

Characterization and Application of Bismuth-Film Modified Graphite-Polyurethane Composite Electrodes

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Abstract

Bismuth films (BiF) deposited in situ on graphite-polyurethane composite electrodes were successfully used for the determination of Zn, Cd, Pb, Cu and Hg, simultaneously in acetate buffer solution pH 4.5 using square wave anodic stripping voltammetry. It is possible to determine metals reoxidized at potentials more negative and more positive than Bi using in situ deposited BiF; reoxidation was studied by electrochemical impedance spectroscopy. The BiF-modified electrode was applied to analyse tap water. The influence of surface-active compounds, Triton X-100 and bovine serum albumin, on the stripping of these metals was investigated; Nafion coatings did not significantly improve the performance.

Keywords: Bismuth film, Carbon composite electrodes, Trace metal determination, Stripping voltammetry, Electrochemical impedance spectroscopy, Bismuth

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Dedicated to a Decade of Bismuth Electrodes in Modern Electroanalysis

1. Introduction

Bismuth film electrodes (BiFEs) have constituted an attractive subject for electroanalytical research as a potential replacement for mercury electrodes in stripping voltammetry for the last decade. Bi has a low toxicity and, as a film on a solid electrode substrate, has similar electrochemical properties to mercury films in terms of potential window and ability to electrodeposit other substances on its surface [1–7].

BiFEs have been deposited on carbon substrates, particularly on glassy carbon [1, 8–18], carbon fibre [1, 13], screen-printed electrodes [19, 20], carbon paste electrodes [13, 21–24], electrically heated carbon paste electrodes [25], and boron-doped diamond electrodes [24], showing some advantages with respect to mercury-based electrodes. Bismuth bulk electrodes have also been studied and compared with BiFEs [26]. The BiFE can be deposited under in situ or ex situ conditions depending on the target analyte or the aim of the analysis.

These electrodes have been used for anodic stripping voltammetry [1, 7, 9, 10, 13–15, 17, 27–29], adsorptive stripping voltammetry [28, 19–25], potentiometric stripping analysis [26] as well for cathodic stripping voltammetry [15, 27, 28]. The positive potential region cannot be used at ex situ deposited bismuth films due to dissolution of the film itself, since the Bi stripping potential is at ca. -0.3 V vs.

SCE, depending on the medium. Such films were used for the determination of heavy metals, mostly Cd and Pb, as well as of some organic compounds [3–5], where mercury film electrodes had been previously employed.

BiFEs as well as mercury film electrodes (MFEs) allow the determination of several metals at the same time. The preconcentration time of submicromolar concentrations of the heavy metal ions can vary between 1–5 min, but usually the accumulation time is from 30 to 120 s, depending on the electrode substrate and electrolyte medium [1–7].

Graphite-castor oil polyurethane composite electrodes (GPCE) were introduced 7 years ago as a new type of composite electrode material [30]. This electrode material, prepared from graphite powder and polyurethane obtained from vegetable oil, has several advantages: i) resistance to organic solvents; ii) mechanical resistance; iii) reduced risks to the environment; and iv) easy surface renewal. Moreover, the binding polymer is prepared from a bicomponent liquid system containing a resin and a hardener which is prepared by simply mixing the binder with graphite powder and possibly modifiers (if needed). The oily nature of the resin also produces a composite with a hydrophobic character, preventing the swelling effect observed for composites made with epoxy resins when such electrodes are used in aqueous media. It can be used with different compositions, depending on the application [30, 31].

In this work, bismuth films have been electrochemically in situ deposited onto a graphite-castor oil polyurethane composite electrode substrate. GPCE modified with BiF was applied for the determination of five heavy metals, Zn, Cd, Pb, Cu and Hg, in acetate buffer pH 4.5, by square wave anodic stripping voltammetry (SWASV). The role of Bi in this case was the formation of co-deposits with these metals [23] as well as simultaneous electrodeposition, ensuring better preconcentration at the electrode surface, since the stripping potentials of Cu and Hg are more positive than that of Bi. The BiFE was applied to the determination of heavy metals in tap water samples and the effect of surfactants together with Nafion coatings was studied.

2. Experimental

2.1. Chemicals and Solutions

Graphite powder of 1–2 μm particle size (Aldrich, Germany) and polyurethane resin (Poliquil, Araraquara, SP, Brazil) were used for the preparation of the composite, see below.

Standard 1000 mg L^{-1} solutions (Tec-Lab, Brazil) of Cd^{2+} (traceable to SRM 3108 NIST, USA), Pb^{2+} (traceable to SRM 3128 NIST, USA), Cu^{2+} (traceable to SRM 3114 NIST, USA), and Hg^{2+} (traceable to SRM 3133 NIST, USA) were used for the preparation of the working cadmium, lead, copper and mercury solutions. Bismuth(III) nitrate and zinc(II) chloride were obtained from Sigma (Germany).

