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Effect of Bi(III) concentration on the stripping voltammetric response of in situ bismuth-coated carbon paste and gold electrodes

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Abstract

The effect of Bi(III) concentration (over the wide concentration range of 10^{-7} to 10^{-4} M) on the determination of Pb and Cd metal ions (in the 10^{-8} to 10^{-5} M range), by means of anodic stripping voltammetry (ASV) at in situ bismuth-coated carbon paste (CPE) and gold electrodes, has been studied. It is shown that in square wave anodic stripping voltammetry (SWASV) experiments the sensitivity of the technique generally depends on the Bi(III)-to-metal ion concentration ratio. It was found that, unlike the usually recommended at least 10-fold Hg(II) excess in anodic stripping experiments at in situ prepared mercury film electrodes, Bi(III)-to-metal ion ratios less than 10 are either optimal or equally effective at CPE and Au electrode substrates. Detection limits down to $0.1 \,\mu g \, L^{-1}$ for Pb(II) and $0.15 \,\mu g \, L^{-1}$ for Cd(II) were estimated at CPEs under conditions of small or moderate Bi(III) excess. Depending on Bi(III) concentration and deposition time, multiple stripping peaks attributed to Bi were recorded (especially in the case of Au substrates), indicating various forms of Bi deposits.

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1. Introduction

Since their introduction in the beginning of this decade as alternatives to mercury film electrodes for stripping voltammetry and potentiometry [1-3], bismuth-coated electrodes are being intensively studied and the first related reviews have already appeared in the literature [4–6]. This ever increasing interest is due to low Bi toxicity as opposed to Hg, its reasonably wide potential window (similar negative potential limit and slightly lower positive limit than that of Hg) and its ability to form alloys with many metal ions [7]. Such properties make it an environmentally friendly alternative to Hg for the determination of many heavy and toxic metal ions by anodic stripping voltammetry (ASV) and potentiometry.

Among the variety of electrode materials that have been used as substrates for Bi film plating, glassy carbon and graphitic materials have been the most common choices [1-3,8,9]. Carbon paste electrodes (CPE) have also been proven another useful

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class of electrode supports for Hg and Bi stripping voltammetry applications [10–12]. On the contrary, Au electrodes have rarely been used as substrates for Bi film electrodes [13], mainly due to their higher catalytic activity for hydrogen evolution. The latter limits the efficiency of Bi and/or metal ion deposition during the plating/accumulation step and also results in higher background currents at remaining uncovered Au regions at negative potentials. However, Au is a common and reliable electrode material that could be useful as a Bi substrate for specific metal ion detection applications (e.g. Pb, Tl, In, etc.) that are stripped-oxidised at intermediate (not too negative) potentials.

The effect of Hg film thickness on the ASV response is well established [14,15] and similar effects have been assumed for Bi films without any discrimination for the type of electrode support [1,8,9]. An optimum Hg film thickness is usually sought for the analyte concentration targeted, since too thin films would be saturated by the metal ion depositing and diffusing into the film, while too thick films (or large mercury drops) would pose mass transfer limitations to metal ion diffusing out of the film during the stripping step. In cases that the Hg or Bi films are formed in situ by addition of these ions in the sample then (for all other plating parameters kept constant)

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film thickness is controlled by added Hg or Bi concentration. An empirical rule of thump that resulted from Florence's early work on Hg anodic stripping voltammetry [15] and has been followed ever since for Hg and recently for Bi electrodes too [1–11,13], suggests that mercury and bismuth ions should be added in a 10-fold at least excess with respect to metal ion analyte concentration. This is again irrespective to the type of electrode support and despite the different nature of Bi films whose solid state should certainly limit metal diffusion into and out of the bulk of the film. There are very few papers that present the effect of Bi concentration on the ASV signal and only for a particular analyte concentration level and graphite or glassy carbon electrodes [1,8,9]. To the best of our knowledge, there is no detailed study of the effect of the metal ion-to-Bi(III) bulk concentration ratio on the ASV response over a wide metal ion analyte concentration range, neither at CPE nor at Au electrode substrates. Furthermore, this effect has yet to be studied on the "normalised" ASV response, i.e. on the metal analyte stripping peak current (or charge) divided by that of co-deposited Bi [16].

The aim of the present work has been to carry out a more detailed study of the effect of the Bi(III) levels on the square wave anodic stripping voltammetry determination (SWASV) of metal ions, over a wide analyte concentration range and for electrode substrates other than graphite or glassy carbon. In more detail, its objectives have been: (i) to identify the dependence of the SWASV picture at CPE and Au electrodes, on Bi(III) ion levels and on time of deposition, (ii) to determine the effect of Bi(III) ion/metal ion concentration ratio (in the 1–400 range) on the sensitivity of Pb(II) and Cd(II) determination in the 10^{-8} to 10^{-5} M range, (iii) to determine the effect of Bi(III) ion/metal ion concentration ratio on the "normalised" (with respect to Bi [16]) SWASV response of Pb and Cd and (iv) to establish the optimum Bi(III) ion/metal ion concentrates.

