



Disposable screen-printed sensors modified with bismuth precursor compounds for the rapid voltammetric screening of trace Pb(II) and Cd(II)

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ABSTRACT

In this article, a study of novel screen-printed electrodes bulk-modified with five potential bismuth precursor compounds (bismuth citrate, bismuth titanate, bismuth oxide, bismuth aluminate and bismuth zirconate) is presented for the determination of Cd(II) and Pb(II) by anodic stripping voltammetry. During the electrolytic deposition step, the precursor was reduced and served as the source of bismuth. Different key parameters were investigated in detail such as the nature of the bismuth precursor compound, the precursor content in the carbon ink, the polarisation range of the sensors, the supporting electrolyte, the stripping waveform, the deposition time, the deposition potential and the long-term stability of the sensors under continuous use. Using bismuth citrate as the precursor, the limit of detection was $0.9 \mu\text{g L}^{-1}$ for Pb(II) and $1.1 \mu\text{g L}^{-1}$ for Cd(II). The reproducibility on the same sensor (expressed as % relative standard deviation, ($n=8$)) was 5.4% for Pb(II) and 7.2% for Cd(II) at the $20 \mu\text{g L}^{-1}$ level. Finally, the sensors were applied to the determination of Cd(II) and Pb(II) in water samples.

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1. Introduction

Over the last decade, bismuth has emerged as a promising electrode material for the fabrication of voltammetric sensors [1–4]. The main attractive property of bismuth-based sensors is the low toxicity of bismuth and its compounds while their performance closely resembles that of their mercury counterparts. Therefore, bismuth electrodes can serve as environmentally friendly replacements for mercury electrodes in stripping analysis.

Different types of bismuth-based sensors have appeared but the most ubiquitous and widely used configuration in stripping analysis is the bismuth-film electrode (BiFE) [1–3]. BiFEs are normally fabricated by electroplating which involves coating of a conductive support material with a thin bismuth film. The electroplating step can be performed by reduction of Bi(III) to metallic bismuth either from a separate Bi(III) plating solution prior to the analysis (*ex-situ* plating) or by adding directly Bi(III) into the sample solution and co-deposition of bismuth and the target metals during the analysis (*in-situ* plating); the main strengths and weaknesses of these alternative approaches have been discussed previously [1,3]. However, the main drawbacks of electroplating are the requirement to use and manipulate a Bi(III) plating solution (with

the associated limitations imposed by the tendency of Bi(III) to hydrolyse and form complexes [5]) and the notoriously strong dependence of the morphology of the bismuth deposit on the plating conditions [5–9]. In order to address these limitations, microengineering thin-layer deposition techniques have been applied to form bismuth films but such approaches require expensive instrumentation and clean-room facilities [10–13].

The use of bismuth precursor compounds is a convenient alternative approach to fabricate a BiFE. The principle of operation is the modification of the working electrode with a bismuth precursor (a Bi(III) compound). Generation of the bismuth film occurs by reductive potentiostatic polarisation of the electrode during which the Bi(III) in the precursor is reduced to metallic bismuth. However, the utilisation of bismuth precursor compounds for bismuth film formation has attracted only limited attention. The first report of such a sensor was a carbon paste electrode loaded with Bi_2O_3 [14,15] followed by reports of a graphite–epoxy composite electrode containing $\text{Bi}(\text{NO}_3)_3$ [16], and carbon paste electrodes modified with ammonium tetrafluorobismuthate [17] or BiF_3 [18]. Screen-printing technology enables the rapid fabrication of disposable, inexpensive electrodes and allows convenient modification of the electrode by simply mixing the modifier with the base electrode material (normally carbon ink) [19,20]. Screen-printed electrodes bulk-loaded with Bi_2O_3 [21–24] have been reported for the determination of trace metals by voltammetric techniques; however, all the screen-printed sensors reported so far utilise exclusively

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Bi_2O_3 as the bismuth precursor compound. Recently, preliminary results from our group have demonstrated that alternative bismuth modifiers could be used to good effect in conjunction with screen-printed electrodes for trace metal analysis by stripping voltammetry [25].

The aim of the present work was to assess five different bismuth(III) compounds (bismuth citrate $[\text{O}_2\text{CCH}_2\text{C}(\text{OH})(\text{CO}_2)\text{CH}_2\text{CO}_2]\text{Bi}$, bismuth titanate ($\text{Bi}_2\text{O}_3 \cdot 2\text{TiO}_2$), bismuth oxide (Bi_2O_3), bismuth aluminate ($\text{Bi}_2(\text{Al}_2\text{O}_4)_3 \cdot \text{H}_2\text{O}$) and bismuth zirconate ($2\text{Bi}_2\text{O}_3 \cdot 3\text{ZrO}_2$)) as potential bismuth precursors for the fabrication of disposable modified screen-printed electrodes for the voltammetric determination of trace $\text{Pb}(\text{II})$ and $\text{Cd}(\text{II})$. The selection of these compounds was made in terms of their low solubility in aqueous media and appropriate mean particle size, compatible with the screen-printing process. Different critical parameters related to both the electrode fabrication and the measurement procedure were investigated, the analytical features of the respective sensors were derived and the sensors were applied to the analysis of water samples.

