

A Study of Bi₂O₃-Modified Screen-Printed Sensors for Determination of Cd(II) and Pb(II) by Anodic Stripping Voltammetry

**Nikolitsa Lezi¹, Anastasios Economou^{1*}, Constantinos E. Efstathiou¹,
and Mamas Prodromidis²**

¹ *Laboratory of Analytical Chemistry, Department of Chemistry, University of Athens, 15771 Athens, Greece*

² *Laboratory of Analytical Chemistry, Department of Chemistry, University of Ioannina, 45110 Ioannina, Greece*

Abstract: In this article, a study of Bi₂O₃-modified screen-printed electrodes is given presenting the determination of Cd(II) and Pb(II) by anodic stripping voltammetry (ASV). Initially, the electrode was subjected to cathodic polarisation to reduce the Bi₂O₃ to metallic bismuth. Then, the target metal cations were electrolytically preconcentrated on the electrode by alloying with bismuth. Following the deposition step, an anodic voltammetric scan was applied in which the metals were oxidised and stripped back into the solution; the voltammogram recorded and the stripping peak heights being related to Pb(II) and Cd(II) concentrations in the sample. Different key parameters were investigated in detail such as the medium used for the Bi₂O₃ reduction, the Bi₂O₃ 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 the optimum conditions, the limit of detection was 1.1 µg l⁻¹ for Pb(II) and 2.1 µg l⁻¹ for Cd(II). The reproducibility of measurements on the same chip (expressed as the RSD [%], for *n* = 8) was 7.7 % for Pb(II) and 8.4 % for Cd(II) at the 20 µg l⁻¹ level.

Keywords: Anodic stripping voltammetry, Screen-printed sensors; Bi₂O₃-modified electrodes; Cd(II) and Pb(II).

*) Author to whom correspondence should be addressed. E-mail: aeconomou@chem.uoa.gr

Introduction

Bismuth film electrodes (BiFEs) have been introduced in 2000 as environmentally-friendly alternatives to mercury electrodes in stripping analysis [1]. In the last decade, extensive research has shown that BiFEs exhibit analytical properties comparable to their mercury

counterparts, mercury film electrodes (MFEs), in electrochemical stripping analysis [2-5]. The main advantage of BiFEs is the low toxicity of bismuth and its salts compared to that of mercury and its compounds.

By far, the commonest approach to fabricate BiFEs is electroplating which involves plating of the bismuth film by reduction of Bi(III) 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) [2-5]. The main disadvantage of electroplating seem to be the experimental complexity associated with the use and manipulation of the Bi(III) plating solution.

The use of bismuth precursors is an elegant way to avoid the use of external Bi(III) solutions. This method for the generation of the bismuth layer involves the modification of the working electrode with a bismuth-precursor compound (a Bi(III) salt or Bi₂O₃); generation of the bismuth film occurs *in-situ* by applying a reductive potential to the working electrode. The very first report of such as sensor was a carbon paste electrode loaded with Bi₂O₃ [6]. More recently, screen-printed electrodes bulk-loaded with Bi₂O₃ [7-10] or surface-modified with BiPO₄ [11] have been reported for the determination of trace metals by voltammetric techniques. Screen-printing technology enables rapid fabrication of disposable, inexpensive electrodes, allowing one convenient modification of the electrode properties by simply mixing the modifier with the base electrode material (normally carbon ink) [12,13].

This work presents a systematic study of Bi₂O₃-modified screen-printed electrodes for the determination of Cd(II) and Pb(II) by ASV. Different key parameters were investigated in detail such as the medium used for the Bi₂O₃ reduction, the Bi₂O₃ 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.

Experimental

Chemicals, Reagents, Stock and Standard Solutions

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). 0.1 mol l⁻¹ stock solutions of acetate buffer (pH 4.5) and ammonia buffer (pH 9.2) and 0.05 mol l⁻¹ stock solutions of nitric acid, phosphoric acid and sulphuric acid and 0.1 mol l⁻¹ of KOH were used as supporting electrolytes.