2. Experimental

2.1. Chemicals and sample preparation

All chemicals used in the preparation of stock solutions were of analytical reagent grade and obtained from Merck (Damstadt, Germany) and Fluka. Concentrated CH₃COOH p.a. (Fluka) and CH₃COONa p.a. (Fluka) were used for the preparation of 1 M stock acetate buffer. Stock solutions for in situ bismuth plating, were prepared from Bi(NO₃)₃·5H₂O (Merck, Germany), while Pb(NO₃)₂ p.a. and Cd(NO₃)₂·4H₂O p.a. (Merck, Germany) were employed in the preparation of metal ion stock solutions in 0.01 mol L⁻¹ concentrations. Where appropriate, the respective solutions were diluted as needed. All the solutions of diluted standards were always stabilised by acidifying with approximatelly 1–2 mL of 65% HNO₃ (Fluka). In the preparation of solutions redistilled water was used.

2.2. *Bi film electrode substrates: carbon paste electrodes and Au electrodes*

The carbon paste used was prepared by intimate handmixing of 1.0 g spectroscopic graphite powder ("CR-5", Maziva, Tynn.Vltavou, Czech Republic) with approximately 0.6 mL highly viscous silicone oil ("SO", LUKOIL MV 800 product; Lucebni zavody Kolin, Czech Republic). Freshly made carbon paste mixtures were checked with respect to their ohmic resistance; all values were within the 5–50 Ω range, indicating sufficient compactness and homogeneity of the individual mixtures. Subsequently the paste was packed into piston-driven carbon paste holders made in the laboratory. The carbon paste electrode surface was renewed before starting a new series of experiments or prior to analysis of each sample by extruding approximately 0.5 mm of carbon paste from the holder followed by wiping with wet filter paper. The diameter of the carbon paste electrode was 2 mm.

A gold disc electrode of a 2 mm diameter (BAS Inc.) was employed. It was polished on emery paper of varied roughness and then on velvet pads soaked with alumina sluries of different alumina powder grain size (1, 0.05, 0.03 μ m; Buehler, Ltd.). Prior to each set of SWASV experiments the gold disk electrode was tested/activated by fast cyclic voltametry (at 1 V s⁻¹) between hydrogen and oxygen evolution.

2.3. In situ Bi plating procedure and anodic stripping square wave voltammetry parameters

In situ bismuth films were prepared by spiking the sample with the required Bi(III) concentration in the beginning of each set of experiments. Following that, increasing metal ion concentrations were studied by incremental spiking of the sample with the appropriate volume of mixed Pb(II) and Cd(II) stock solutions.

At a CPE the following SWASV parameters were employed:

- i. For Pb(II) and Cd(II) concentrations in the 10^{-6} to 10^{-5} M range: $E_{dep} = -1.10$ V versus Ag/AgCl; $E_{fin} = 0.00$ V (+0.2 V for the highest Bi(III) concentration used); $t_{dep} = 30$ s (under stirring); $t_{eq} = 15$ s; frequency = 25 Hz; potential step = 4 mV; amplitude = 20 mV. Before each measurement $E_{cond} = +0.10$ V was applied on the electrode for 30 s under stirring. Acetate buffer (1 M, pH 4.5) was used as a supporting electrolyte.
- ii. For Pb(II) and Cd(II) concentrations in the 10^{-7} to 10^{-6} M range: $E_{dep} = -0.95$ V versus Ag/AgCl; $E_{fin} = +0.10$ V (+0.45 V for the highest Bi concentration used); $t_{dep} = 90$ s (under stirring); $t_{eq} = 15$ s; frequency = 25 Hz; potential step = 4 mV; amplitude = 20 mV. Before each measurement $E_{cond} = +0.10$ V was applied on the electrode for 30 s under stirring. Acetate buffer (0.1 M, pH 4.5) was used as a supporting electrolyte.
- iii. For Pb(II) and Cd(II) concentrations in the 10^{-7} to 10^{-6} M range: conditions identical to those of (ii) above except that $t_{dep} = 120$ s.

