

Disposable Screen-Printed Electrodes with in-Built Bismuth Precursors for Lead(II) Determination by Anodic Stripping Voltammetry

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Abstract: The utility of disposable screen-printed electrodes modified with three bismuth-precursor compounds (bismuth titanate, bismuth oxide and bismuth aluminate) was assessed for the determination of Pb(II) by anodic stripping voltammetry. It was found that, in principle, both bismuth oxide and bismuth aluminate could be successfully used as bismuth precursors but the latter yielded higher sensitivity for the detection of Pb(II). The instrumental parameters for Pb(II) determination (deposition time and potential and stripping waveform mode) were investigated and the effect of different co-existing metals was studied. Using the selected conditions, the limit of detection for Pb(II) was $0.6 \mu\text{g l}^{-1}$ and the % relative standard deviation at the $20 \mu\text{g l}^{-1}$ level was 5.2 % ($n=8$). The sensors were successfully utilised for the determination of Pb(II) in tap-water.

Keywords: Screen-printed electrodes; Bismuth-precursors modified electrodes; Anodic stripping voltammetry; Lead(II); Determination.

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Introduction

Bismuth film electrodes (BiFEs), introduced in 2000 for stripping voltammetric detection [1], have been the subject of numerous and thorough studies over the last decade [2-6]. It has been demonstrated that BiFEs exhibit favourable analytical properties in electro-

chemical stripping analysis, in many ways comparable to those of mercury film electrodes (MFEs) with the notable drawback of a narrower anodic potential window [2-6]. The most significant attraction of BiFEs is that they are environmentally-friendly, since the toxicity of bismuth and its salts (commonly used to generate BiFEs) is lower than that declared for mercury and its compounds.

Regarding the way to fabricate BiFEs, there are three main routes:

- i) Electroplating: this is the commonest method to generate a BiFE. It involves plating of the bismuth film by Bi(III) reduction to metallic bismuth on a conductive support material 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) [2-6]. The main drawback of electroplating is the added experimental complexity and the requirement for Bi(III) salts while the morphology of the bismuth deposit is strongly dependent on the electroplating conditions [7,8].
- ii) Thin-film microfabrication: this approach is based on application of microelectronic thin-film deposition techniques and involves deposition of a thin layer of bismuth on a silicon support material by sputtering or thermal evaporation while the geometry of the electrodes is defined by photolithography [9-12]. Microfabricated BiFEs do not require Bi(III) solutions for bismuth plating, are disposable and possess controlled surface morphology but require rather expensive instrumentation for their fabrication.
- iii) Use of bismuth precursors: this method for the generation of the bismuth layer involves bulk-modification of an electrode with a bismuth-precursor compound (typically a Bi(III) compound); generation of the bismuth film occurs *in-situ* during the reductive deposition step. The first report of such as sensor was a carbon paste electrode loaded with bismuth oxide [13] while a composite electrode modified with bismuth nitrate [14] and a carbon paste electrode modified with ammonium tetrafluorobismuthate [15] have been reported more recently. Lately, the concept of electrode modification with bismuth precursors has been combined with screen-printing leading to screen-printed strips loaded with bismuth oxide [16-19]. These sensors are disposable and do not require a separate bismuth plating step whereas their construction is easier and less expensive than thin-film microfabrication.

However, there is no report in the literature of alternative modifiers to bismuth oxide for the fabrication of screen-printed BiFE sensors. The aim of the present work was to assess three bismuth(III) compounds bismuth titanate ($\text{Bi}_2\text{O}_3 \cdot 2\text{TiO}_2$), bismuth oxide (Bi_2O_3) and bismuth aluminate ($\text{Bi}_2(\text{Al}_2\text{O}_4)_3 \cdot x\text{H}_2\text{O}$) as potential bismuth precursors for the fabrication of disposable modified screen-printed electrodes and to present some initial results with the view to determine Pb(II) by anodic stripping voltammetry.