Bismuth oxide (Bi_2O_3 , grain size $\leq 10 \mu\text{m}$) was purchased from Sigma-Aldrich. Working stock solutions containing $20 \text{ mg l}^{-1} \text{ Cd(II) + Pb(II)}$ were prepared from the standards for AAS ($1.000 \pm 0.001 \text{ g l}^{-1}$). All stock and standard solutions were diluted as required with doubly-distilled water.

Electrochemical Apparatus

A Pamlens potentiostat (Palm Instruments BV; Houten, The Netherlands) was used in combination with the PStTrace 2.1 software (PalmSens). 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 served during the deposition step.

Screen-Printed Electrodes

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). Inks were forced through an emulsion (13–20 μm thick) with the desired pattern using a polyurethane 75 durometer squeegee. As illustrated in Fig. 1, screen-printed electrodes were printed in arrays of five (working) electrodes and consisted of two layers, which were printed in the following order: i) a layer made of graphite that acted as the conductive track; ii) the Bi_2O_3 -bearing graphite layer (working layer). Each layer was cured in an oven according to the following conditions: graphite layer, $90 \text{ }^\circ\text{C}$ for 30 min; working layer, $90 \text{ }^\circ\text{C}$ for 120 min. The Bi_2O_3 -bearing printed ink was prepared by mixing 4.9 g of graphite ink with 100 mg of Bi_2O_3 (2 % w/w), 4.8 g of graphite ink with 200 mg of Bi_2O_3 (4 % w/w) or 4.7 g of graphite ink with 300 mg of Bi_2O_3 (6 % w/w).

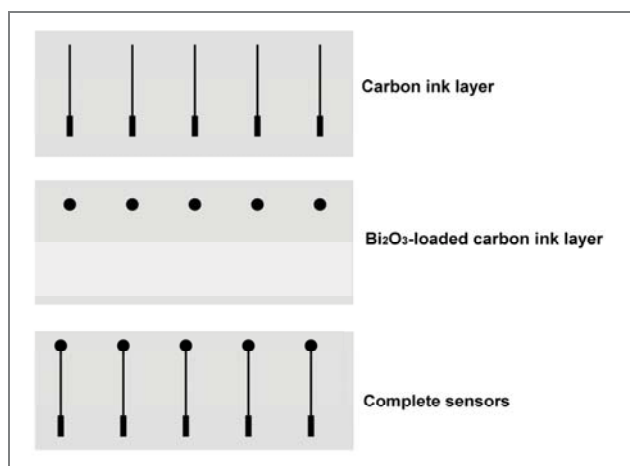


Fig. 1:

*Process of fabrication
for the Bi_2O_3 -modified
screen-printed electrodes*

(From authors' archives)

Electroanalytical Measurements and Related Procedures

Oxygen Removal. For the cyclic voltammetric experiments, the solutions were deoxygenated by bubbling with N₂ (purity of 99.9%) for approx. 10 min. Anodic stripping voltammetry experiments were carried out in the presence of oxygen.

Conditioning of the Working Electrode. The screen-printed working electrodes containing Bi₂O₃ required a potentiostatic conditioning step to convert the precursor compound to metallic bismuth. Two procedures were used to perform the conditioning step: (i) *ex situ* conditioning, which involved immersion of the electrodes in a cell containing 0.1 M KOH and polarisation of the working electrode to -1.4 V vs. ref. for 120 s under stirring at approx. 1000 rpm.; then, the electrode was transferred to the sample solution for analysis, and; (ii) *in situ* conditioning, which did not necessitate any additional steps and could be carried out simultaneously and together with the deposition step as described below – in the following section.

Voltammetric Measurements

Cyclic Voltammetry (CV). The polarisation range and electrode processes related to the Bi₂O₃-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 $v=50 \text{ mV s}^{-1}$ after potentiostatic polarisation at -1.4 V for 120 s.

Anodic Stripping Voltammetry (ASV). For ASV experiments, 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 -0.35 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, $v=10 \text{ mV s}^{-1}$; 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: 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 $v=50 \text{ mV s}^{-1}$; step increment $E_s=4 \text{ mV}$.

Processing and Evaluation of the Measurements. The individual analytical signals were evaluated as the peak heights using the automatic base-line settings by the software. Where applicable, the measurements were evaluated statistically by means of standardised procedures and criteria.