Chemical reagents were all of analytical grade and were used without further purification. Sodium acetate and acetic acid (Riedel–de Haën, Germany) were used to prepare 0.1 mol L^{-1} acetate buffer pH 4.45. Stock solutions of the metal ions mentioned above were diluted as required before measurements in acetate buffer and stored at room temperature. All solutions were prepared with water purified in a Millipore Milli-Q system (resistivity $\geq 18 \text{ M}\Omega \text{ cm}$).

2.2. Instrumentation and Methods

All voltammetric measurements were carried out in a 20.0 mL total capacity glass cell at $25 \pm 1^\circ\text{C}$, using the graphite–polyurethane composite as working electrode, a saturated calomel electrode (SCE) as reference, and platinum wire (1.0 cm length, 0.5 mm diameter) as auxiliary electrode. Square-wave anodic stripping voltammetry was performed with an $\mu\text{Autolab Type II}$ (Ecochemie, Netherlands) potentiostat/galvanostat coupled to a personal computer and controlled with GPES 4.9 software. The geometric area of the electrode was 0.126 cm^2 .

Electrochemical impedance measurements were carried out in the same electrochemical cell with a PC-controlled Solartron 1250 frequency response analyser coupled to a Solartron 1286 electrochemical interface using ZPlot 2.4 software (Solartron Analytical, UK). A sinusoidal voltage perturbation of amplitude 10 mV was applied, scanning

from 65 kHz to 0.1 Hz with 10 points per frequency decade. Fitting to equivalent electrical circuits was performed with ZView 3.0 software.

2.3. Electrode Preparation

The polyurethane (PU) resin was prepared by mixing 0.8 parts of the prepolymer (A-249) with 1.0 part of the polyol (491-ID), according to the manufacturer's instructions. Previous results [30] showed that the best composition of the material was 60% (w/w) graphite and 40% (w/w) PU; corresponding amounts of PU and graphite were mixed together in a mortar for 5 min. The electrode was prepared from rods of the composite (4 mm diameter) extruded in a press. For this purpose, 50 mm long rods were cut and attached to a copper wire using silver epoxy (Electron Microscopy Sciences, Hatfield, PA, USA) and left to cure for 24 h. The electrode was then sealed in a glass tube using epoxy resin (Silaex, São Paulo, SP, Brazil) and used only after at least 24 h. After curing, the excess of polymer was removed using 600-grit abrasive paper. Finally, the electrode surface was polished with $\gamma\text{-Al}_2\text{O}_3$ suspension down to 1 μm particle size on a polishing wheel and sonicated for 5 min in water.

A Bi film (BiF) was deposited in situ with the other metals from a solution containing 0.1 mol L^{-1} acetate buffer pH 4.45, 48 $\mu\text{mol L}^{-1}$ Bi(III), and the other metal ions. The SWASV conditions were: for the in situ deposition, accumulation time 120 s at -1.4 V vs. SCE, equilibration time 15 s and, for the SW sweep pulse amplitude 25 mV, frequency 25 Hz, step potential 4 mV, and potential sweep from -1.4 to $+0.5 \text{ V}$ vs. SCE.

2.4. Nafion Coated Bismuth Film Electrode

The Nafion coating was made by applying 5 μL of a solution of 0.25 wt% Nafion in alcohols, followed by 3 μL of *N,N'*-dimethylformamide, directly on top of the graphite-polyurethane composite electrode, with a motorized electronic micropipette (EDP-Plus, Rainin, USA). After evaporation of the solvents, the film was cured with a jet of warm air for about 1 min. This procedure leads to a film of ca. 1 μm thickness. The bismuth film was then deposited through the Nafion-coated composite electrode, the bismuth layer being formed between the composite electrode substrate and the Nafion coating.

3. Results and Discussion

3.1. Determination of Heavy Metals at Graphite-Polyurethane Modified Electrodes with Bi Films

3.1.1. Influence of Bismuth on Metal Ion Determination

Usually, metals which have a stripping potential more negative than that of Bi are determined at Bi film electrodes.

However, it has been proved that it is also possible to determine metals that are stripped after Bi, in particular Cu [32]. A metal ion with a more positive stripping potential was added to the solution in order to evaluate BiFE sensitivity and selectivity to metal ions with more positive stripping potentials: Hg(II) was chosen for this purpose. Thermodynamically, Hg would be deposited first and would form a MFE rather than a BiFE. The concentration of all metals (except Bi(III)) was $0.5 \mu\text{mol L}^{-1}$ in 0.1 mol L^{-1} acetate buffer pH 4.45. The experimental results, see Figure 1, showed that Bi has the biggest influence on the electrode sensitivity. The dashed curve shows electrode performance without Bi(III): all peaks are well-defined and separated, only Pb(II) has a double peak under these conditions. After addition of $48 \mu\text{mol L}^{-1}$ of Bi(III) to the same solution, the peaks increased significantly in height including that of Hg, the exception being Cu, which remained almost the same. In addition, most peak positions were slightly shifted in the positive direction, depending on the metal: the stripping peak of Zn remained at -1.125 V , Cd was shifted from -0.799 to -0.773 V , Pb was shifted from -0.584 to -0.541 V , and Cu from -0.099 to -0.079 V , and, finally, the Hg stripping peak remained at the same position, at 0.244 V .