At the Au disc electrode the following SWASV parameters were employed:

 $E_{dep} = -1.20 \text{ V}$ versus Ag/AgCl; $E_{fin} = +0.50 \text{ V}$; $t_{dep} = 300 \text{ s}$ (under stirring); $t_{eq} = 15 \text{ s}$; frequency = 20 Hz; potential



Fig. 1. SWASVs at Bi–CPEs in solutions of: (A) 10^{-6} M Pb²⁺ and Cd²⁺ + 10^{-5} M Bi(III), (B) 10^{-7} M Pb²⁺ and Cd²⁺ + 10^{-6} M Bi(III) and (C) 10^{-8} M Pb²⁺ and Cd²⁺ + 10^{-7} M Bi(III), for varied deposition–accumulation times at -1.10 V (A) and -0.95 V (B and C) vs. Ag/AgCl as shown in the graphs. Insets: (a) the variation of the Bi stripping current with time for different Bi(III) bulk concentrations. (b) The variation of the Pb stripping current with time from (A) 10^{-6} M Pb²⁺, (B) 10^{-7} M Pb²⁺ and (C) 10^{-8} M Pb²⁺, for different Bi(III) bulk concentrations.

step = 5 mV; amplitude = 25 mV. Before each measurement E_{cond} = +0.30 V was applied on the electrode for 30 s under stirring. Acetate buffer (0.05 M, pH 4.5) was used as a supporting electrolyte.

The relative standard deviation of the SWASV response as calculated from five repetitive measurements was better than 2, 3 and 5% for 10^{-6} , 10^{-7} and 10^{-8} M Pb(II) and Cd(II), respectively.

2.4. Electrochemical cell and instrumentation

A three-electrode cell was used, consisting of the CPE or Au disc working electrode (see Section 2.1), a Ag/AgCl (3 M NaCl; BAS Inc.), reference electrode and a Pt coil auxiliary electrode (BAS Inc.). All experiments were performed under stirring conditions, using an electrical stirrer (Metrohm E 549; 400 rpm) equipped with a magnetic bar ($1.5 \text{ cm} \times 0.5 \text{ cm}$). Samples were spiked using a 20–100 µL micropipette (WPI). The potentiostat used was a Model PGSTAT 100 Autolab (Ecochimie, Utrecht, Holand), connected to a personal computer and controlled by GPES, Version 4.8 software (Ecochimie).

3. Results and discussion

3.1. Effect of deposition time on the square wave anodic stripping voltammetry of Pb(II) and Cd(II) of Bi–CPE and Bi–Au electrodes

3.1.1. Bi-CPE electrodes

Fig. 1(A–C) shows SWASVs at Bi–CPEs in 10^{-6} , 10^{-7} and 10^{-8} M Pb²⁺ + Cd²⁺ solutions, respectively, in the presence of a 10-fold Bi(III) excess (10^{-5} , 10^{-6} and 10^{-7} M, respectively), for varied deposition–accumulation times at -1.10 V (A) and -0.95 V (B and C) versus Ag/AgCl. It can be seen that in all cases, as the accumulation time and deposited Bi quantity increases, the Bi stripping peak shifts from potential values in the -0.20 to -0.15 V versus Ag/AgCl (3 M NaCl) region (similar to that reported in general for graphite, glassy carbon and carbon paste electrodes [1-3,8-12]), towards -0.05 to 0.00 V versus Ag/AgCl (3 M NaCl) (i.e. close to the formal potential of +0.22 V versus SHE calculated for the Bi/Bi³⁺ couple in acetate buffer of pH 4.5 [5]). Closer inspection of the Bi stripping peak reveals that at longer times this peak is either deformed (Fig. 1(A and B)) or even split in two (Fig. 1(C)), with a hump or an over-



Fig. 2. SEM micrographs of CPE (A) and Bi–CPE (B–D) surfaces, at magnifications indicated by the scale bars. Deposition was carried out for 300 s at -1.00 V vs. Ag/AgCl under stirring, from solutions of (B) 1×10^{-4} M and (C and D) 4×10^{-4} M Bi(III), in the presence of 1×10^{-5} M Pb(II) + Cd(II).

lapping peak in the -0.20 to -0.15 V range. It is reasonable to assume that the peak or hump at more negative potentials corresponds to weakly bonded Bi on carbon paste (preferentially formed at low coverage values) while the peak at less negative potentials corresponds to bulk Bi (formed on top of the former, at higher coverage values and thicker films). This picture sets the grounds for a first criterion used in this work for the choice of deposition time for each concentration range: only times short enough to avoid the formation of two types of Bi deposits and deformed stripping peaks were considered. In that case metal ions are expected to co-deposit with/on highly dispersed Bi. Also, symmetrical Bi stripping peaks would allow normalisation of metal ion stripping currents by the associated (single) Bi peak current (see [16] and discussion below).