2. Experimental

2.1. Chemicals and reagents

All chemicals used for the preparation of stock and standard solutions were of analytical reagent grade and purchased from Merck (Darmstadt, Germany) or Sigma–Aldrich (USA). 1.0 and 0.1 mol L^{-1} stock solutions of acetate buffer (pH 4.5) and ammonia buffer (pH 9.2) as well as 0.05 mol L^{-1} stock solutions of nitric acid, hydrochloric acid, phosphoric acid and sulphuric acid were used as supporting electrolytes. Bismuth oxide (Bi_2O_3 , grain size $\leq 10 \mu\text{m}$), bismuth zirconate ($2\text{Bi}_2\text{O}_3 \cdot 3\text{ZrO}_2$, 325 mesh) and bismuth titanate ($\text{Bi}_2\text{O}_3 \cdot 2\text{TiO}_2$, 325 mesh) were purchased from Sigma–Aldrich. Bismuth aluminate ($\text{Bi}_2(\text{Al}_2\text{O}_4)_3 \cdot \text{H}_2\text{O}$, $x \approx 10$, grain size $\leq 2 \mu\text{m}$) and bismuth citrate ($[\text{O}_2\text{CCH}_2\text{C}(\text{OH})(\text{CO}_2)\text{CH}_2\text{CO}_2]\text{Bi}$, grain size $\leq 10 \mu\text{m}$) were purchased from Alfa Aesar. A 0.1 mol L^{-1} $\text{K}_4[\text{Fe}(\text{CN})_6]$ solution was prepared in doubly distilled water. Metal cation 20 mg L^{-1} working stock solutions were prepared from 1000 mg L^{-1} atomic absorption standard solutions. All standard and stock solutions were diluted as required with doubly distilled water.

2.2. Apparatus

A Pamsens potentiostat (Palm Instruments BV, The Netherlands) was used in combination with the PStTrace 2.1 software (Pamsens). Measurements were performed in a standard glass voltammetric cell. A Ag/AgCl (sat. KCl) reference electrode and a Pt wire auxiliary electrode completed the cell; all potentials in the text are referred vs the Ag/AgCl (sat. KCl) reference electrode. A magnetic stirrer operating at approx. 1000 rpm provided stirring during the deposition step. An optical microscope (Karl Suss PA 200, SUS Microtec) was used for imaging of the surface of the microelectrodes. Transmission electron microscope (TEM) images were obtained using a high resolution instrument (JEOL JEM-2100, Tokyo, Japan) equipped with a LaB_6 filament operating at 200 kV. Samples were deposited on a holey carbon grid, after dissolving the screen-printed electrodes in acetone.

2.3. Working electrode fabrication

Screen-printed electrodes were fabricated over a polyester substrate (Mac Dermid, UK) using a DEK Model 247 screen printer (UK) and polyester screens with 230 mesh for the graphite ink (Electrodag PF-407A, Acheson Colloiden, NL) and 280 mesh for

the dielectric ink (D2000222D2, Gwent Ltd., UK). Inks were forced through an emulsion ($13\text{--}20 \mu\text{m}$ thick) with the desired pattern using a polyurethane 75 durometer squeegee. Screen-printed electrodes were printed in arrays of five (working) electrodes and consisted of three layers, which were printed in the following order: (i) a layer made of graphite that acted as the conductive track; (ii) the graphite layer loaded with the bismuth precursor (working layer), and; (iii) the dielectric layer with openings allowing external electric contact to one end of the sensor and access of analyte to bismuth layer at the other. Each layer was cured in an oven according to the following conditions: graphite layer, 90°C for 30 min; working layer, 90°C for 120 min, and dielectric layer, 60°C for 30 min. The graphite layer loaded with the bismuth precursor was produced by mixing appropriate amounts of the bismuth precursor compound and graphite ink. Screen-printed electrodes in which the working layer was graphite without the addition of modifier were also fabricated and used as supports for *in situ* plated BiFEs.

2.4. Sample preparation

18.0 mL of the certified lake water sample (TM 24.3, Environment Canada, Burlington, Canada) was adjusted to pH 4.5 with ammonia solution. The sample was spiked with ferrocyanide ions to a final concentration of 0.05 mmol L^{-1} . Finally, the sample was diluted with 1 mol L^{-1} acetate buffer (pH 4.5) to a final volume of 20.0 mL .

18.0 mL from a tap water sample collected in our laboratory was spiked with ferrocyanide ions to a final concentration of 0.05 mmol L^{-1} and the sample was diluted with 1 mol L^{-1} acetate buffer (pH 4.5) to a final volume of 20.0 mL .

2.5. Measurement procedure

For the cyclic voltammetry experiments, the solutions were deoxygenated by bubbling with N_2 (purity of 99.9%) for approx. 10 min. Anodic stripping voltammetry experiments were carried out in the presence of oxygen.

2.6. Cyclic voltammetry

The polarisation range and electrode processes related to the bismuth precursor-modified screen-printed electrodes was investigated by cyclic voltammetry in different supporting electrolytes by potential scanning from -1.4 to 0.6 V and back at a scan rate $\nu = 50 \text{ mV s}^{-1}$ after potentiostatic polarisation at -1.4 V for 120 s.

2.7. Anodic stripping voltammetry

For anodic stripping voltammetry (ASV) experiments, involving *in situ* plating of a BiFE, screen-printed electrodes without addition of modifier were used and the sample was spiked with $\text{Bi}(\text{III})$ to a final concentration of 1 mg L^{-1} . The electrodes were immersed in the cell containing the sample and preconcentration took place at -1.4 V for 120 s (unless stated otherwise) under stirring at approx. 1000 rpm. Then, the stirring was stopped and, after an equilibration period of 10 s, an anodic voltammetric scan was performed from -1.2 V to 0.2 V . Finally, the electrode was cleaned from any remaining traces of metals at 0.2 V for 20 s under stirring at approx. 1000 rpm.

For ASV experiments with the precursor-modified screen-printed sensors, the electrodes were immersed in the cell containing the sample and preconcentration took place at -1.4 V for 120 s (unless stated otherwise) under stirring at approx. 1000 rpm.