Experimental

Chemicals

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). A 1 mol l⁻¹ stock solution of acetate buffer (pH 4.5) were used for the preparation of the 0.1 mol l⁻¹ acetate buffer (pH 4.5) supporting electrolyte.

Bismuth oxide (Bi₂O₃, grain size ≤ 10 μm) and bismuth titanate, (Bi₂O₃·2TiO₂, 325 mesh) were purchased from Sigma-Aldrich while bismuth aluminate hydrate (Bi₂(Al₂O₄)₃·xH₂O, x≈10, grain size ≤ 2 μm) was purchased from Alfa Aesar. Cu(II), Cd(II), Pb(II), Zn(II), Sn(II), In(III) and Tl(I) standard 20 mg l⁻¹ stock solutions were prepared from (1.000 ± 0.001 g l⁻¹) atomic absorption standard solutions. All standard and stock solutions were diluted as required with double-distilled water.

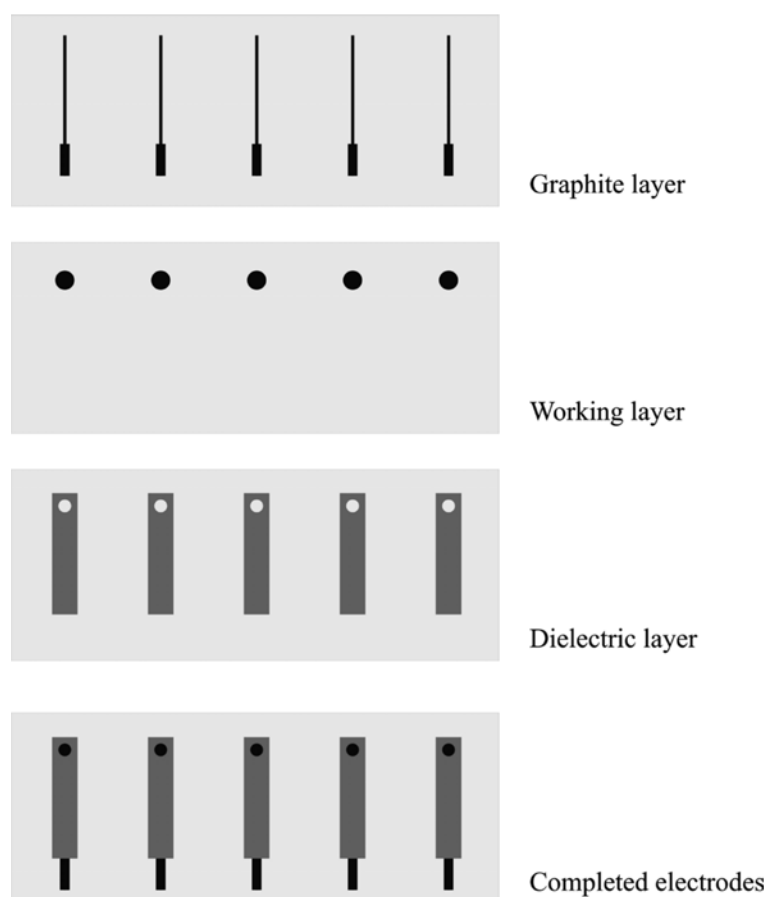
Apparatus

A Pamlens potentiostat (Palm Instruments BV, Houten, The Netherlands) was used in combination with the PSTrace 2.1 software (Palmsens). Measurements were performed in a standard glass voltammtric cell. A Ag/AgCl (sat. KCl) reference electrode and a Pt wire auxiliary electrode completed the cell. A magnetic stirrer operating at approx. 1000 rpm provided stirring during the deposition step.

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 (13–20 μm thick) with the desired pattern using a polyurethane 75 durometer squeegee. As illustrated in Scheme 1, 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 acts as the conductive track; ii) the bismuth-bearing graphite layer (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 bismuth bearing printed ink was produced by mixing 100 mg of the bismuth precursor compound and 4.9 g of graphite ink.