Insets (a) in Fig. 1(A–C) show the variation of the Bi (main) stripping peak current with time of deposition at Bi–CPEs from solutions in the wide 1×10^{-4} to 1×10^{-6} M Bi(III) range. It can be seen that in all cases there is no linearity over the entire time period studied and indeed saturation begins at times longer than ca. 50 s (for 10^{-4} to 10^{-5} M Bi(III)), 100 s (for 10^{-5} to 10^{-6} M Bi(III)) and 200 s (for 10^{-5} to 10^{-6} M Bi(III)), depending on bismuth concentration. This is another indication of a

change in the morphology and type of the deposit. At short times and/or low concentrations, Bi is expected to be dispersed as thin patches and/or nuclei on carbon regions of the CPE. As the time of deposition and/or Bi concentration increases, and since the deposition is carried out under conditions of mass transfer control at potentials more negative than -0.95 V, the deposit is expected to thicken in a non-uniform way as it grows preferentially on top of already deposited patches (see Fig. 2). This uneven development may result in high local current densities which in turn may decrease the current efficiency of Bi deposition in favour of the parasitic hydrogen evolution reaction (such effects are well established for metal deposition at substantially negative potentials-under mass transfer control). Hence, the rate of Bi deposition gradually falls. Insets (b) in Fig. 1(A–C) show the variation of the Pb stripping peak current with time of deposition at Bi–CPEs from 1×10^{-6} , 1×10^{-7} and 1×10^{-8} M solutions of Pb²⁺, respectively, in the presence of a 10- and 100-fold excess of Bi(III). It can be seen that linearity is restricted to periods shorter than ca. 100 s for the highest Pb^{2+} concentration and ca. 200 s for the two lower concentrations and that signal saturation is observed again at longer times (similar results were obtained for Cd too). The

fact that the metal ion stripping peak current follows the same time variation as that of Bi can be rationalised if one takes into account the variation of deposited Bi area with time and the fact that Pb and Cd are preferentially deposited on the surface of the solid Bi deposits where they form stable alloys [7].

The changes in Bi deposit morphology with changing Bi(III) bulk concentration, used to interpret the variation of Bi (and Pb) stripping currents, are supported by the SEM pictures shown in Fig. 2 which depicts deposits from 1×10^{-4} and 4×10^{-4} M Bi(III) solutions (in the presence of 1×10^{-5} M Pb(II) + Cd(II)), formed under stirring during a 300 s accumulation time at CPEs. (It should be noted that only for these higher range Bi(III) concentrations and for such relatively long deposition periods was it possible to observe by SEM significant quantities of Bi on CPEs). Fig. 2(A) shows the surface of a bare CPE substrate with the carbon particles and their agglomerates bound together by the viscous silicone oil. Fig. 2(B) depicts a Bi-covered part of the CPE after a 300 s accumulation period from a 10^{-4} M Bi(III) solution. The Bi deposits can be seen as white/grey patches/islands or near-spherical agglomerates that partially cover the carbon particles' surface. At the higher concentration of Fig. 2(C) $(4 \times 10^{-4} \text{ M Bi(III)})$, a thin skin-underlayer of coalescing islands is seen to cover a large part of the surface but the deposit has started to thicken in a non-uniform manner forming dendritic structures, typical of uneven deposition under conditions of mass transfer control. Finally, Fig. 2(D) presents a larger scale view of the surface of the substrate shown in Fig. 2(C).

A very useful approach in SWASV at Bi electrodes, recently introduced by Wang et al. [16] to account for signal variations due to changes in mass transfer rate and deposition time, is based on the normalisation of the metal ion stripping current with Bi stripping peak current. A constancy of this ratio implies a similar effect of these parameters on metal and Bi deposition and most likely a constant deposit morphology and metal-Bi interactions too. It should also allow comparison of data obtained at different deposition times, provided that this ratio stays constant within the corresponding time range for each set of data. Fig. 3(A and B) and their insets show the variation of the normalised Pb and Cd stripping peak current with time of deposition at Bi-CPE, from 1×10^{-8} and 1×10^{-6} M Pb(II) + Cd(II) solutions in the presence of a 10- and 100-fold excess of Bi(III). It can be seen that, for times not exceeding 200 s, the normalised peak current remains almost constant with deposition time in all cases. (A more complex variation, depending on the type of metal ion and Bi(III) concentration, was observed at longer periods but this is beyond the scope of this paper.) It should be noted that for both high and low Pb(II) and Cd(II) concentrations, the normalised current is always higher in the presence of a 10-fold excess than in a 100-fold one, indicating a higher utilisation of Bi deposit for SWASV purposes at a lower Bi coverage. This is because metal occlusion, which may occur during co-deposition within the three-dimensional structures of thicker Bi deposits (see Fig. 2(C)), should be limited at thin Bi deposits.

Based on the requirements set above (a single Bi stripping peak, near-linearity of Bi and metal ion peak current variation with time and constancy of the normalised current in that



Fig. 3. Variation of the normalised (with respect to Bi signal) Pb (A) and Cd (B) stripping peak current with time of deposition at Bi–CPEs, from 1×10^{-8} M and (inset) 1×10^{-6} M solutions, in the presence of a 10- and 100-fold excess of Bi(III), as indicated on the graphs.

timescale) and the results of Figs. 1–3, the deposition times chosen for the three Pb and Cd ion ranges studied, i.e. 10^{-8} to 10^{-7} , 10^{-7} to 10^{-6} and 10^{-6} to 10^{-5} M, were 120, 90 and 30 s, respectively.