Results and Discussion

Characterisation of the Sensors by Cyclic Voltammetry and Polarisation Range

Initially, the Bi_2O_3 -loaded screen-printed electrodes (4 % w/w) were characterised by cyclic voltammetry in the range -1.4 to 0.6 V after reduction of the Bi_2O_3 modifier to metallic bismuth at -1.4 V for 120 s in three different supporting electrolytes: 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 (Fig. 2). As illustrated in Fig. 2, the forward anodic scan gave rise to an oxidation peak which was due to the oxidation of the metallic bismuth formed during the cathodic polarisation step preceding the cyclic voltammetry; the peak potentials were: 0.16 V (in 0.1 mol l^{-1} acetate buffer (pH 4.5)); -0.19 V (in 0.1 mol l^{-1} ammonia buffer (pH 9.2)), and; 0.42 V (in 0.05 mol l^{-1} nitric acid). In the reverse cathodic scan, reduction peaks appeared as a result of reduction of species formed in the forward anodic scan. The peak potentials were: -0.91 V (in 0.1 mol l^{-1} ammonia buffer (pH 9.2)), and; -0.48 V (in 0.05 mol l^{-1} nitric acid) while the 0.1 mol l^{-1} acetate buffer (pH 4.5) electrolyte produced a wide and ill-defined reduction peak. These results indicate that reduction of the Bi_2O_3 precursor to metallic bismuth does, indeed, occur in a wide range of pH values under conditions of cathodic polarisation of the electrode.

The polarisation range of the Bi_2O_3 -modified screen-printed electrodes (4 % w/w) at the three supporting electrolytes is illustrated as an inset in Fig. 2. In all three electrolytes, the anodic limit was dictated by the oxidation of the metallic bismuth and the cathodic limit by the reduction of hydrogen ions. The polarisation ranges in the three supporting electrolytes were: -1.17 to -0.24 V in 0.1 mol l^{-1} acetate buffer (pH 4.5); -1.27 to -0.35 V in 0.1 mol l^{-1} ammonia buffer (pH 9.2), and; -0.86 to -0.11 V in 0.05 mol l^{-1} nitric acid (Fig. 2). Therefore, the polarisation window is shifted to more anodic values in acidic media and to more cathodic values in basic media.

Electrode Conditioning and Effect of the Bi_2O_3 Loading

In previous work utilising screen-printed or carbon-paste electrodes loaded with Bi_2O_3 for ASV, the reduction of the precursor compounds has been usually carried out *in situ* during the cathodic electrolytic deposition step (in acidic media) [6,8-10]. However, there is one report of the use of a Bi_2O_3 -modified screen-printed electrode, in which the reduction of the precursor compound to form metallic bismuth has been carried out *ex situ* in a separate

solution containing 0.1 M KOH [7]; the authors claiming that their method of the formation of metallic bismuth layer on the electrode surface had resulted in the electrodes with improved sensing features.