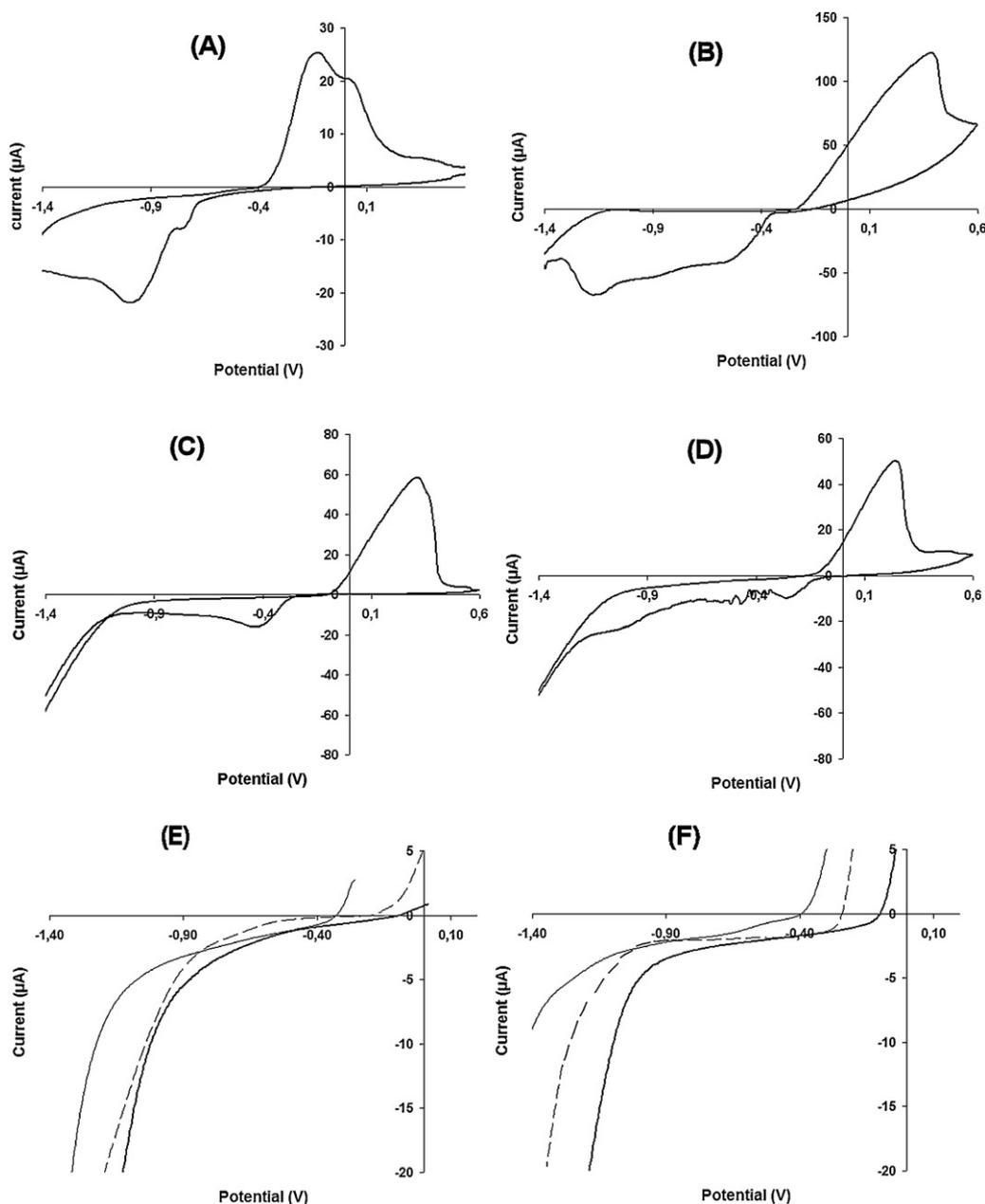


Fig. 1. Cyclic voltammograms in the range -1.4 V to 0.6 V on a screen-printed electrode modified with 6% (w/w) bismuth citrate after cathodic polarisation at -1.4 V for 120 s in: (A) 0.1 mol L^{-1} ammonia buffer (pH 9.2), (B) 0.1 mol L^{-1} acetate buffer (pH 4.5), (C) 0.05 mol L^{-1} nitric acid, (D) 0.05 mol L^{-1} hydrochloric acid; anodic linear sweep voltammograms in the range -1.4 V to 0.1 V: (E) before, and (F) after cathodic polarisation at -1.4 V for 120 s in: 0.1 mol L^{-1} ammonia buffer (pH 9.2) (—), 0.1 mol L^{-1} acetate buffer (pH 4.5) (---), 0.05 mol L^{-1} nitric acid (— · —). Scan rate 0.05 V s^{-1} .

Then, the stirring was stopped and, after an equilibration period of 10 s, an anodic voltammetric scan was performed from -1.2 V to -0.35 V. Finally, the electrode was cleaned from any remaining traces of metals at -0.35 V for 20 s under stirring at approx. 1000 rpm.

Differential pulse (DP) voltammograms were recorded using the following waveform parameters: scan rate, $\nu = 10 \text{ mV s}^{-1}$; pulse height, $E_p = 20 \text{ mV}$; pulse duration, $t_p = 50 \text{ ms}$. Square wave (SW) voltammograms were recorded using the following waveform parameters: scan frequency, $f = 50 \text{ Hz}$; pulse height, $E_p = 20 \text{ mV}$; step increment, $E_s = 4 \text{ mV}$. Linear sweep (DC) voltammograms were recorded using the following waveform parameters: scan rate $\nu = 50 \text{ mV s}^{-1}$; step increment $E_s = 4 \text{ mV}$.