Using a GPCE modified with Bi film, no evidence of Zn-Cu intermetallic compound formation was obtained as observed in [32]: no additional peaks appeared after that of Cu. Moreover, Zn and Cu peaks were well defined and linearly dependent on concentration. The results above lead to the conclusion that Bi(III) improves the preconcentration of heavy metals by co-deposition as intermetallic compound(s) and/or fused alloys, including those that are stripped after Bi itself.

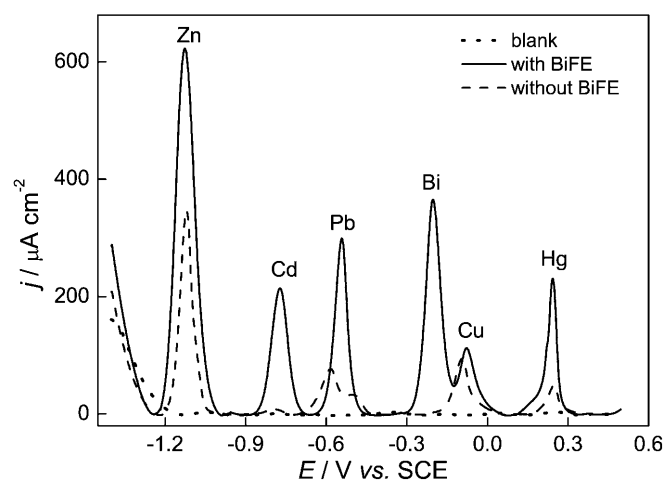


Fig. 1. SWASVs at BiFE/GPCE in the presence (dashed line) and absence (dotted line) of $0.5 \mu\text{mol L}^{-1}$ of Zn(II), Cd(II), Pb(II), Cu(II), and Hg(II), and $48 \mu\text{mol L}^{-1}$ of Bi(III) in 0.1 mol L^{-1} acetate buffer pH 4.45.

3.1.2. Calibration of the Bi Film Electrode

SWASV was carried out with various concentrations of the heavy metal ions at the BiFE, determining them simultaneously as shown in Figure 2a, the stripping peak current increasing with increase in concentration, as expected. Figure 2b shows calibration curves in the nanomolar range for all metals. The sensitivity to Cu and Hg was significantly lower than that of the other metals, but is still sufficient for the determination of trace concentrations. Calibration data such as sensitivity, limit of detection, and correlation coefficient are presented in Table 1. Surprisingly, Pb(II) in the concentration range down to 6 nmol L^{-1} had a high response and the intercept did not pass through the origin. The high positive intercept might be related either to Pb(II) interaction with polyurethane at the electrode surface or to formation of some stronger intermetallic interactions at lower concentrations of this metal.