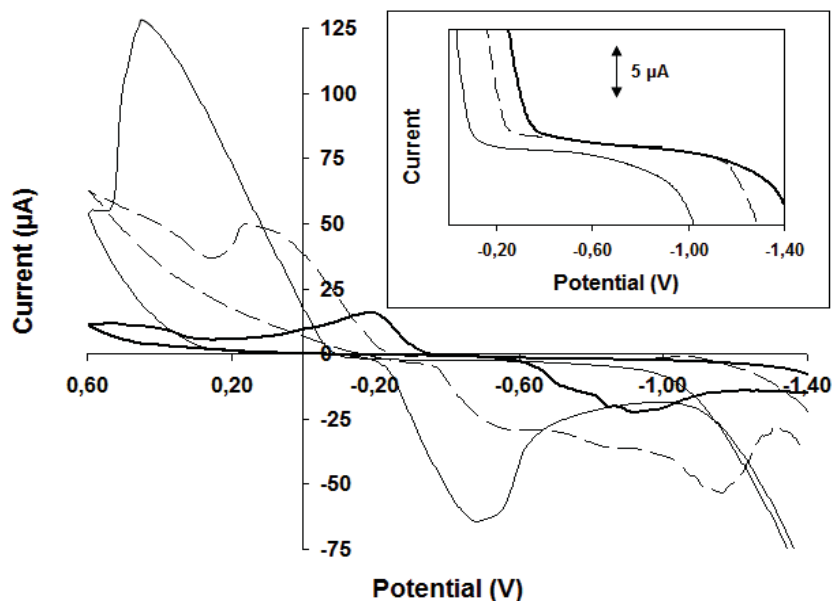


Fig. 2: Cyclic voltammograms at a Bi_2O_3 -modified screen-printed electrode (4 % w/w) in different electrolytes (polarisation range shown in inset). Legend: (---) 0.1 M acetate buffer (pH 4.5), (—) 0.05 M nitric acid, (- · -) 0.1 M ammonia buffer (pH 9.2). Experimental conditions: E_{INIT} and $E_{\text{FIN}} = -1.4$ V, vertex potential, $E_{\text{VX}} = 0.6$ V; scan rate $\nu = 50$ mV s^{-1} ; potentiostatic polarisation at -1.4 V vs. ref. for 120 s before cyclic voltammetry (for other details, see *Experimental*).

In this work, *ex situ* conditioning in 0.1 mol l^{-1} KOH and *in situ* conditioning in 0.1 mol l^{-1} acetate buffer (pH 4.5) were compared for the determination of Pb(II) and Cd(II) by square wave ASV using screen-printed electrodes modified with 2 %, 4 % and 6 % (w/w) Bi_2O_3 (Fig. 3). It was found that the *ex situ* conditioning in 0.1 mol l^{-1} KOH improved the Cd peak height at all the Bi_2O_3 loadings but did not significantly effect the Pb peak height. On the other hand, the electrodes modified with 4 % (w/w) Bi_2O_3 produced the highest Pb and Cd peaks, as well as the most satisfactory background characteristics and resolution (Fig. 3(B)). Therefore, the 4 % (w/w) Bi_2O_3 loading, combined with *ex situ* conditioning in 0.1 mol l^{-1} KOH, was selected for the following experiments.