Fig. 4. SWASVs at a Bi–Au disc electrode in 10^{-6} M Bi(III) solutions, for varied deposition–accumulation times at -0.8 V vs. Ag/AgCl (3 M NaCl), as indicated on the graph. Inset: SWASVs at a Bi–Au disc electrode in 1×10^{-6} and 5×10^{-6} M Bi(III) solutions, after a 300 s deposition–accumulation time at -1.2 V vs. Ag/AgCl (3 M NaCl).

3.1.2. Bi-Au disk electrodes

Fig. 4 shows SWASVs at a Bi–Au disc electrode in 10^{-6} M Bi(III), for varied deposition-accumulation times at -0.80 V versus Ag/AgCl (3 M NaCl). It can be seen that, even at the shorter times of 30 s used, at least three Bi stripping peaks are recorded: a peak at ca. 0.00 V versus Ag/AgCl (3 M NaCl), a peak at ca. +0.10 V versus Ag/AgCl (3 M NaCl) and a hump at ca. +0.30 V versus Ag/AgCl (3 M NaCl). The first of these peaks, whose height increases with increasing deposition time, occurs at the position expected for the stripping of bulk Bi [5] (an ill-defined shoulder to this peak, recorded at longer times at potentials ca. -0.10 V, may be attributed to some form of weakly bonded Bi). The broad peak recorded in the +0.10 to +0.15 V range should be due to strongly bonded Bi deposits on Au and its decrease with deposition time may be explained by the increased Bi-Bi interactions as bulk Bi is deposited, at the expense of strong Bi-Au interactions. A similar anodic stripping behaviour and metal-substrate interaction postulation has been reported for the stripping of Hg from Au [17]. Finally,

the hump at ca. +0.30 V versus Ag/AgCl (3 M NaCl) lies in the region were underpotentially deposited Bi has been reported to strip off [18,19] (recording of UPD features in the same scale as those attributed to the bulk deposit is possible for such low Bi(III) concentrations and hence small deposit quantity). A rather unexpected feature of the SWASVs of Fig. 4 is that the total area of the Bi stripping peaks (hence the amount of Bi deposited too) hardly increases as the deposition time increases from 30 to 300 s, indicating a decrease in Bi deposition efficiency as this starts to grow on Bi pre-deposited layers than on Au sites of strong Bi-Au interactions. The inset to Fig. 4 presents the effect of Bi(III) concentration on the shape and magnitude of the Bi stripping peak; it can be seen that upon increasing the Bi(III) concentration from 10^{-6} to 5×10^{-6} M, the bulk Bi peak at 0.00 V dominates, the strongly bound Bi peak at +0.10 V is suppressed/hidden in the former, while the shoulder of weakly bound Bi at -0.10 V is still present.

The multiplicity or deformation of Bi stripping peaks recorded at Bi–Au electrodes for all deposition times and Bi(III)



Fig. 5. (A) SWASVs at Bi–CPEs from solutions of Pb²⁺ and Cd²⁺ of increasing concentration in 1×10^{-8} M steps in the 2×10^{-8} to 1×10^{-7} M range. Bi(III) concentration is 10^{-7} M and deposition time at -0.95 V vs. Ag/AgCl (3 M NaCl) is 120 s. Insets: calibration plots for Pb²⁺ and Cd²⁺ in the presence of 10^{-7} , 10^{-6} and 4×10^{-6} M Bi(III). (B) Same as in (A) but for increasing concentration in 1×10^{-7} M steps in the 1×10^{-7} to 1×10^{-6} M range. Bi(III) concentration is 10^{-6} M and deposition time at -0.95 V vs. Ag/AgCl (3 M NaCl) is 90 s. Insets: calibration plots for Pb²⁺ and Cd²⁺ in the presence of 10^{-6} , 10^{-5} and 4×10^{-5} M Bi(III). (C) Same as in (A) but for increasing concentration in 1×10^{-6} M steps in the 1×10^{-6} M range. Bi(III) concentration is 10^{-5} M and deposition time at -1.10 V vs. Ag/AgCl (3 M NaCl) is 30 s. Insets: calibration plots for Pb²⁺ and Cd²⁺ in the presence of 10^{-5} M and deposition time at -1.10 V vs. Ag/AgCl (3 M NaCl) is 30 s. Insets: calibration plots for Pb²⁺ and Cd²⁺ in the presence of 10^{-5} M and deposition time at -1.10 V vs. Ag/AgCl (3 M NaCl) is 30 s. Insets: calibration plots for Pb²⁺ and Cd²⁺ in the presence of 10^{-5} , 10^{-4} and 4×10^{-4} M Bi(III).

concentration values studied led to the following two choices: first, since even at short times a single Bi peak could not be recorded, the time of deposition was chosen at the relatively long time of 300 s. (Preliminary tests have proven long accumulation periods necessary to improve the Cd and Pb response at a Bi film formed on the smooth-small area and hydrogen evolving Au substrate.) Second, the normalisation of the metal stripping response could only be done with respect to the total area–charge under the Bi stripping peaks (hence the metal ion signal should also be expressed in that case as the corresponding stripping peak area).