3. Results and discussion

3.1. Characterisation of the sensors by cyclic voltammetry and microscopy

Initially, the screen-printed electrodes modified with the five different precursor compounds (4%, w/w) were characterised by cyclic voltammetry in the range -1.4 to 0.6 V after reduction of the precursor to metallic bismuth at -1.4 V for 120 s in four different supporting electrolytes: 0.1 mol L^{-1} acetate buffer (pH 4.5), 0.1 mol L^{-1} ammonia buffer (pH 9.2), 0.05 mol L^{-1} nitric acid and 0.05 mol L^{-1} hydrochloric acid. As illustrated in Fig. 1(A–D), which shows typical cyclic voltammograms at a screen-printed electrode modified with bismuth citrate (6%, w/w), the forward anodic scan

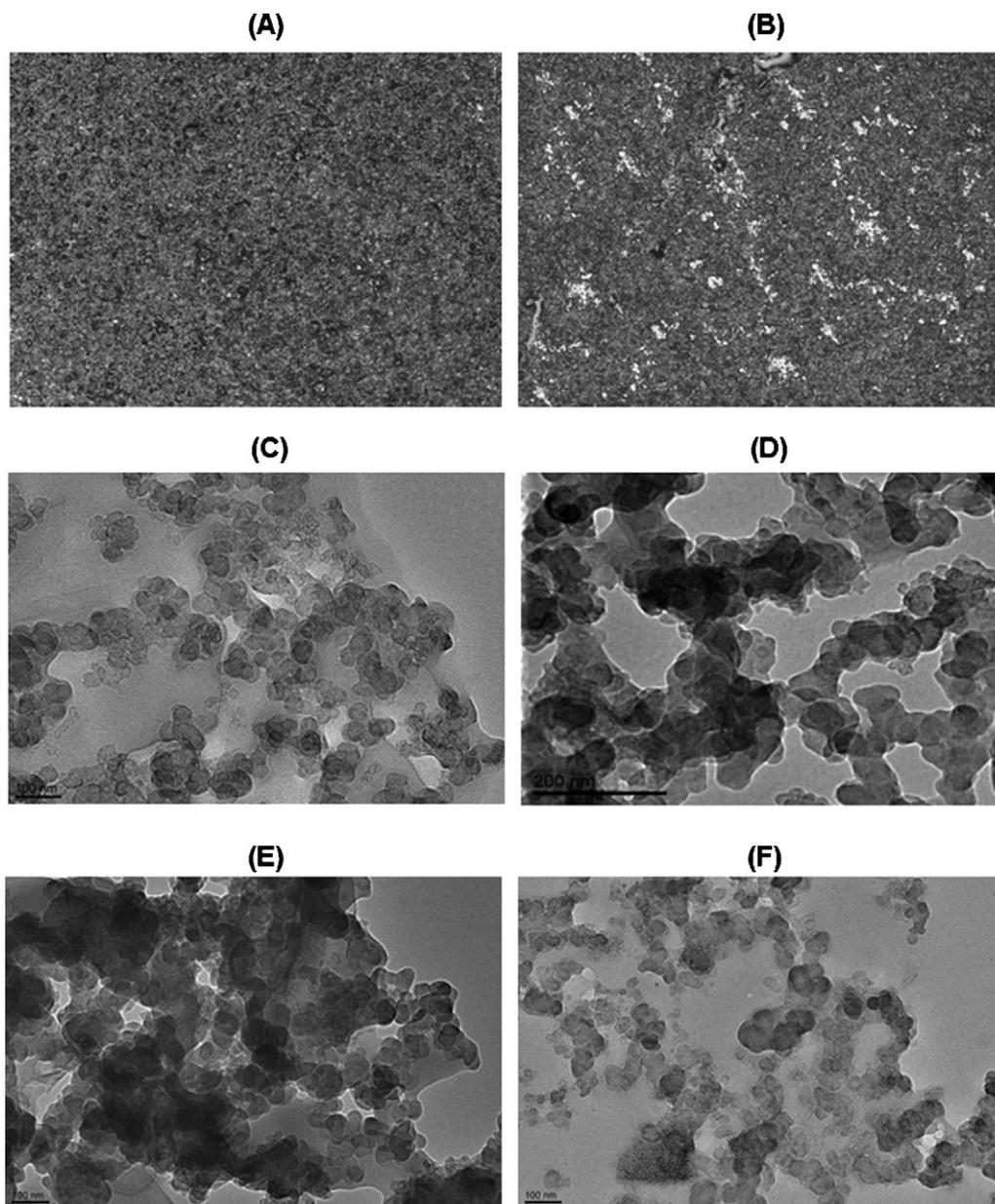


Fig. 2. Optical micrograph of a screen-printed electrode modified with 6% (w/w) bismuth citrate taken (A) before, and (B) after cathodic polarisation at -1.4 V for 120 s in 0.1 mol L^{-1} acetate buffer (pH 4.5); and TEM images of electrodes modified with 4% (w/w): (C) bismuth citrate, (D) bismuth zirconate, (E) bismuth oxide and, (F) bismuth aluminate after cathodic polarisation at -1.4 V for 120 s in 0.1 mol L^{-1} acetate buffer (pH 4.5).

in all the supporting electrolytes gave rise to an oxidation peak which was due to the oxidation of the metallic bismuth formed during the cathodic potentiostatic polarisation step preceding the cyclic voltammetry scan (Fig. 1(A–D)). This suggests that reduction of the precursor compound to metallic bismuth took place during the cathodic polarisation of the electrode. In the reverse cathodic scan, reduction peaks appeared (Fig. 1(A–C)) as a result of reduction of the Bi(III) species formed in the forward anodic scan except in 0.05 mol L^{-1} hydrochloric acid medium (Fig. 1(D)). The weak reverse cathodic peak in 0.05 mol L^{-1} hydrochloric acid was attributed to the formation of BiOCl during the cathodic scan which could not be reversibly reconverted to metallic bismuth. The formation of irreversibly reduced Bi⁰ species (notably of BiOCl in Cl⁻ containing media) has been reported before [6,8]. The formation of BiOCl has been experimentally verified at bismuth nanopowder-modified electrodes in hydrochloric acid and was considered the reason for the rapid degradation of the electrode performance [26].