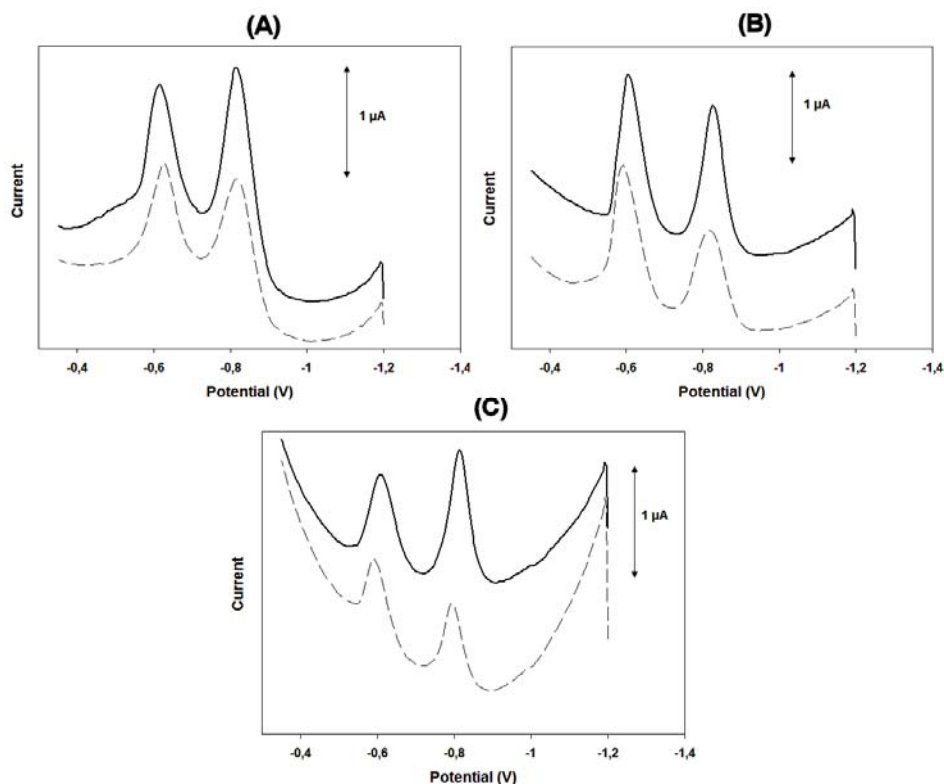


Fig. 3: Square wave stripping voltammograms of $20 \mu\text{g l}^{-1}$ Pb(II) and $40 \mu\text{g l}^{-1}$ Cd(II) at screen-printed electrodes modified with Bi_2O_3 at different loadings using *in situ* and *ex situ* conditioning. Legend: **A**) 2 % (w/w) Bi_2O_3 , **B**) 4 % (w/w) Bi_2O_3 , **C**) 6 % (w/w) Bi_2O_3 ; (---) *in-situ* conditioning at -1.4 V vs. ref. for 120 s in 0.1 M acetate buffer (pH 4.5), (—) *ex-situ* conditioning at -1.4 V for 120 s in 0.1 M KOH (for other details, see *Experimental*).

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 and sulphuric acids at a screen-printed electrode modified with 4 % (w/w) Bi_2O_3 (Fig. 4(A)). The 0.1 mol l^{-1} acetate buffer (pH 4.5) exhibited the best background response at the cathodic side 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 Pb and was, therefore, selected for the following experiments.

Regarding the stripping waveform, a comparison was made between the square-wave (SW), differential pulse (DP) and linear sweep (DC) modulations (Fig. 4(B)). The DC waveform suffered from an excessively sloping baseline while the SW-modulation produced the highest response for 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 to 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.

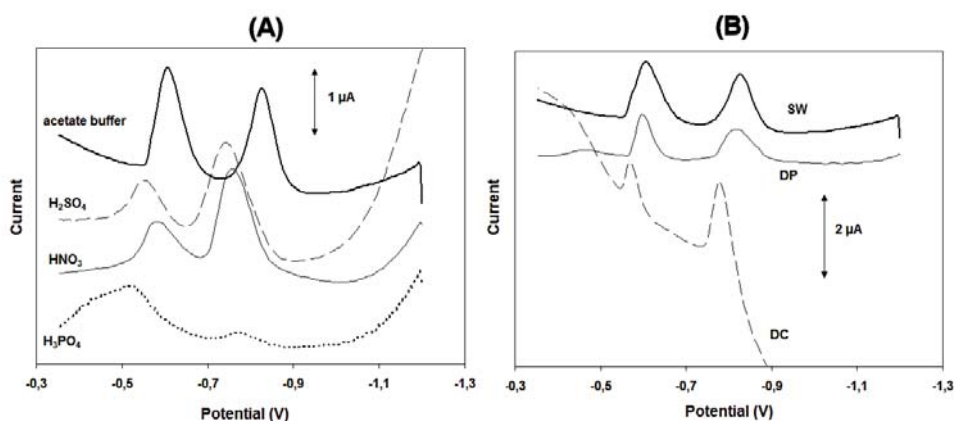


Fig. 4: Effect of the supporting electrolyte and of the stripping waveform (square wave, SW, differential pulse, DP, and linear sweep, DC) on the stripping voltammograms of $20 \mu\text{g l}^{-1}$ Pb(II) and $40 \mu\text{g l}^{-1}$ Cd(II) at a Bi_2O_3 -modified screen-printed electrode (4 % w/w). Legend: **A**) Supporting electrolytes, **B**) Stripping waveform. Experimental conditions: 0.1 M acetate buffer (pH 4.5), 0.05 M nitric acid, phosphoric acid and sulphuric acids; electrode conditioning at -1.4 V vs. ref. for 120 s in 0.1 M KOH (for other details, see *Experimental*).