3.2. Effect of Bi(III) ion concentration on the determination of Pb(II) and Cd(II) at Bi–CPE electrodes

Fig. 5(A–C) shows SWASVs for Pb(II) and Cd(II) determination at Bi–CPEs from metal ion solution concentrations in the 10^{-8} to 10^{-7} , 10^{-7} to 10^{-6} and 10^{-6} to 10^{-5} M ranges in the presence of 10^{-7} , 10^{-6} and 10^{-5} M Bi(III), respectively (i.e. depending on metal ion concentration, in the presence of a 10:1 to 1:1 Bi(III)-to-metal ion concentration ratio, $c_{\text{Bi}}/c_{\text{M}}$). The insets show the respective calibration curves, which include results for higher Bi(III) concentrations too (for each concentration range $c_{\text{Bi}}/c_{\text{M}}$ takes values from 400 to 1). The slight curvature of these plots (especially for medium and high metal ion concentrations) highlights the effect of $c_{\text{Bi}}/c_{\text{M}}$ on the response of Bi–CPEs even when this ratio is changing simply due to the analyte concentration changing within a single calibration plot.

From the calibration plots of Fig. 5(A) it follows that, for the lower Pb(II) and Cd(II) levels studied $(10^{-8} \text{ to } 10^{-7} \text{ M})$ the response was not very sensitive to Bi ion levels in the entire 400-1 excess range (especially in the case of Pb). This indicates that, for Bi(III) ion concentrations in the 10^{-7} to 4×10^{-6} M range and an accumulation time of 120 s, the deposit morphology does not change significantly and the increase in available Bi surface area is probably offset by metal ion codeposition/entrapment within the inner layers of Bi particles. The calibration plots of Fig. 5(B) show that for the medium concentration range of 10^{-7} to 10^{-6} M Pb(II) and Cd(II), although the response was again similar whether 10^{-6} or 10^{-5} Bi(III) was used, the response deteriorated for the higher concentration of 4×10^{-5} Bi(III) to very low levels both for Cd and (in particular) for Pb. This is an indication that at Bi(III) ion concentrations around 4×10^{-5} M and accumulation times of 90 s there is a change in deposit morphology, as the deposit changes from a thin layer of a highly dispersed and easily accessible structure to a denser layer, consisting of irregular three-dimensional structures of lower specific surface area. The calibration plots of Fig. 5(C) show that for the higher concentration range of 10^{-6} to 10^{-5} M Pb(II) and Cd(II), the response was insensitive to Bi(III) levels (in the 10^{-5} to 4×10^{-4} M range) in the case of Cd but deteriorated for the higher concentration of Bi(III) in the case of Pb (but to a lower extent than in the previous case). Thus, one could infer a slight deposit change at Bi(III) ion concentrations around 4×10^{-4} M and accumulation times of 30 s (in a way similar to that of Fig. 2), which is only detected during Pb determination since this is apparently more sensitive to Bi concentration and resulting deposit morphology.

The detection limits (S/N=3), calculated from 10^{-8} M Pb(II) + Cd(II) data according to the procedure of Reference [20], were estimated as 5×10^{-10} M (ca. 0.1 µg L⁻¹) for Pb(II) and 1.3×10^{-9} M (ca. 0.15 µg L⁻¹) for Cd(II) which are lower than those reported for CPEs [5,21,22] and comparable (or even lower) to those of glassy carbon and graphite electrodes [1–3,8,9,23]. Table 1 presents a comparison of Pb(II) and Cd(II) detection limits reported in selected works of ASV at Bi-coated electrodes of various types.

What is important to note from Fig. 5 is that, irrespective of the metal ion concentration targeted, a slight Bi(III) excess in the 1-10 range is adequate in obtaining high quality and sensitivity data at CPE electrodes, equal or better to those obtained for an excess in the 10-100 range. This is further stressed by the results of Fig. 6(A-C) which present SWASVs for the same Pb(II) + Cd(II) concentration in each case (10⁻⁷ M (A), 10⁻⁶ M (B) and 10^{-5} M (C)) but for a varied Bi ion excess (1-, 10- and 40-fold). Surprisingly, even a Bi(III)-to-metal ion ratio of 1:1 is enough to produce the highest Pb and Cd stripping peaks in all cases, whereas when this ratio exceeded the 40:1 value, a signal deterioration was obtained in most cases. This is again and indication of better Bi deposit utilisation for metal ion accumulation on its surface at low coverage-dispersed morphology Bi deposits. This is also reflected in the results of the insets to Fig. 6(A-C) which show the variation of the ratio of the metal stripping current to the Bi stripping current with metal ion concentration, for two different Bi ion concentrations in each case: one corresponding to an excess in the 1-10 range and one in the 10-100range. It can be seen that in all cases the sensitivity-slope of the normalized calibration plots is much higher for the lower con-

