to the bare sputtered BiFEs. These results demonstrate the ability of the Nafion-modified sensors to properly operate in samples containing surfactants.

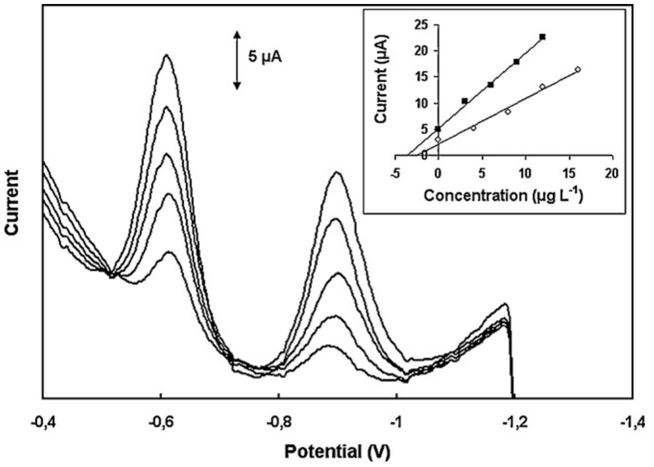

Fig. 5. SWASV responses for the determination of Pb(II) and Cd(II) in a certified lake water sample on a sputtered BiFE modified with a 0.4 µm Nafion membrane. From below: sample and 4 additions of 3 µg l^{-1} Pb(II) and 4 µg l^{-1} Cd(II). The standard addition plot is shown as an inset. Conditions as in Fig. 2 with addition of 0.02 mmol l^{-1} of ferrocyanide.

3.5. Interference study

The interference of Cu(II) in the determination of Pb(II) and Cd(II) has been reported previously on electroplated and microfabricated BiFEs and has been attributed both to the formation of mixed compounds and on the undesired deposition of the target metals on electroplated Cu instead of Bi [6,22,23]. In this work, the presence of Cu(II) affected mostly the Pb peak which was evident even at a two-fold concentration of Cu(II) over Pb(II) and almost completely suppressed the Pb peak at a 5:1 Cu(II)-to-Pb(II) concentration ratio. This interference was alleviated by the addition of ferrocyanide ions that form a stable complex with Cu(II) but do not affect the Cd and Pb peaks, as suggested previously [6,24]. Following previous recommendations, 0.02 mmol l^{-1} of ferrocyanide was added in samples known or suspected to contain Cu(II). In(III) produced a stripping peak at −0.79 V and Tl(I) produced a stripping peak at −0.73 V; both these peaks overlapped severely with the Cd peak and only slightly with the Pb peak. Sn(II) has been shown to produce a stripping peak that overlaps with the Pb peak but this peak is only observed in highly acidic solutions or media including complexing agents that prevent hydrolysis of Sn(II) [25,26]; in the acetate buffer used in this work, no Sn peak was obtained in agreement with earlier studies [26]. Other metals such as, Sb(III), Mn(II), Co(II), Ni(II), Na(I), K(I), Ca(II), Mg(II), Zn(II), at a ten-fold excess over Cd(II) and Pb(II) did not affect the stripping peaks of Pb and Cd (the criterion for interference was ±10% change of the stripping peak heights).

3.6. Application

The Nafion-coated sputtered BiFEs were applied to the analysis of a certified lake water sample for the determination of Pb(II) and Cd(II). Representative stripping voltammograms are illustrated in Fig. 5 (in which the respective standard additions plot is shown as an inset). The determined concentrations of Cd(II) and Pb(II) were 3.6 ± 0.3 µg l^{-1} for Pb(II) and 2.4 ± 0.3 µg l^{-1} for Cd(II) ($n = 3$) while the certified values are 3.2 and 2.5 µg l^{-1}, respectively. This sample, also contained Cu(II) with a certified concentration 9.1 µg l^{-1} and 0.02 mmol l^{-1} ferrocyanide was used to alleviate this interference, as discussed previously.

4. Conclusions

In this work, the utility of Nafion-modified sputtered BiFEs was investigated for the simultaneous determination of Pb(II) and Cd(II) by SWASV in the presence of surfactants. This study has indicated that the presence of the polymer modifier afforded higher sensitivity and improved performance in the presence of surfactants without hindering mass-transport to the electrode surface but the concentration of the Nafion coating solution should be carefully selected to avoid widening of the stripping peaks. Therefore, the Nafion-coated sputtered BiFEs can serve as disposable, environmentally friendly sensors for trace metal analysis in surfactant-rich samples.

Acknowledgments

The contribution of Dr. Ioannis Raptis and Dr. Thanassis Speliotis for the fabrication and optical characterization of the sputtered BiFEs is gratefully acknowledged. Financial support was provided by the Special Account of Research of the University of Athens (Grant No. 70/4/9800).

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