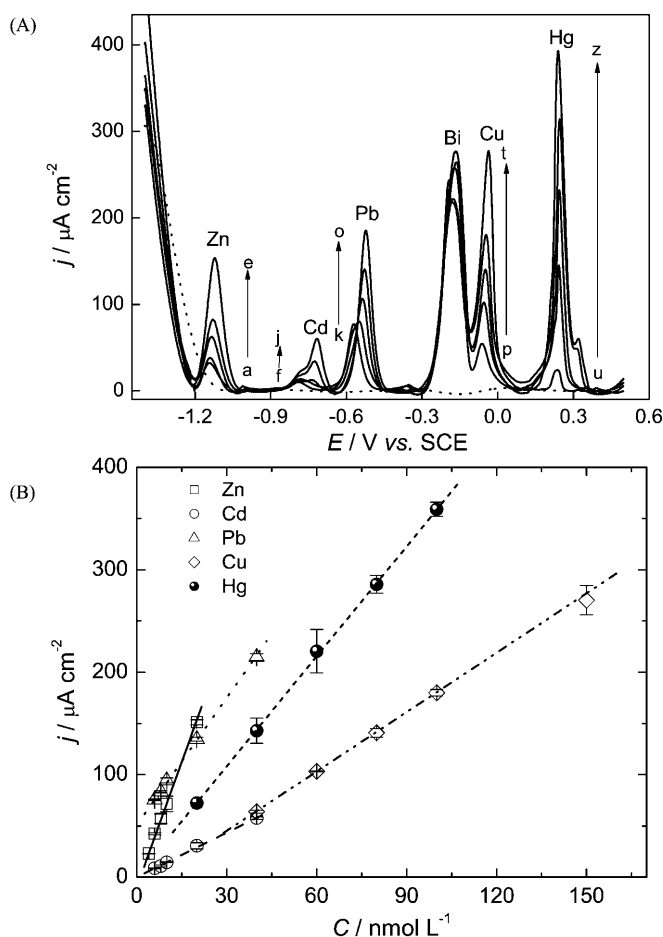


Fig. 2. (A) SWASV in 0.1 mol L^{-1} acetate buffer pH 4.45 at GPCE (dotted line) and at BiFE in the presence of different concentrations of Zn(II), Cd(II), Pb(II), Cu(II), and Hg(II); Bi(III) constant concentration $48 \mu\text{mol L}^{-1}$. Concentrations in nmol L^{-1} : a, p) 4; b, q) 6; c, r) 8; d, s) 10; e) 20; f, k) 6; g, l) 8; h, m) 10; i, n) 20; j, o) 40; t) 15; u) 20; v) 40; x) 60; y) 80; z) 100. (B) Calibration curves for Zn (squares), Cd (circles), Pb (triangles), Cu (diamonds), and Hg (dark balls) at BiFE.

Table 1. Calibration parameters of Zn, Cd, Pb, Cu, and Hg at GPCE modified with Bi film. Data calculated from Figure 2b. Standard deviations are given for $n = 3$.

Metal	Sensitivity ($\mu\text{A cm}^{-2} \text{ nmol}^{-1} \text{ L}$)	Correlation coefficient (R^2)	LOD (nmol L^{-1})
Zn	7.94 ± 0.24	0.997	0.6
Cd	1.43 ± 0.08	0.999	2.2
Pb	4.13 ± 0.08	0.999	1.1
Cu	1.91 ± 0.08	0.999	2.7
Hg	3.57 ± 0.08	0.999	2.5

The data in Table 1 show that the electrode was most sensitive to Zn, and the lowest sensitivity was to Cd; Zn also had the lowest limit of detection. The fact that the GPCE modified with a Bi film is extremely sensitive to Zn, is unlike the other BiFEs reported [33–35]. Commonly, the electrode sensitivity to Zn is limited by hydrogen evolution since Zn is accumulated at -1.4 V and stripped at -1.1 V, where H_2 evolution starts and interferes with both the preconcentration and the stripping processes [33, 34]. Thus glassy carbon electrodes modified with bismuth films are most sensitive either to Cd or to Pb [33, 35]. It seems that hydrogen evolution does not interfere with Zn accumulation at the GPCE modified with Bi film, because noticeable hydrogen evolution starts at potentials more negative than -1.5 V (vs. SCE) at GPCE [30].

3.1.3. Electrochemical Impedance Spectroscopy Study of the Bismuth Film Electrode

Electrochemical impedance spectra were recorded in acetate buffer solutions at bare GPCE and at BiFE in the absence of and in the presence of all the heavy metals simultaneously at different potentials, corresponding to where the following processes were occurring: -1.4 V, preconcentration of heavy metals and BiF formation; -1.1 V, reoxidation peak of Zn; -0.8 V, reoxidation peak of Cd; -0.6 V, reoxidation peak of Pb; -0.1 V, reoxidation peak of Cu; $+0.2$ V, reoxidation peak of Hg. The selected spectra are presented as complex plane plots (Figure 3a) and imaginary impedance vs. logarithm of frequency (Figure 3b), a plot which represents a powerful way of examining the time constants of interfacial processes, since the peaks in the plots correspond to when $\omega RC = 1$ for situations where charge separation (capacitance, C) and charge transfer (resistance, R) are in parallel, with ω the frequency of the voltage perturbation in radians [33, 34].

The spectra at -1.4 and at -1.1 V (the latter not shown) give evidence that, besides the other processes (metal preconcentration and Zn reoxidation), some hydrogen evolution takes place, since the spectra in the low frequency region do not give stable values, due to the formation of a tiny quantity of H_2 gas bubbles, especially visible at -1.4 V. Misshaped semicircles are obtained (Figure 3a) and the impedance values are much lower compared with other potentials studied. The time constants at these potentials are in the middle frequency region (Figure 3b). Moving to less negative potentials, impedance values increase up to

-0.6 V, then decrease slightly until $+0.2$ V but the semi-circle continues to become large and the time constants shift to lower frequencies.