Qualitatively similar cyclic voltammograms were obtained at screen-printed electrodes loaded with the other precursor compounds (not shown) with the exception of the bismuth titanate-modified electrodes which did not give rise to any peaks in any of the supporting media. It was assumed that reduction of Bi(III) in this precursor was not favored for thermodynamic or kinetic reasons; this assumption was confirmed by the fact that no stripping peaks for Pb or Cd were obtained at these electrodes in stripping voltammetry experiments (see Section 3.2).

The polarisation ranges of the bismuth citrate-modified screen-printed electrode (6%, w/w) in 0.1 mol L^{-1} acetate buffer (pH 4.5), 0.1 mol L^{-1} ammonia buffer (pH 9.2) and 0.05 mol L^{-1} nitric acid before and after cathodic polarisation at -1.4 V are illustrated in Fig. 1(E and F), respectively. In every case, the anodic limit was dictated by the oxidation of the metallic bismuth and the cathodic range by the reduction of hydrogen ions. Without polarisation, the cathodic polarisation window in all the media was rather limited (Fig. 1(E)) but, after cathodic polarisation, the cathodic limit

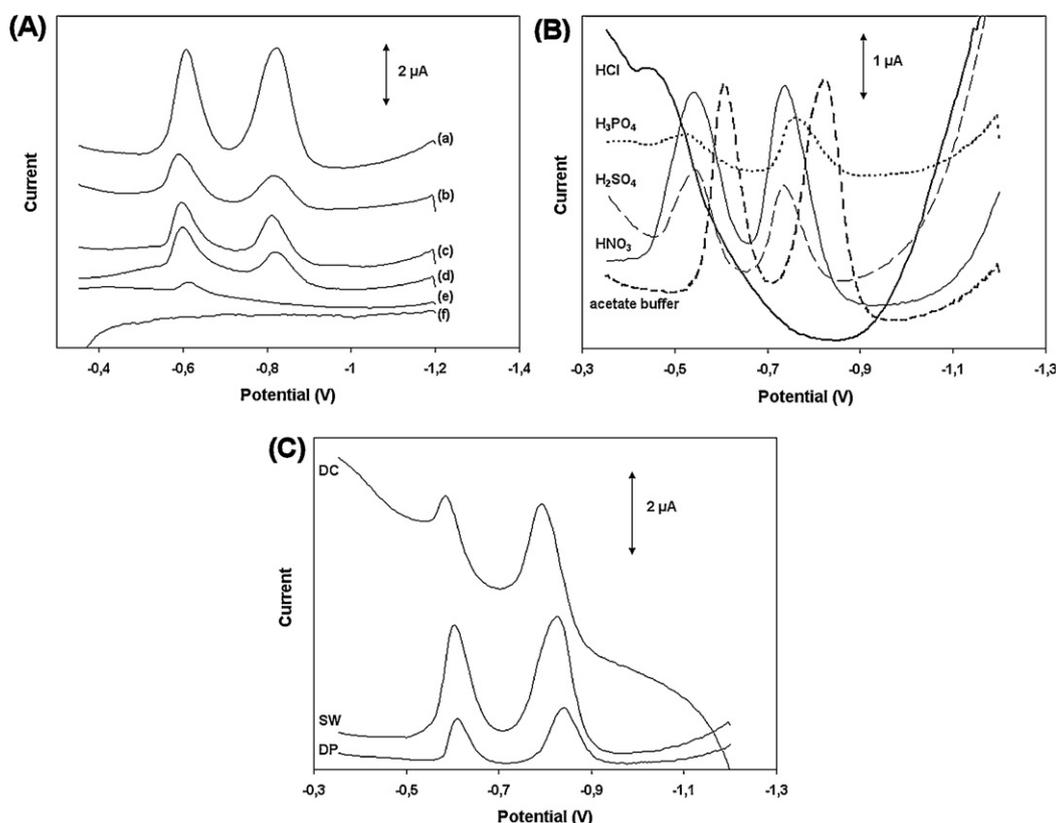


Fig. 3. (A) Comparative square wave voltammograms at screen-printed electrodes modified with: (a) 6% (w/w) bismuth citrate; (b) 4% (w/w) bismuth oxide; (c) 2% (w/w) bismuth aluminate; (d) 2% (w/w) bismuth zirconate; (e) an unmodified screen-printed electrode; (f) 6% (w/w) bismuth titanate. (B) Comparative square wave voltammograms at screen-printed electrodes modified with 6% (w/w) bismuth citrate in: 0.05 mol L⁻¹ nitric acid, 0.05 mol L⁻¹ sulphuric acid, 0.05 mol L⁻¹ hydrochloric acid, 0.05 mol L⁻¹ phosphoric acid and 0.1 mol L⁻¹ acetate buffer (pH 4.5). (C) Comparative square wave voltammograms at screen-printed electrodes modified with 6% (w/w) bismuth citrate in the square wave (SW), differential pulse (DP) and linear sweep (DC) modes. 0.1 mol L⁻¹ acetate buffer (pH 4.5) containing 20 μg L⁻¹ Pb(II) and 40 μg L⁻¹ Cd(II), preconcentration time 120 s, preconcentration potential -1.4 V.

range was extended to more negative potentials (Fig. 1(F)). This was accounted for by the fact that cathodic polarisation resulted in the generation of metallic bismuth and formation of a bismuth film that lowered the cathodic overpotential of hydrogen reduction.

Formation of bismuth particles was also corroborated by inspection with optical microscopy. Photos taken with an optical microscope of the surface of a bismuth citrate-modified screen-printed electrode (6%, w/w) in 0.1 mol L⁻¹ acetate are illustrated before cathodic polarisation (Fig. 2(A)) and after cathodic polarisation at -1.4 V (Fig. 2(B)). The electrode before polarisation exhibited a uniform surface but the formation of bismuth particles was evident after cathodic polarisation at -1.4 V. Further investigation by TEM of the screen-printed electrodes, modified with 4% (w/w) bismuth precursors after cathodic polarisation at -1.4 V, indicates a higher degree of dispersion of the bismuth particles in the cases of bismuth citrate and bismuth aluminate modified electrodes (Fig. 2(C and F)) while larger aggregates were observed for the electrodes modified with bismuth zirconate (Fig. 2(D)) and bismuth oxide (Fig. 2(E)).