Effect of the Deposition Time and the Deposition Potential

The effect of the deposition time on the stripping peak heights for Pb and Cd was investigated in the range 20-240 s at a screen-printed electrode modified with 4 % (w/w) Bi_2O_3 (Fig. 5 A). The stripping peak heights followed a 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 on the stripping peak heights for Pb and Cd was studied in the range -1.5 V to -0.9 V at a screen-printed electrode modified with 4 % (w/w) Bi_2O_3 (Fig. 5 B). The deposition potential affected both the reduction of Bi_2O_3 to metallic bismuth and the deposition efficiency of the target metal cations. The stripping peaks were negligible at potentials more positive than -0.9 V and increased rapidly as the deposition potential became more negative until -1.3 V. More negative potentials did not induce significant change in the stripping peak heights as both the Bi_2O_3 at the electrode and the target metal cations reaching the electrode surface were quantitatively reduced. A deposition potential of -1.4 V was finally selected for further work.

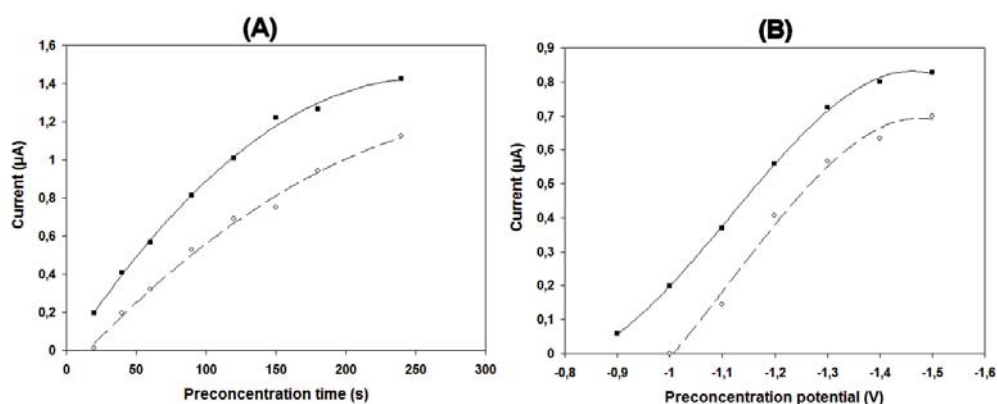


Fig. 5: Effect of the preconcentration time and of the preconcentration potential on the stripping response of $20 \mu\text{g l}^{-1}$ Pb(II) and $40 \mu\text{g l}^{-1}$ Cd(II) at a Bi_2O_3 -modified screen-printed electrode (4 % w/w). Legend: **A)** Preconcentration time, **B)** Preconcentration potential; (—■—) Pb, (—○—) Cd. Experimental conditions: 0.1 M acetate buffer (pH 4.5); DP stripping; deposition time 120 s; deposition potential -1.4 V vs. ref.; electrode conditioning at -1.4 V for 120 s in 0.1 M KOH (for other details, see *Experimental*).

Calibration Features of the Sensors

Calibration for Pb(II) and Cd(II) was performed using the following conditions: screen-printed electrode modified with 4 % (w/w) Bi_2O_3 ; electrode conditioning at -1.4 V for 120 s in 0.1 mol l^{-1} KOH; supporting electrolyte, 0.1 mol l^{-1} acetate buffer (pH 4.5); deposition potential -1.4 V; deposition time 120 s. DP stripping voltammograms for the simultaneous determination of $0\text{--}80 \mu\text{g l}^{-1}$ of Pb(II) and $0\text{--}160 \mu\text{g l}^{-1}$ of Cd(II) are illustrated in Fig. 6 (the calibration plot is shown as an inset).