At almost all potentials, except -1.4 V, the lowest impedance values were obtained at unmodified GPCE, with a low charge transfer resistance and a high capacitance. A different behaviour was found at -1.4 V at the bare composite electrode due to a small amount of hydrogen evolution in the absence of heavy metal ions (without disturbance by metal deposition). Modification of the electrode surface with the Bi film increased the impedance values at almost all potentials. Addition of the other heavy metal ions to solution did not give any significant changes at -0.2 V or at other less negative potentials, and the spectra were similar to that of the BiF, except at -1.4 V. This is probably due to changes in the hydrogen evolution rate: more metal ions disturb H_2 production and increase the capacitance at the electrode surface.

Electrochemical impedance spectra were analysed using equivalent circuits. The same equivalent circuit was applied to nearly all spectra, consisting of the cell resistance, R_Ω , in series with a charge transfer resistance, R_{ct} , describing the reduction/reoxidation of metal ions, in parallel with a constant phase element, CPE, modelled as a nonideal capacitor:

$$\text{CPE} = 1/(C i \omega)^\alpha \quad (1)$$

where C is the capacitance, i is the square root of -1 , ω is the radial frequency, and α is a CPE exponent expressing nonuniformity. The spectra at -0.1 and $+0.2$ V at bare composite electrode were extended with an additional capacitance C_2 in series to describe processes in the low frequency region. The data obtained from equivalent circuit analysis of the spectra are presented in Table 2; the errors in the fitting of the experimental values to the equivalent circuit varied between 1–7% for R_{ct} , 0.9–4% for C , and less than 1% for α and R_Ω . R_Ω was ca. $29 \Omega \text{ cm}^2$ for bare GPCE and ca. $25 \Omega \text{ cm}^2$ for BiF modified electrodes in the presence or in the absence of the other heavy metal ions, independent of applied potential.

The EIS results lead to the conclusion that bismuth deposition at GPCE at -1.4 V occurs together with hydrogen evolution but that simultaneous heavy metal electro-deposition decreases hydrogen evolution. Time constants are not altered by the interfacial metal film composition (Figure 3b).