3.2. Comparison of the precursor compounds and effect of the Bi₂O₃ loading

The precursor compounds at different loadings in the screen printed electrode in the range 2–6% (w/w) were compared for the determination of Pb(II) and Cd(II) by square wave ASV. The sensitivity towards Cd and Pb was maximum for the bismuth citrate at the 6% (w/w) loading, for the bismuth oxide at the 4% (w/w) loading, for the bismuth aluminate at the 2% (w/w) loading and at the

bismuth zirconate at the 2% (w/w) loading while bismuth titanate did not produce stripping peak for Cd and Pb at any loading. SW stripping voltammograms at screen-printed electrodes modified with precursors at their optimum loadings and at an unmodified screen-printing electrode are illustrated in Fig. 3(A); the unmodified electrode only exhibited a small peak for Pb (always lower than the peak at the modified electrodes except the bismuth titanate-modified electrode) and no peak for Cd. Bismuth citrate at 6% (w/w) was selected as the best precursor-loading combination and was used for further work. The better performance of the electrodes modified with bismuth citrate is attributed to the release of citrate ions in solution during the cathodic deposition step in which Bi(III) in the salt is converted to metallic bismuth. It has been shown before that the presence of citrate ions in the solution assist in the formation of more homogeneous bismuth films consisting of smaller particles and by better adherence to the substrate [7]. This earlier finding was supported by the TEM images in Fig. 2(C–F) and is speculated that the citrate salts serve as effective pre-organised material for the formation of well-dispersed nanoparticles in the surface of the electrode.

3.3. Effect of the supporting electrolyte and the stripping waveform

The effect of the supporting electrolyte was investigated by monitoring the square wave stripping voltammograms in different media: 0.1 mol L⁻¹ acetate buffer (pH 4.5) and 0.05 mol L⁻¹ of nitric acid, phosphoric acid, hydrochloric acid and sulphuric acid at a screen-printed electrodes modified with 6% (w/w) bismuth citrate

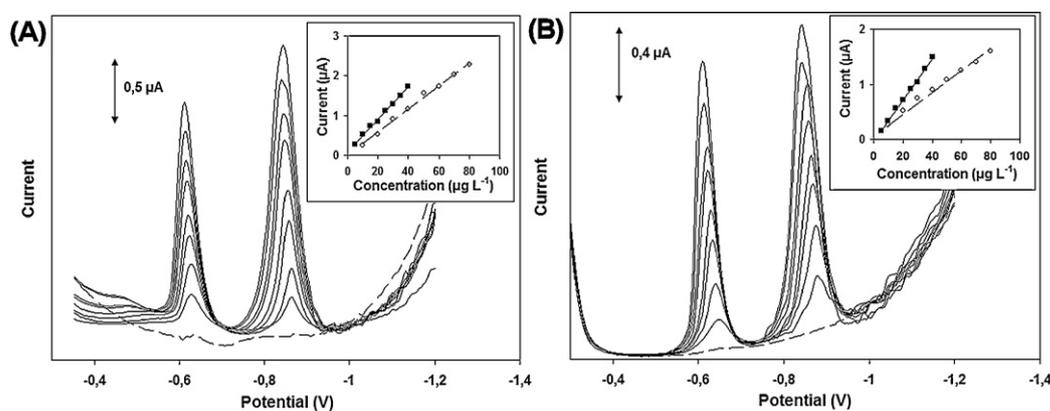


Fig. 4. DP stripping voltammograms and calibration plots for Cd (—○—) and Pb (—■—) at (A) a screen-printed electrode modified with 6% (w/w) bismuth citrate, and (B) BiFE electroplated *in situ* on an unmodified screen-printed electrode. 0.1 mol L⁻¹ acetate buffer (pH 4.5) without Pb(II) and Cd(II) (---) and with successive additions of 5 μg L⁻¹ Pb(II) and 10 μg L⁻¹ Cd(II). Preconcentration time 120 s, preconcentration potential -1.4 V.

(Fig. 3(B)). The 0.1 mol L⁻¹ acetate buffer (pH 4.5) exhibited the best background response at the cathodic region of the Cd peak since the relatively higher pH suppressed the hydrogen evolution which was more pronounced in the acidic solutions. Also, the 0.1 mol L⁻¹ acetate buffer (pH 4.5) produced the highest response for the Pb and Cd peaks followed by the 0.05 mol L⁻¹ of nitric acid medium; however, in the latter, the separation between the two stripping peaks was not adequate. No peaks were obtained in 0.05 mol L⁻¹ of hydrochloric acid and this was attributed to the electrode inactivation by the formation of irreversibly reducible BiOCl as discussed in Section 3.1 and experimentally verified previously [26]. Therefore, the 0.1 mol L⁻¹ acetate buffer (pH 4.5) was selected for the following experiments.

Regarding the stripping waveform, a comparison was made between the SW, DP and DC modulations (Fig. 3(C)). The DC waveform suffered from an excessively sloping baseline while the SW modulation produced the highest response for both Cd and Pb. The DP scan benefited from the best baseline characteristics and, more importantly, produced narrower peaks and better separation between the Cd and Pb peaks compared with the SW waveform; this latter attribute was particularly critical at higher concentrations of the target cations where the SW modulation provided inadequate separation. In addition, the DP scan provided better

concentration linearity and was, therefore, selected for subsequent work.