Scheme 1. *Fabrication of bismuth-precursor modified screen-printed electrodes*

Experimental procedure

The sample was introduced in the cell and the accumulation (preconcentration) step was performed under stirring at -1.50 vs Ag/AgCl for a pre-defined time period (usually 120 s). After a 10 s equilibration period in static solution, an anodic voltammetric scan was performed from -1.20 V to -0.35 V. Then, the electrode was cleaned from remaining traces of deposited metals by holding the potential at -0.35 V for 10 s under stirring.

Results and Discussion

Comparative SW anodic stripping voltammograms recorded in a solution containing $20 \mu\text{g l}^{-1}$ of Pb(II) at screen-printed electrodes modified with 2 % (w/w) of the three bismuth precursor compounds are illustrated in Fig. 1.

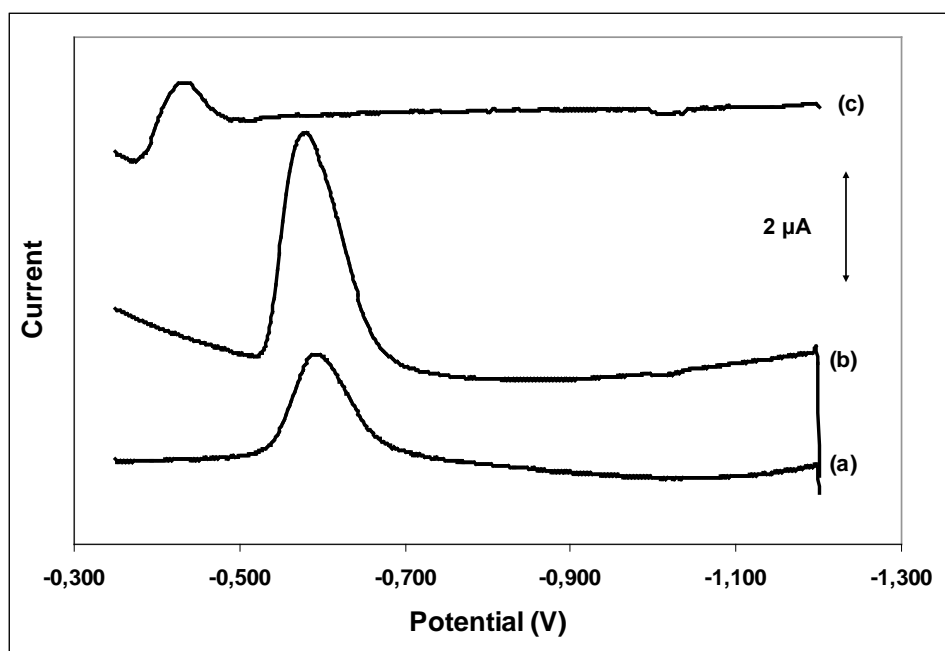


Figure 1. SW anodic stripping voltammograms of a solution containing $20 \mu\text{g l}^{-1}$ of Pb(II) at screen-printed electrodes modified with 2 % (w/w): (a) bismuth oxide; (b) bismuth aluminate; (c) bismuth titanate. Experimental conditions: 0.1 mol l^{-1} acetate buffer (pH 4.5); deposition potential, -1.5 V ; final potential, -0.35 V (both vs Ag/AgCl); deposition time, 120 s; equilibrium period, 10 s; square-wave frequency, 100 Hz; pulse height, 20 mV; step increment, 2 mV.

The screen-printed electrode modified with bismuth aluminate (Fig. 1b) offered higher sensitivity than the bismuth oxide electrode (1a). The electrode modified with bismuth titanate yielded an even weaker ill-defined peak at more positive potential (1c). Hence, the electrodes loaded with the bismuth aluminate precursor were selected for further work.