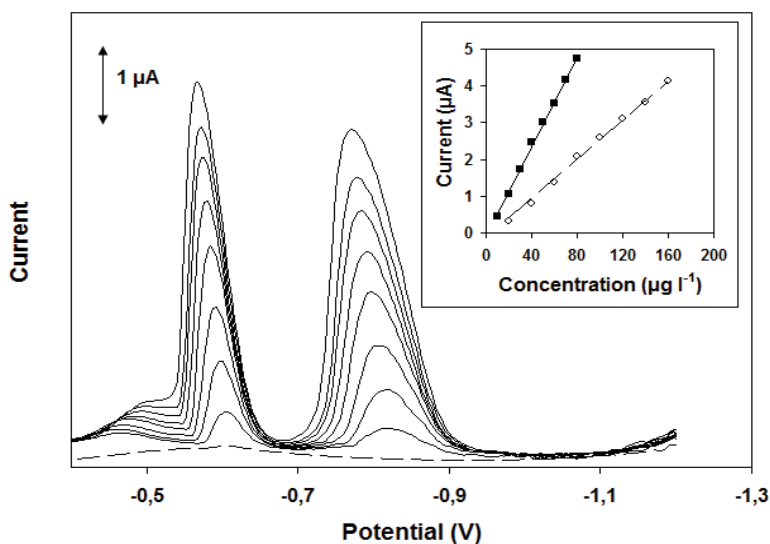


Fig. 6: DP stripping voltammograms for the simultaneous determination of 0–80 $\mu\text{g l}^{-1}$ Pb(II) and 0–160 $\mu\text{g l}^{-1}$ Cd(II) (calibration plot shown as inset). Legend: (– – –) blank, (—) successive additions of 10 $\mu\text{g l}^{-1}$ Pb(II) and 20 $\mu\text{g l}^{-1}$ Cd(II); (– o –) Cd(II), (—■—) Pb(II). Experimental conditions: screen-printed electrode modified with 4 % (w/w) Bi_2O_3 ; electrode conditioning at –1.4 V vs. ref. for 120 s in 0.1 M KOH; supporting electrolyte, 0.1 M acetate buffer (pH 4.5); deposition potential –1.4 V vs. ref.; deposition time 120 s (for other details, see *Experimental*).

In the range examined, the calibration plots were linear and obeyed the equations:

$$\text{Pb: } I_{\text{Pb}}(\mu\text{A}) = (6.1 \pm 0.2) \times 10^{-2} \times C_{\text{Pb}}(\mu\text{g l}^{-1}) + (9.9 \pm 2.3) \times 10^{-2} \quad R^2 = 0.997$$

$$\text{Cd: } I_{\text{Cd}}(\mu\text{A}) = (2.7 \pm 0.1) \times 10^{-2} \times C_{\text{Cd}}(\mu\text{g l}^{-1}) + (5.2 \pm 1.9) \times 10^{-2} \quad R^2 = 0.996$$

The limits of detection (calculated as $\text{LOD} = 3s_b/S$, where " s_b " was the standard deviation of the intercept and " S " the slope of calibration plot) were 1.1 $\mu\text{g l}^{-1}$ Pb(II) and 2.1 $\mu\text{g l}^{-1}$ Cd(II). The reproducibility of measurements at the same sensor (expressed as the RSD [%], for $n = 8$) was $\pm 7.7\%$ for Pb and $\pm 8.4\%$ for Cd, respectively, for the model content of 20 $\mu\text{g l}^{-1}$.

The electrodes were stable for around 10 successive preconcentration / stripping / cleaning cycles and then responses started to decrease gradually. Therefore, these electrodes could be used as semi-disposable sensors enabling a complete analysis to be conducted at a single device in the regime (i) measurement in the original sample and (ii) in sample after the respective standard additions.

Conclusions

In this article, Bi₂O₃-modified screen-printed disposable voltammetric sensors are presented and their electroanalytical utility to determine Pb(II) and Cd(II) ions using ASV demonstrated. It has been found that the best results were obtained with a 4 % (w/w) Bi₂O₃ loading in the carbon ink and with *ex-situ* reduction of Bi₂O₃ in 0.1 M KOH. A 0.1 M acetate buffer (with pH 4.5) was selected as the supporting electrolyte, with stripping in the DPV mode. The LODs, 1.1 µg l⁻¹ Pb(II) and 2.1 µg l⁻¹ Cd(II), and the reproducibility of measurements, ±7.7% for Pb and ±8.4% for Cd, are deemed satisfactory for the rapid quantitative screening of heavy metal traces with a useful sensing lifetime of about ten measuring cycles. Finally, compared to some previous configurations of the Bi₂O₃-SP(C)E type [7-10], or also [14,15], the sensors developed herein have shown comparable or even superior practical applicability.

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