3.4. Effect of the deposition time and the deposition potential

The effect of the deposition time was investigated in the range 20–240 s on the stripping peak heights for Pb and Cd at a screen-printed electrode modified with 6% (w/w) bismuth citrate. The stripping peak heights followed a typical rectilinear dependence on the deposition time with a rapid increase of the response at low deposition times and gradual levelling-off as saturation of the electrode was eventually reached.

The effect of the deposition potential was studied in the range -1.5 V to -0.9 V on the stripping peak heights for Pb and Cd at a screen-printed electrode modified with 6% (w/w) bismuth citrate. The deposition potential affected both the reduction of the precursor to metallic bismuth and the deposition of the target metal cations. The stripping responses were negligible at potentials more positive than -0.9 V and increased rapidly as the deposition potential became more negative until -1.4 V. More negative potentials did not induce significant change in the stripping peak heights as both the bismuth citrate in the electrode and the target metal cations reaching the electrode surface were quantitatively reduced.

Table 1
Calibration data for Pb(II) and Cd(II) on screen-printed electrodes modified with bismuth precursor compounds and on a BiFE electroplated *in situ* on an unmodified screen-printed electrode. The calibration plots are of the form: $I_p = (a \pm s_a) \times c + (b \pm s_b)$, where I_p is the peak current and c is the metal concentration in the sample.

Modifier	$(a \pm s_a) \times 10^{-3} (\mu\text{A} \mu\text{g}^{-1} \text{L})^a$	$(b \pm s_b) \times 10^{-3} (\mu\text{A})^b$	r^2^c	LOD ^d ($\mu\text{g L}^{-1}$)	RSD% ^e
Pb(II)					
Bismuth oxide 4% (w/w)	17.0 ± 0.5	31.1 ± 5.7	0.995	1.0	10.4
Bismuth aluminate 2% (w/w)	15.9 ± 0.5	19.1 ± 6.0	0.994	1.1	6.2
Bismuth citrate 6% (w/w)	40.1 ± 0.9	50.1 ± 12.3	0.996	0.9	5.4
Bismuth zirconate 2% (w/w)	18.2 ± 0.8	16.0 ± 8.3	0.990	1.4	10.1
<i>In situ</i> bismuth-plated SPE	37.6 ± 0.9	35.5 ± 14.7	0.996	1.2	5.8
Cd(II)					
Bismuth oxide 4% (w/w)	5.5 ± 0.2	8.6 ± 3.7	0.995	2.0	14.6
Bismuth aluminate 2% (w/w)	9.7 ± 0.2	1.7 ± 4.8	0.997	1.5	5.8
Bismuth citrate 6% (w/w)	28.1 ± 0.9	34.3 ± 10.2	0.993	1.1	7.2
Bismuth zirconate 2% (w/w)	3.7 ± 0.3	21.3 ± 4.0	0.985	3.2	15.5
<i>In situ</i> bismuth-plated SPE	18.6 ± 0.6	13.5 ± 12.8	0.993	2.1	8.2

^a a is the slope of the calibration plot and s_a is the standard deviation of the slope.

^b b is the intercept of the calibration plot and s_b is the standard deviation of the intercept.

^c r^2 is the coefficient of correlation.

^d LOD is the limit of detection (calculated as $\text{LOD} = 3s_b/a$).

^e RSD% is the % relative standard deviation ($n=8$) at $20 \mu\text{g L}^{-1}$.

A deposition potential of -1.4V was finally selected for further work.

3.5. Calibration features of the sensors

Calibration for Pb(II) and Cd(II) was performed using the following conditions: screen-printed electrode modified with 6% (w/w) bismuth citrate; supporting electrolyte, 0.1 mol L^{-1} acetate buffer (pH 4.5); deposition potential -1.4V ; deposition time 120 s. For comparison, calibration was performed at screen-printed electrodes loaded with 4% (w/w) bismuth oxide, 2% (w/w) bismuth aluminate and 2% (w/w) bismuth zirconate as well as with unmodified screen-printed electrodes electroplated *in situ* with bismuth. The calibration features of these sensors for the determination of Pb(II) and Cd(II) are summarised in Table 1. The sensitivities and LODs for Pb(II) were similar on the different electrodes with the screen-printed electrode modified with 6% (w/w) bismuth citrate yielding the lowest value. Regarding Cd(II), the screen-printed electrode modified with 6% (w/w) bismuth citrate produced by far the highest sensitivity and the lowest LOD whereas the screen-printed electrode modified with 2% (w/w) bismuth zirconate produced the lowest sensitivity and the highest LOD.

Comparative DP stripping voltammograms for the simultaneous determination of Pb(II) and Cd(II) are illustrated at screen-printed electrode modified with 6% (w/w) bismuth citrate (Fig. 4(A)) and at a BiFE electroplated *in situ* on an unmodified screen-printed electrode (Fig. 4(B)); the calibration plots are shown as insets in Fig. 4(A and B). It is interesting to point out that the DP voltammograms at the screen-printed electrode modified with 6% (w/w) bismuth citrate were characterised by lower background in the cathodic range than the voltammograms at the screen-printed electrode coated *in situ* with a bismuth film.

The reproducibility for the screen-printed electrodes modified with different precursors (expressed as the % relative standard deviation of successive measurements ($n=8$) on the same sensor at the $20\text{ }\mu\text{g L}^{-1}$ level) is also shown in Table 1. The best overall reproducibility was observed on the bismuth citrate-loaded electrode followed by the bismuth aluminate-modified electrode. Both these electrodes were comparable, in terms of reproducibility, with the screen-printed electrode coated *in situ* with a bismuth film. The electrodes were stable for around 10 successive preconcentration/stripping/cleaning cycles and then the response started to decrease gradually. Therefore, these electrodes could be used as semi-disposable sensors enabling a complete analysis (*i.e.* standard addition method) to be conducted at a single device.