The SW, DP and DC voltammetric stripping modes for the determination of Pb(II) at the bismuth aluminate-modified screen-printed electrode were compared (Fig. 2). The DP mode (Fig. 2(b)) produced the flattest baseline but the SW (Fig. 2(c)) modulation provided much higher sensitivity with better baseline characteristics than the DC mode (Fig. 2(a)) and was selected for subsequent experiments.

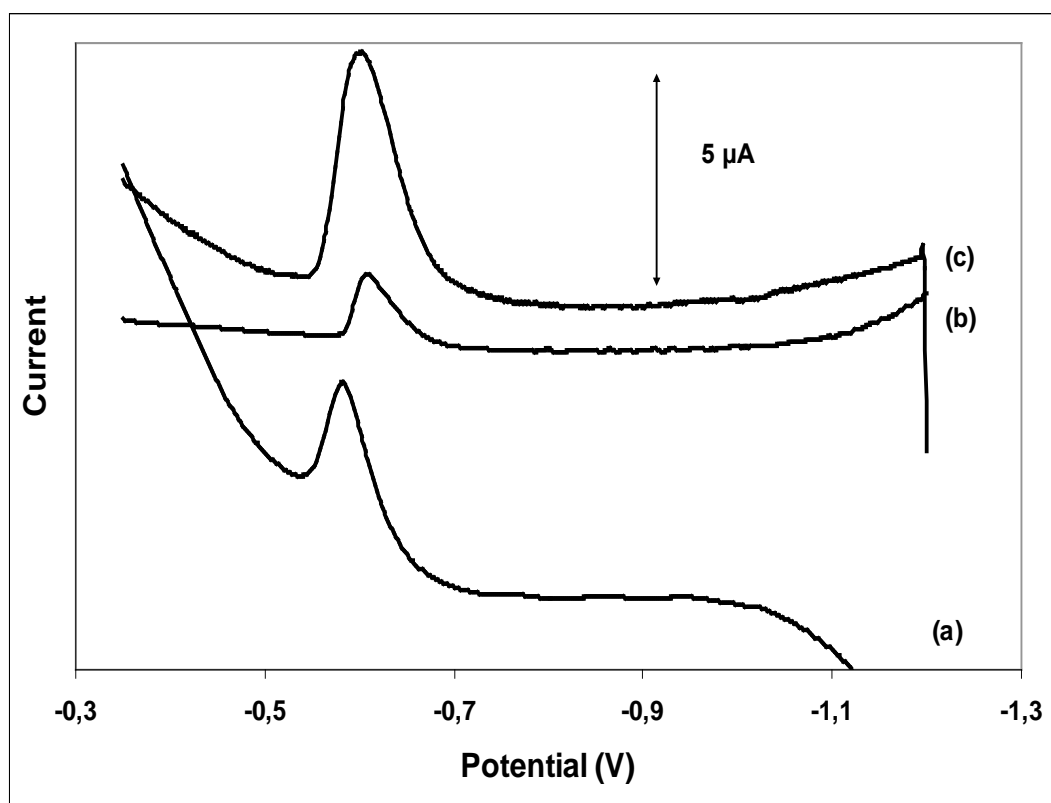


Figure 2. Anodic stripping voltammograms of a solution containing $20 \mu\text{g l}^{-1}$ of Pb(II) at a screen-printed electrodes modified with 2 % (w/w) bismuth aluminate with the stripping step conducted with (a) linear sweep (DC); (b) differential pulse (DP), (c) square wave (SW) mode. Experimental conditions as in Fig. 1; DCASV scan rate, 100 mV s^{-1} ; DPASV scan rate, 10 mV s^{-1} ; pulse height, 20 mV; pulse duration , 50 ms.