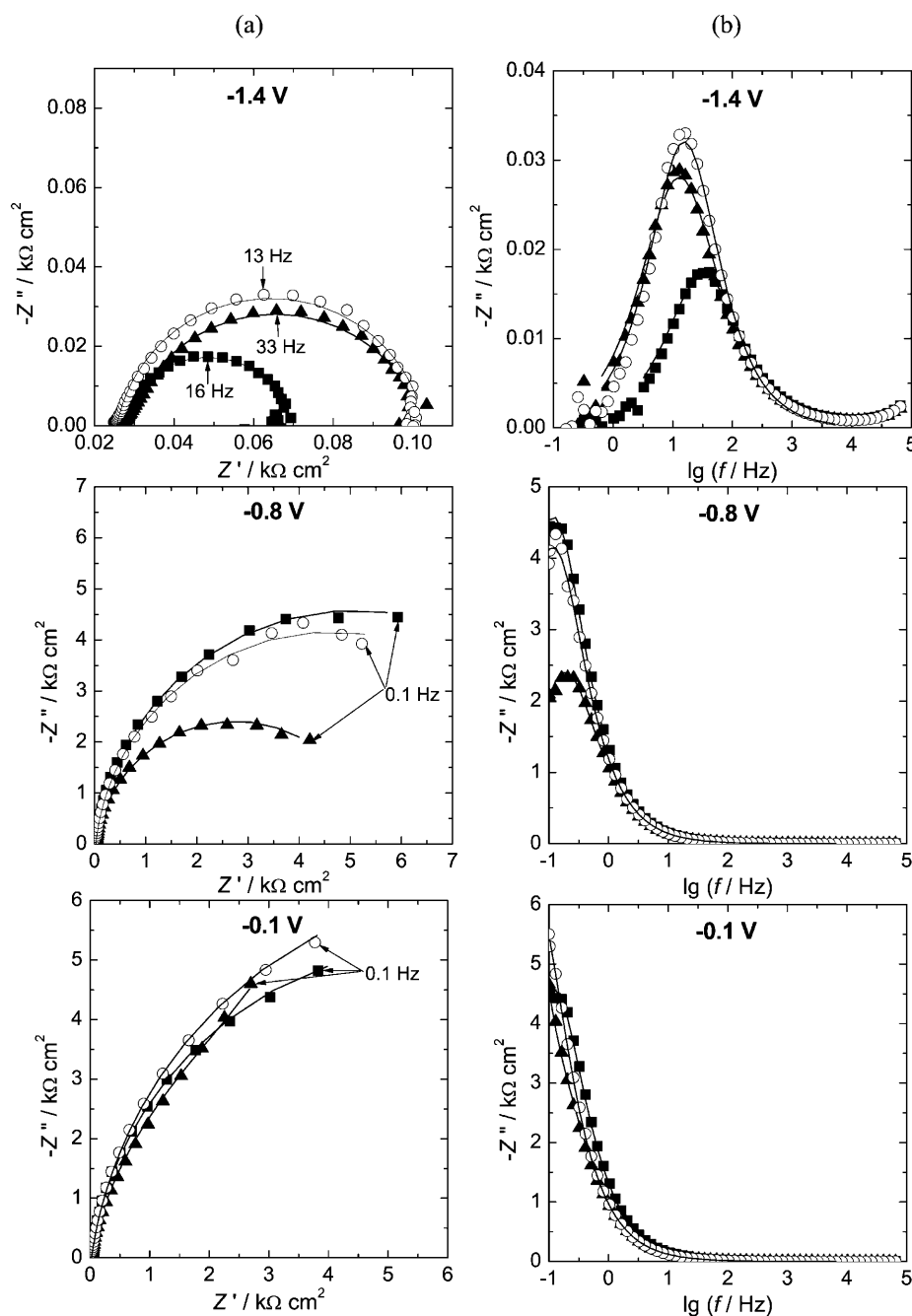


Fig. 3. (a) Complex plane and (b) imaginary impedance vs. log frequency plots at (\blacktriangle) GPCE, GPCE modified with BiF (\blacksquare) in the absence and (\circ) the presence of 50 nmol L^{-1} of heavy metal ions at different potentials. Lines indicate fitting by electrical equivalent circuit models.

3.1.4. Determination of Heavy Metals in Tap Water

Analysis of tap water samples was performed using stagnant (overnight) tap water samples collected first thing in the morning. The water was then left to run for 5 min and a second sample was taken. These two samples were analysed by adding 5 mL of the water sample to 5 mL of 0.1 mol L^{-1} acetate buffer solution pH 4.45, and SWASV was performed, using preconcentration for 120 s. The SWASVs

obtained for both samples are presented in Figure 4. As seen, both samples have only Zn, in the first sample $48.1 \pm 0.5 \text{ nmol L}^{-1}$ and in the second sample $24 \pm 1 \text{ nmol L}^{-1}$. The stagnant tap water sample has more of this metal ion, explained since the supply system in the building is made zinc-galvanised piping. It seems that this metal ion accumulates overnight in tap water due to corrosion, and that after running it in the morning its quality improves significantly.

Table 2. Parameters from equivalent circuit fitting of the impedance spectra of Figure 3. R_{Ω} : cell resistance, C : capacitance from CPE, α : roughness exponent, R_{ct} : charge transfer resistance.

E (V) vs. SCE	R_{ct} (k Ω cm 2)	C (μ F cm $^{-2}$ s $^{\alpha-1}$)	α
GPCE			
-1.4	0.07	360	0.82
-1.1	0.21	231	0.87
-0.8	5.48	158	0.92
-0.6	9.56	161	0.91
-0.1	4.83	270	0.87
+0.2	4.81	389	0.83
GPCE + BiF			
-1.4	0.04	257	0.84
-1.1	0.46	169	0.90
-0.8	10.2	130	0.94
-0.6	19.0	161	0.94
-0.1	11.8	186	0.92
+0.2	21.2	284	0.88
GPCE + BiF + heavy metals			
-1.4	0.08	225	0.89
-1.1	1.05	189	0.90
-0.8	9.21	144	0.94
-0.6	25.1	149	0.93
-0.1	14.3	186	0.91
+0.2	20.8	272	0.88

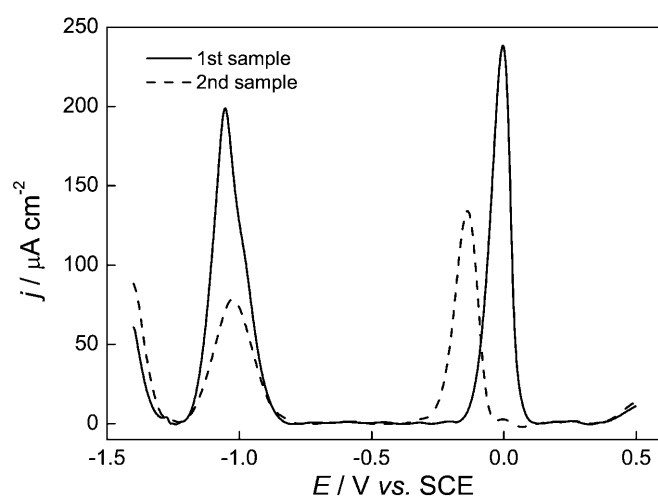


Fig. 4. SWASV of tap water samples at GPCE modified with BiF. 1st sample is stagnant tap water; 2nd sample is tap water collected after 5 min running water (counting immediately after the 1st sampling). 5 mL of sample in 5 mL of 0.1 mol L $^{-1}$ acetate buffer pH 4.45.