3.6. Interference study

In previous work on Bi_2O_3 -loaded screen printed electrodes, the only interference investigated has been the well-known adverse effect of Cu(II) on the determination of Pb(II) and Cd(II) [19,20]. In this work, the presence of a number of heavy metals known to interfere with the determination of Cd(II) and Pb(II) through competitive deposition, formation of intermetallic compounds and peak overlap were examined. The effect of different concentrations of Cu(II), Tl(I), In(III), Sn(II), Sb(III) and Zn(II) on the stripping response $20\text{ }\mu\text{g L}^{-1}$ of Pb and $40\text{ }\mu\text{g L}^{-1}$ of Cd was investigated at the screen-printed electrode modified with 6% (w/w) bismuth citrate. In the case of Pb(II), the only serious interference was Cu(II) but the determination of Cd(II), in addition to Cu(II), was also affected by the presence of Tl(I). The interference due to Cu(II) was efficiently alleviated by addition of ferrocyanide ions as discussed before [11,21,22] while in most real samples the Tl(I) concentrations is much lower than the Cd(II) concentration. The presence of other common cations such as Mn(II), Co(II), Ni(II), Na(I), K(I), Ca(II), Mg(II), at a ten-fold excess

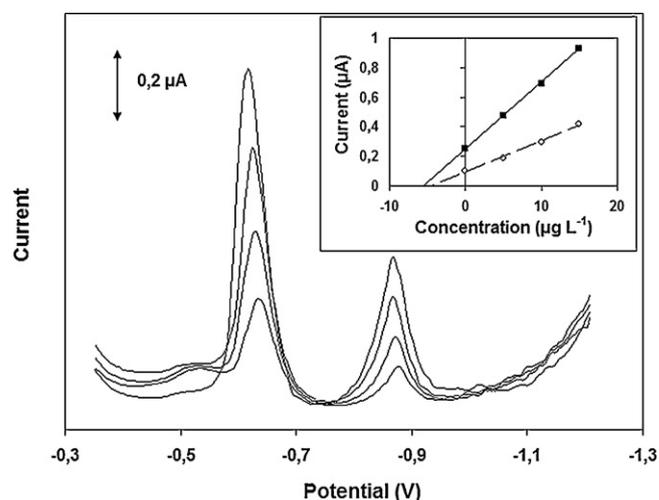


Fig. 5. DP stripping voltammograms and standard addition plots for Cd ($--\circ--$) and Pb ($--\blacksquare--$) at a screen-printed electrode modified with 6% (w/w) bismuth citrate for the TM-24.3 lake water. Sample + 3 additions of $5\text{ }\mu\text{g L}^{-1}$ Pb(II) and Cd(II), preconcentration time 120 s, preconcentration potential -1.4V .

over Cd(II) and Pb(II) did not have a statistically significant affect upon the stripping peaks of Pb and Cd.

Electroplated and sputtered BiFEs are prone to adsorption on surfactants that cause deactivation of their surface [11,27] but the effect of surfactants at screen printed electrodes modified with bismuth precursors has not been studied so far. Triton X-100 was selected as a “model” surfactant and its effect was studied at different concentrations in the range 0.1 to 10 mg L^{-1} on the stripping response of $20\text{ }\mu\text{g L}^{-1}$ of Pb and $40\text{ }\mu\text{g L}^{-1}$ of Cd at the screen-printed electrode modified with 6% (w/w) bismuth citrate. The presence of the surfactant caused a sharp drop in the peak heights of Cd and Pb even at the lower surfactant concentrations and the loss in sensitivity was more than 50% at 1 mg L^{-1} of Triton X-100. Also, wider and distorted Cd and Pb peaks were obtained at Triton X-100 concentrations higher than 2 mg L^{-1} .

3.7. Applications

The screen-printed electrodes modified with 6% (w/w) bismuth citrate were finally applied to the analysis of water samples. In all cases, ferrocyanide ions were added to the sample solutions to alleviate the interference by Cu(II). In the TM-24.3 lake water sample, the determined concentrations for Pb(II) and Cd(II) were $5.5 \pm 0.6\text{ }\mu\text{g L}^{-1}$ and $4.4 \pm 0.5\text{ }\mu\text{g L}^{-1}$, respectively, while the certified concentrations were $5.82\text{ }\mu\text{g L}^{-1}$ and $3.97\text{ }\mu\text{g L}^{-1}$. Representative DP stripping voltammograms for the determination of Pb(II) and Cd(II) in the TM-24.3 lake water sample are illustrated in Fig. 5. In tapwater, the determined Pb(II) concentration was $6.7 \pm 0.7\text{ }\mu\text{g L}^{-1}$ and the reference value (established by ASV on a glassy carbon BiFE according to the procedure described earlier [28]) was $6.5 \pm 0.6\text{ }\mu\text{g L}^{-1}$. The Cd(II) concentration in tapwater was lower than the LOD and the accuracy was established by the calculation of the recovery after spiking the sample with $4\text{ }\mu\text{g L}^{-1}$ of Cd(II); the calculated recovery value was 97.1%, which was considered satisfactory.

4. Conclusions

In this article, the fabrication of disposable screen-printed voltammetric modified sensors with bismuth precursor compounds is presented and their analytical utility for the determination of Pb(II) and Cd(II) by anodic stripping voltammetry is demonstrated. It was found that the nature of the precursor

compound and its content in the carbon ink critically affected the sensitivity. The best results, in terms of sensitivity and peak shape, were obtained with bismuth citrate as the precursor at a 6% (w/w) loading in the carbon ink. 0.1 mol L⁻¹ acetate buffer (pH 4.5) was selected as the supporting electrolyte and stripping was performed in the DP mode. The limit of detection (0.9 µg L⁻¹ for Pb(II) and 1.1 µg L⁻¹ for Cd(II)) and the reproducibility were comparable to, or better than, those on electroplated BiFEs on screen-printed supports which can extend the scope of these sensors for rapid screening of metal pollutants. The useful life-time of the sensors was 10 stripping cycles.

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