The effect of the deposition potential on the Pb SW stripping peak current was studied in the range -0.9 to -1.6 V and the results are shown in Fig. 3(A). The SW response increased as the deposition potential became more negative and leveled-off at -1.4 V. Considering that the peak potential for the Pb peak was at -0.60 V, levelling-off at rather more positive potentials was expected, as indeed observed in previous studies involving electroplated and micro-fabricated BIFEs [8,11]. The observation that more negative preconcentration potentials were necessary to achieve the maximum response for Pb on the bismuth-precursor modified screen-printed electrode was attributed to the fact that the reduction of the precursor to metallic bismuth required a rather negative potential. The effect of the deposition time on the SW stripping peak current in the interval 20-240 is illustrated in Fig. 3(B); a typical rectilinear dependence was observed.

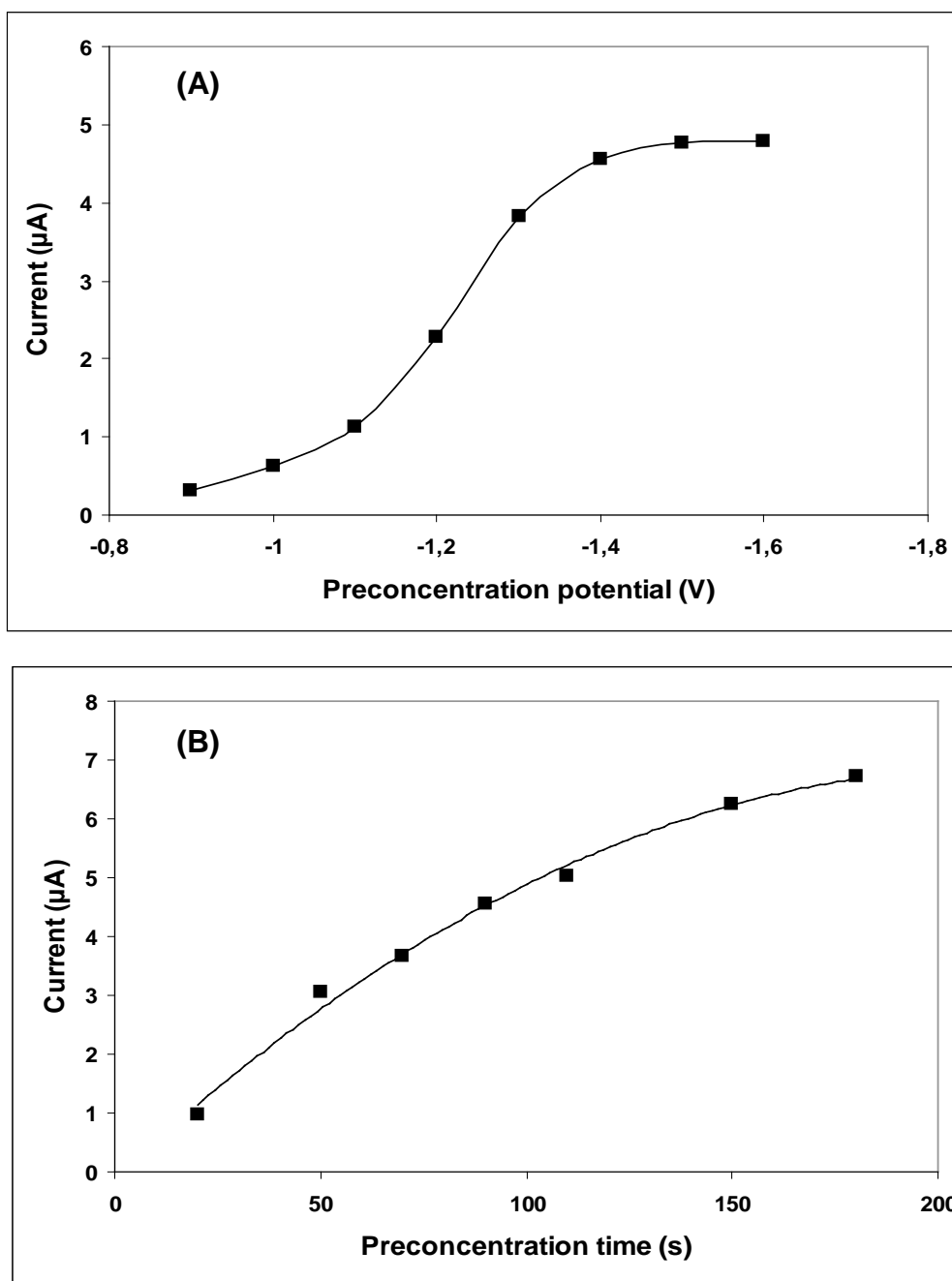


Figure 3. Effect of (A) the deposition potential and (B) deposition time, on the SW anodic stripping peak of Pb in a solution containing $20 \mu\text{g l}^{-1}$ of Pb(II) at a screen-printed electrodes modified with 2 % (w/w) bismuth aluminate. Experimental conditions as those in Fig. 1.