Table 1

Pb(II) and Cd(II)	detection limits	by anodic s	stripping te	chniques at l	Bi-coated	carbon-	based	electrode	substrates
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Electrode substrate	Bi plating method	Analytical technique	Accumulation time (s)	$\begin{array}{c} Pb(II) \\ (\mu g L^{-1}) \end{array}$	$\begin{array}{c} Cd(II) \\ (\mu g L^{-1}) \end{array}$	Reference
Carbon paste	In situ	SWASV	120	0.1	0.15	This work
Carbon paste	In situ	Anodic stripping potentiometry	600	0.5		[5]
Carbon paste (heated)	In situ	SWASV	120	3.16		[22]
Graphite-epoxy composite	In situ	SWASV	120	23.1	2.2	
Carbon fibre In situ		SWASV	600	0.3		[1]
Screen-printed carbon	Ex situ	SWASV	600	0.3		[2]
Glassy carbon	Ex situ	SWASV	600	0.2	0.2	[8]
Pencil-lead carbon	In situ	SWASV	600	0.4	0.3	[9]



Fig. 6. SWASVs at Bi–CPEs from (A) 10^{-7} M, (B) 10^{-6} M and (C) 10^{-5} M Pb²⁺ + Cd²⁺ solutions, for varied Bi(III) excess values (1-, 10- and 40-fold) as indicated on the graphs. Deposition at -0.95 V vs. Ag/AgCl (3 M NaCl) for (A) 120 s, (B) 90 s and at -1.10 V for (C) 30 s. Insets: (a) the variation (with respect to Bi signal) of the normalised stripping current of Pb with Pb(II) bulk concentration. (b) Similar to (a) results for Cd.

centrations of Bi(III) used and that, in the low and medium Pb(II) and Cd(II) concentration ranges $(1 \times 10^{-8} \text{ to } 1 \times 10^{-6} \text{ M})$, the linearity of the plots is also improved. These findings suggest that, if Wang's approach for stripping peak normalisation is to be followed (to correct for experimental conditions variations), then the use of a low rather than high Bi excess is more appropriate. Also, a comparison of the (normalized) sensitivities for the three metal ion concentration range studied, reveals that these get higher as the concentration range decreases, suggesting that the effect of higher Bi utilisation for low Bi(III) concentrations is more pronounced in the detection of low metal concentrations (which is of course more relevant to trace metal applications).

3.3. Determination of Pb(II) and Cd(II) a Bi–Au electrode for two different Bi ion concentration levels

Fig. 7(A and B) shows the SWASVs for Pb(II) and Cd(II) determination at a Au disc electrode from their solutions in the 10^{-8} to 10^{-6} and 5×10^{-8} to 10^{-6} M range, respectively, in the presence of 10^{-6} M (A) and 5×10^{-6} M (B) Bi(III). Two immediate observations can be made. First, a Cd peak could

not be obtained for concentrations lower than 1×10^{-7} M and this may be due to the fact that this occurs at potentials close to the hydrogen evolution reaction and/or to a low Cd deposition efficiency. The latter may arise from the lower diffusivity of Cd(II) ions (when compared to Pb(II) [24]) or their lower affinity for Au and co-deposited Bi, which may be accentuated under conditions of low metal ion deposition efficiencies due to the parasitic hydrogen evolution reaction that is known to occur at Au (at rates higher than at CPE).

The second observation is related to the multiplicity (Fig. 7(A)) or deformation (Fig. 7(B)) of the Bi stripping peak(s) and their area change as the calibration proceeds. The increase in Bi stripping peak(s) area was found to occur both at successive experiments in blank (only Bi-containing) solutions and in calibration experiments, irrespective of whether these were they were performed for descending or ascending metal ion concentrations. Hence, this change is related with the increasing number of experiments and is more likely due to a change in Au electrode roughness as it is pulsed between the negative deposition (-1.1 V versus Ag/AgCl) and positive cleaning (+0.5 V versus Ag/AgCl) potentials before each SWASV. Regarding the multi-



Fig. 7. SWASVs at a Bi–Au disc electrode from solutions of Pb²⁺ and Cd²⁺ in the 10^{-8} to 10^{-6} M and 5×10^{-8} to 10^{-6} M concentration ranges, respectively, in the presence of (A) 10^{-6} M and (B) 5×10^{-6} M Bi(III). Deposition time at -1.1 V vs. Ag/AgCl (3 M NaCl) was 300 s.

plicity of the Bi peak in Fig. 7(A) and as also discussed in Section 3.1, the main peak between -0.2 and +0.2 V is due to bulk Bi whereas that at +0.2 to +0.3 V should be due to underpotentially deposited Bi (hence it is affected more by an increase in roughness). At higher Bi(III) concentrations (Fig. 7(B)) all Bi peaks merge into a wide, deformed peak. The change of Bi peak area (thus of deposited Bi quantity too) between experiments makes Wang's approach for signal normalisation [16] even more relevant for Au electrodes. Also, the multiplicity/deformation of this peak makes the use of peak area mandatory for its accurate quantification and has led to the choice of peak area as the metal ion stripping signal too.