3.2. Influence of Surfactants on Anodic Stripping Voltammetry of Heavy Metals

Since natural environmental samples, in which traces of heavy metals need to be analyzed, usually contain some surface-active substances, it is important to investigate their influence on the analytical performance of bismuth film electrodes. The influence of two surface blocking agents: surfactant, polyethylene glycol *p*-(1,1,3,3-tetramethylbu-

tyl)-phenyl ether (Triton X-100), and protein, bovine serum albumin (BSA), on the performance of GPCE modified with bismuth film was tested.

3.2.1. Unmodified Bi Film Electrode

The influence of the surface active materials was tested by adding different amounts of these compounds to a known amount of the heavy metal ions and carrying out SWASV as described in Section 3.1.1. The results are presented in Figure 5, plotting peak currents in the presence of 0.5 μ mol L $^{-1}$ of the heavy metals normalised to the response without any addition of surface active material, vs. Triton X-100 or BSA concentrations. These experiments were repeated three times and gave the same results. Fig. 5 demonstrates that Triton X-100 and BSA have different effects on all metals and that this effect is different for each metal studied. A stronger negative effect on the metal signal was obtained with Triton X-100 for almost all metals (except Cu) compared to BSA.

Low Triton concentrations of 1–2 mg L $^{-1}$ did not affect the metal signal which even increased a little for Cu(II) and Hg(II). An increase in surfactant concentration led to a decrease of a peak current for Cd(II) and Pb(II) to 50 and 20% of the signal, respectively, for 20 mg L $^{-1}$ Triton. In the case of Zn(II), the signal remained relatively stable up to 8 mg L $^{-1}$ of Triton X-100 and then, by 20 mg L $^{-1}$ Triton, dropped to 40% of the initial value.

A different influence of Triton X-100 was observed for the metals reoxidized after Bi: the metal signal increased to 120% of the initial value of the signal without addition of the surface active compound. Such a positive surfactant effect might be due to an improvement of the preconcentration of these metals by complexation with the surfactant at higher concentrations. A positive surface active compound effect has been obtained before only at mercury film electrodes (MFE) coated with polymer films, in particular for Pb(II) [2].

BSA had a smaller effect on metal reoxidation at BiFE than Triton X-100, except for Hg(II) (Figure 5). In general, up to a concentration of BSA of 5 mg L $^{-1}$, the signal increased for Zn(II), Pb(II), and Hg(II), and remained almost the same for Cd(II). With a further increase in BSA concentration, the signal decreased to the original value for Zn(II) and Hg(II), and in the case of Cd(II) and Pb(II) the signal dropped to 50% of the initial value. A totally different effect of BSA was observed for Cu(II): the signal remained at 100% up to 5 mg L $^{-1}$ of BSA and then dropped to zero by 10 mg L $^{-1}$ of BSA. This probably shows the different nature of the complexation phenomena and stability constants with the various metal ions. The influence of proteins was previously studied only at MFE and with polymer-coated MFEs, there usually being a positive effect of protein at low albumin concentrations [36, 37].

At GPCE in situ modified with Bi films, surface active materials do not have as strong an influence as was reported previously in [34] at BiF deposited on carbon film electrodes. This leads us to conclude that surface active materials