The effect of different trace metals known to form alloys with bismuth and are, therefore, detectable on bismuth electrodes was studied by addition of different metals in a solution containing $20 \mu\text{g l}^{-1}$ of Pb(II) (Fig. 4). $20 \mu\text{g l}^{-1}$ of Cd(II) produced a stripping peak which was well separated from the Pb peak and did not cause any change in the Pb stripping

peak height ((Fig. 4(b)). $40 \mu\text{g l}^{-1}$ of Cu(II), Zn(II) and Sn(II), added simultaneously, produced no stripping peaks in the potential range examined and caused a combined decrease in the Pb peak height by 11 % (Fig. 4(c)). Further addition of $40 \mu\text{g l}^{-1}$ of In(III) caused the appearance of a stripping peak that overlapped with the Cd peak and reduced by a further 11 % the Pb peak height (Fig. 4(d)). However, even in the presence of these cations, a well-developed and analytically useful Pb peak was still observed in contrast to previously reported screen-printed electrodes either electroplated or modified with bismuth oxide which suffer from severe interference due to the presence of Cu(II) [20,16]. Finally, the addition of $40 \mu\text{g l}^{-1}$ of Tl(I) caused a severe drop in the Pb response and produced a wide stripping peak that overlapped with the Cd and In peaks (Fig. 4(e)).