Fig. 8(A) and its inset show the change of Pb and Cd stripping peak areas, respectively, with metal ion concentration for two different Bi(III) levels. Depending on metal ion concentration these two levels correspond to a (100–1)- or (500–5)-fold Bi(III) excess for Pb(II) and to a (10–1)- or (50–5)-fold Bi(III) excess for Cd(II). It can be seen that for Pb, there is virtually no effect of Bi(III) excess on the response whereas for Cd there is some limited effect. (Note also the very poor response of the



Fig. 8. (A) Calibration plots of Pb²⁺ and (inset) Cd²⁺ at a Bi–Au disc electrode in the presence of 10^{-6} and 5×10^{-6} M Bi(III), based on the corresponding metal ion peak area of the SWASVs of Fig. 7. (B) Normalised (with respect to Bi stripping charge) calibration plots of Pb²⁺ and (inset) Cd²⁺ at conditions similar to those of (A).

Bi–Au electrode to Cd for concentrations below 5×10^{-7} M, indicating that SWASV at Bi-Au is inappropriate for Cd trace determination under the conditions employed.) This insensitivity of the response of Bi-Au electrodes to a wide range of Bi(III) excess contrasts the behaviour of Bi-CPE electrodes where it was found that a higher than 40-fold excess is detrimental to the response in most cases (Fig. 6). The difference should arise from the different type of electrode substrate in the two cases and its effect on deposit morphology: in CPEs the electrode material (carbon particles) is of a dispersed type and hence, depending on its coverage, the deposited Bi can be either in the form of dispersed nuclei (low coverage) or of thick dentritic deposits (high coverage) (see SEMs of Fig. 2 and Reference [25]); the Au disc electrode has a uniform surface and hence Bi deposits formed on it are expected to be more uniform (similar to uniformly covered glassy carbon electrodes [6]). What is interesting however is that, for Bi-Au electrodes too, low Bi(III) excess values equal or less than 10 are still adequate to obtain high metal stripping responses.

Finally, Fig. 8(B) and its inset presents the variation of the metal ion stripping peak charge normalised by the Bi stripping peaks area, with metal ion concentration, for the two Bi(III) excess levels studied, for both Pb and Cd. It can be seen that the normalised response for Pb is again higher for the lower Bi(III) excess used indicating better Bi utilisation (but the effect is not as pronounced as for Bi–CPE; see Fig. 6), whereas for Cd the response and utilisation is similar in both cases (in the linear region).

4. Conclusions

- (i) Values of the Bi(III)-to-metal ion concentration ratio in the 10–1 range were adequate for in situ prepared Bi–CPE electrodes in obtaining the higher sensitivity in the square wave anodic stripping voltammetric determination of Pb(II) and Cd(II) ions in a wide 10^{-8} to 10^{-5} concentration range. Detection limits down to $0.1 \,\mu g \, L^{-1}$ for Pb(II) and $0.15 \,\mu g \, L^{-1}$ for Cd(II) were estimated at CPEs under conditions of small or moderate Bi(III) excess. However, at excess values higher than ca. 40, signal deterioration was observed in most cases.
- (ii) The sensitivity of Au–CPE in the SWASV determination of Pb(II) and Cd(II) ions in the 10^{-8} to 10^{-6} M concentration range is almost unaffected by the Bi(III) excess but again, high sensitivities are still attained for excess values less than 10.
- (iii) The findings of (i) and (ii) above that the determination of metal ions by SWASV at in situ formed Bi–CPE and Bi–Au is possible even at Bi(III) excess values less than 10 (the commonly used minimum excess in Hg-based anodic stripping voltammetry and, until now, in its Bi-based variant) may have significant electroanalytical implications: the use of very small quantities of added Bi will make the approach even cleaner and introduce fewer impurities. More importantly, it would limit Bi(III) hydrolysis, hence decrease the concentration of buffer needed and further minimise added impurities.
- (iv) The variation of Bi stripping peaks (and correspondingly, of quantity of deposited Bi) with successive SWASV experiments at Au electrodes, makes the normalisation of the metal ion signal by the Bi signal proposed by Wang et al. [16] essential in that case. The multiplicity or deformation of the Bi peak necessitates then the use of the stripping peak area-charge as the signal, if Wang's approach for data normalisation is to be followed for Au.

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