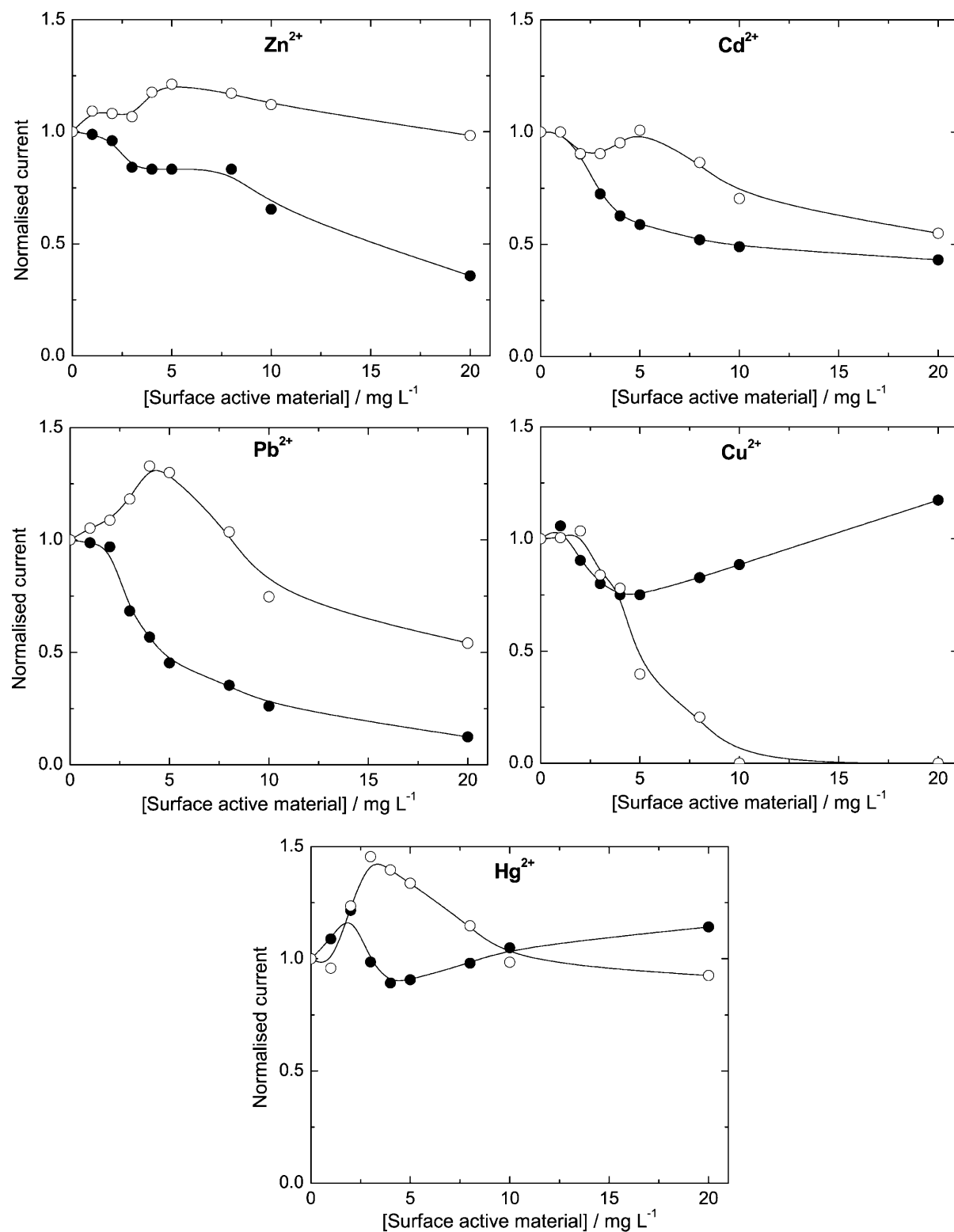


Fig. 5. Influence of surface active materials: Triton X-100 (●) and BSA (○) on 50 nmol L⁻¹ of Zn(II), Cd(II), Pb(II), Cu(II), and Hg(II). All other conditions as in Figure 2.

do not block this type of electrode strongly, which represents an important advantage. Lesser adsorption effects on bare GPCEs have also been observed [38, 39].

3.2.2. Nafion Modified Bi Film Electrode

GPCEs were modified with a Nafion coating using the procedure described in Experimental Section 2.4 and the

influence of surface active compounds was investigated using the same procedure as above, Section 3.2.1. A polymer film is often used to protect the electrode surface from organic substances present in natural samples that adsorb at the electrode surface in this way diminishing the response to analyte [2, 36, 37].

It was found that the Nafion coating improves the response of Zn(II) and Cu(II) at low Triton X-100 concentrations. No significant changes were observed with the Nafion film for Hg(II) determination over the concentration range of Triton tested. For all the other metals, the influence of Triton on the response to the metals was less at the Nafion coated BiFE than without any coating.

BSA at Nafion coated Bi films had a smaller influence on metal determination and the signal decreased by up to 20% at 20 mg L⁻¹ of BSA. However, a change in the presence of small amounts of BSA (up to 5 mg L⁻¹) was observed: higher in the case of Zn(II) and Pb(II) and lower in the case of Hg(II) compared to the BiFE without Nafion film.

In conclusion, surface-active materials appear to have a lesser effect at GPCE/BiFEs than at other electrode substrates with Bi films, such as carbon film electrodes modified with Bi films deposited ex situ [34].

4. Conclusions

Bismuth films were deposited in situ on graphite-polyurethane composite electrodes and tested with respect to the simultaneous determination of five heavy metals, Zn, Cd, Pb, Cu and Hg, in acetate buffer solution pH 4.45 using square wave anodic stripping voltammetry. It was shown that it is possible to determine metals reoxidized at potentials both more negative and more positive than Bi, an advantage of the in situ deposited BiF. The reoxidation was probed by EIS showing the total suppression of hydrogen evolution at the BiF deposition potential, which decreases the capacitance of the GPCE, and that addition of the metal ions tested changes the spectra insignificantly. The BiF modified electrode was applied to analyse tap water.

The influence of the surface active compounds Triton X-100 and BSA on the SWASV of the heavy metal ions was tested. The influence of Triton was greater than that of BSA: at low concentrations of surface active materials a signal increase was found for some metal ions while BSA had a strong influence only on Cu; nevertheless, the effect of surfactants is less than at other electrode substrates. Nafion coatings diminish the influence of BSA slightly but not that of Triton X-100, showing that this approach is of limited value at BiFEs on these composite electrodes.

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