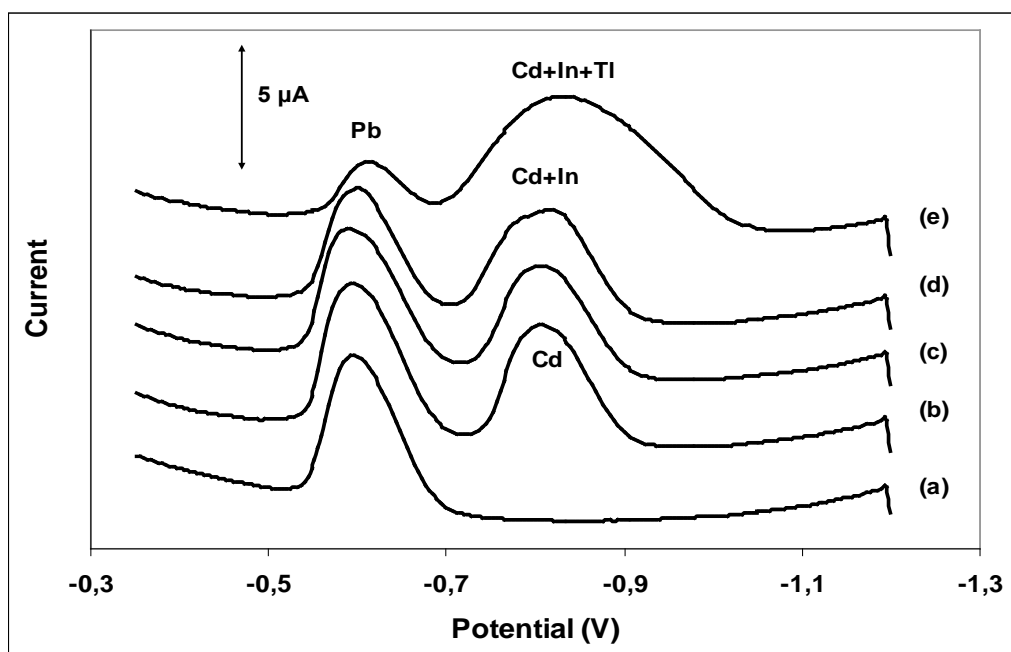


Figure 4. SW stripping voltammograms at a screen-printed electrodes modified with 2 % (w/w) bismuth aluminate in a solution containing: (a) $20 \mu\text{g l}^{-1}$ of Pb(II); (b) as (a) with $20 \mu\text{g l}^{-1}$ of Cd(II); (c) as (b) with $40 \mu\text{g l}^{-1}$ of Cu(II), Zn(II) and Sn(II); (d) as (c) with $20 \mu\text{g l}^{-1}$ of In(III); (e) as (d) with $20 \mu\text{g l}^{-1}$ of Tl(I). Expex. conditions as in Fig. 1.

Calibration for Pb(II) was performed at a screen-printed electrodes modified with 2 % (w/w) bismuth aluminate using a deposition time of 120 s; representative voltammograms in the range $10\text{-}60 \mu\text{g l}^{-1}$ together with the respective calibration plot are shown in Fig. 5. The limit of detection (calculated as $\text{LOD}=3s_b/S$, where s_b is the standard deviation of the intercept and S is the slope of the calibration plot) was $0.6 \mu\text{g l}^{-1}$ and the % relative standard deviation at the $20 \mu\text{g l}^{-1}$ level was 5.2 % ($n=8$).

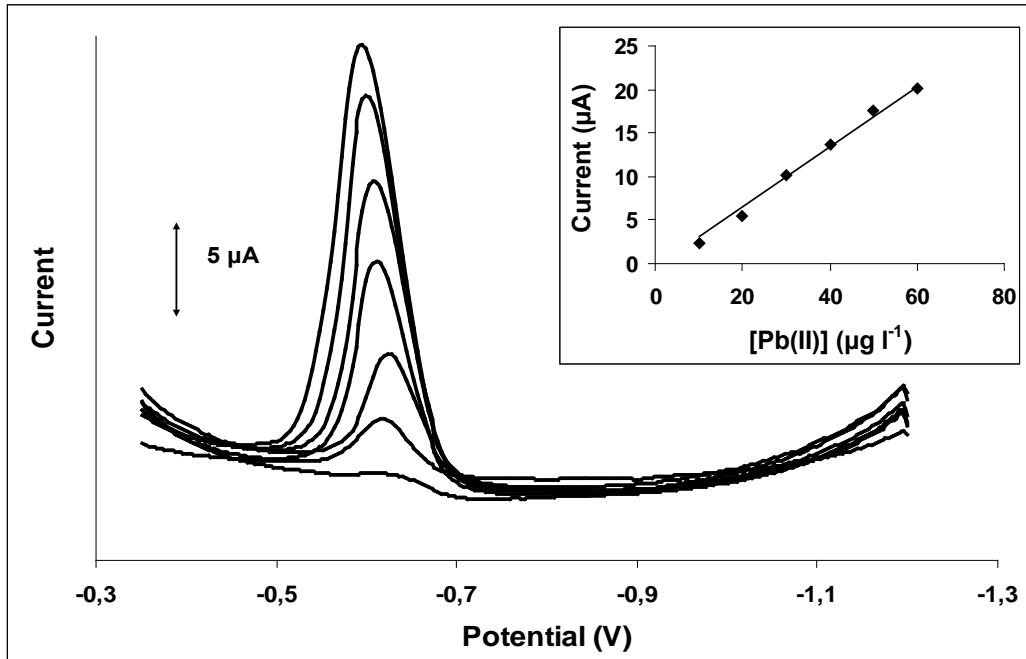


Figure 5. SW stripping voltammograms at a screen-printed electrodes modified with 2 % (w/w) bismuth aluminate in a solution containing (from bottom to top): 0, 10, 20, 30, 40, 50 and 60 $\mu\text{g l}^{-1}$ of Pb(II). Calibration plot as inset. Exp. conditions as in Fig. 1.

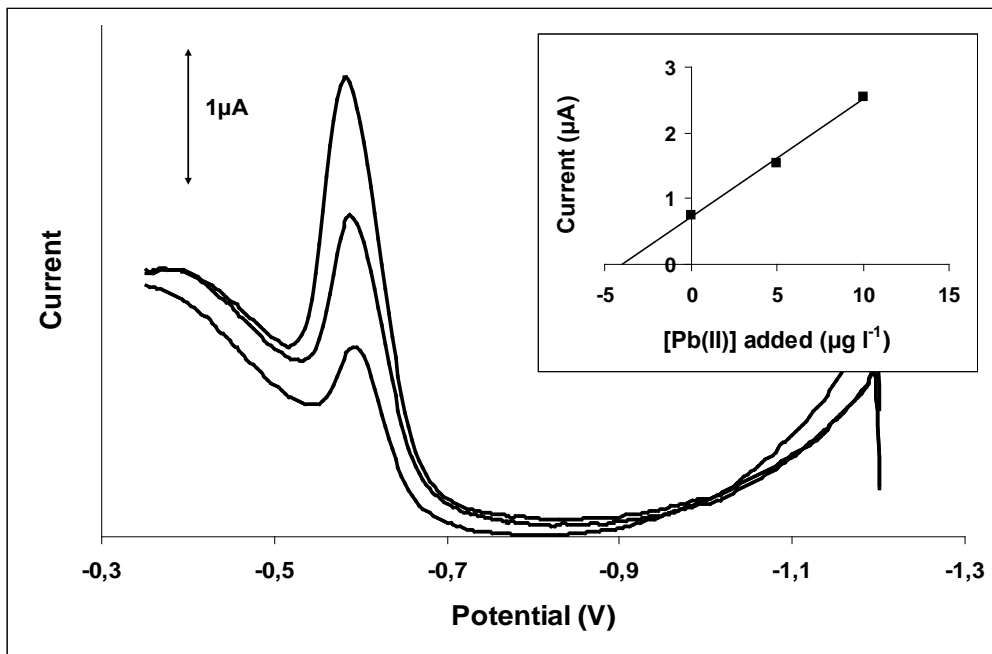


Figure 6. SW stripping voltammograms at a screen-printed electrodes modified with 2 % (w/w) bismuth aluminate in a tap water sample (from bottom to top): sample, 2 standard additions of 5 $\mu\text{g l}^{-1}$ of Pb(II). Standard additions plot as inset. Experimental conditions as in Fig. 1.

The screen-printed electrodes modified with 2 % (w/w) bismuth aluminate were finally used for the determination of Pb(II) in tapwater by SWASV. The tapwater sample was collected from taps in the Laboratory of Analytical Chemistry in the University of Athens. 19.0 ml of the sample and 1.0 ml of the 1 mol l⁻¹ solution of acetate buffer (pH 4.5) were placed in the cell and the analysis was carried out as described in the *Experimental* section.

Conclusions

This work has demonstrated proof-of-principle applicability of alternative bismuth precursors for the fabrication of screen-printed BiFEs. Although the existing screen-printed sensors all utilise bismuth oxide as the modifier, the bismuth aluminate used in this work exhibited superior analytical performance in terms of sensitivity for the determination of Pb(II). Given the numerous bismuth compounds that are commercially available, there is increased scope for extended studies to assess the analytical utility of several additional bismuth precursors for various target metals. Combined with screen-printing technology, these modified electrodes could serve as disposable mercury-free sensors for trace metals with improved performance.

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