

Trace Metal Analysis by Stripping Voltammetry at a Bismuth-Coated Iridium Microdisc Electrode

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Abstract: This work describes an electrochemical sensor prepared by electroplating *in situ* a bismuth film on an iridium disk microelectrode. The iridium-based bismuth-film electrode (BiFE) was applied for the determination of Pb(II) and Cd(II) by square-wave anodic stripping voltammetry (SWASV). The experimental variables (concentration of the bismuth plating solution, preconcentration potential, accumulation time, SW parameters) were investigated. The limits of detection were $1 \mu\text{g L}^{-1}$ for Pb(II) and Cd(II) (at 300 s of preconcentration) and the % relative standard deviations were than 4.2 % and 5.1 %, respectively, at the $20 \mu\text{g L}^{-1}$ level ($n=10$). In addition, preliminary experiments have demonstrated the utility of the sensor for the determination of other heavy metals (In(III) and Tl(I)). Finally, the iridium-based BiFE was applied to the determination of Pb(II) in tap water.

Keywords: Trace metals; Square-wave anodic stripping voltammetry; Bismuth-film electrode; Iridium; Sensor.

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Introduction

Since their initial introduction, bismuth electrodes have attracted significant attention from the electroanalytical community. Bismuth and its salts exhibit much lower toxicity than mercury and its compounds while the electroanalytical performance of bismuth electrodes approaches that of their mercury counterparts. Therefore, bismuth seems to be one of the most attractive materials that can replace mercury for electroanalysis in the cathodic potential regime and the field of electroanalysis on bismuth electrodes has been extensively reviewed [1-4].

The most widely used type of bismuth electrode for stripping analysis is the bismuth-film electrode (BiFE) prepared by *ex-situ* or *in-situ* electroplating of metallic bismuth on a conductive substrate [1,2]. The nature of the support material is very critical for the performance of the resulting BiFEs and a significant amount of work has been devoted in this area. Different forms of carbon (such as carbon paste, wax-impregnated graphite, pencil-lead, boron-doped diamond, carbon fibres, nitrogen-doped diamond-like carbon, carbon nanotubes, graphene, carbon-film resistors, screen-printed carbon ink, edge-plane pyrolytic graphite and carbon-loaded composites) have been predominantly used as supports for bismuth films [5].

Although the metal supports for bismuth films have been reported, such as those based on copper [6,7] and gold, and platinum [8,9,10], their analytical utility seems to be limited because of the fact that even noble metals (*i.e.* gold) exhibit lower chemical inertness compared to carbon, while they are prone to form intermetallic compounds with the bismuth film and the deposited target metals.

On the contrary, iridium is an ideal support for bismuth-films due to its extreme chemical inertness (the highest among all metals) which prevents both deterioration of its surface and the formation of intermetallic compounds with bismuth or heavy metals during the analysis. Indeed, iridium has been successfully used in the form of disks [11], microfabricated plates [12] or microelectrode arrays [13-15] plated with mercury for the detection of trace metals by stripping voltammetry. Iridium has not been considered as a support for bismuth films until recently; indeed, our group has reported the fabrication of an electrochemical sensor consisting of an iridium wire covered with bismuth for electrochemical stripping analysis [5].

The use of microelectrodes (generally considered as electrodes whose critical dimension is comparable to, or smaller than, the diffusion layer thickness) in voltammetry is advantageous resulting in enhanced rates of mass-transport, decreased ohmic drop, enhanced signal-to-noise ratio, and low capacitive currents as discussed in the relevant reviews [16-21]. Bismuth-film microelectrodes have been fabricated by coating carbon fibers or microdisks of noble metals (Au, Pt) with bismuth [10, 22-29].

This contribution deals with a work that can be understood as an extension of our initial study with bismuth-coated iridium wire electrodes [5] in the configuration of iridium microdisk BiFEs which are being examined as the sensors for detection of heavy metals with the aid of square-wave anodic stripping voltammetry (SWASV).

Experimental

Chemicals, Reagents, Stock, and Standard Solutions

All the chemicals were of analytical grade and purchased from Merck (Darmstadt, Germany) or Sigma-Aldrich (USA). Doubly-distilled water was used. Stock Cd(II), Pb(II), Zn(II), In(III) and Tl(I) solutions (1, 5, 10, 20, 50, and 100 mg L⁻¹) were prepared from 1000 mg L⁻¹ atomic absorption standard solutions after appropriate diluting with deionised water.

A 1000 ± 0.01 mg L⁻¹ Bi(III) standard solution (originally AAS standard) was used for the *in-situ* formation of the bismuth film. The working supporting electrolyte was represented by 0.1 mol L⁻¹ acetate buffer (pH 4.5) prepared from a stock solution of 1 mol L⁻¹ acetate buffer (pH 4.5).

Electrochemical Apparatus and Other Instrumentation

Electrochemical experiments were performed with a home-made potentiostat interfaced to a Pentium PC through a multi-function interface card (6025E PCI, National Instruments, TX). Cyclic voltammetry and SWASV were carried out by a purpose-developed application programme developed in LabVIEW 7.1.

The potentiostat was connected to an external electrode stand with the three-electrode cell comprising an iridium microdisc electrode (see below), a Ag|AgCl|3M KCl reference and a Pt-wire serving as the counter. Stirring was accomplished with a magnetic bar agitated at approx. 300 rpm.

The surface of the microdisc electrode was inspected by means of a scanning electron microscope (SEM) (Leo 440, Carl Zeiss, Germany) and an optical microscope (Karl Suss PA 200, SUS Microtec).

Iridium Microdisk Electrode

The iridium microdisc electrode was prepared by sealing an iridium wire (75 µm in diameter; Alfa Aesar GmbH, Karlsruhe, Germany) in borosilicate capillary tubes (WPI Inc., USA) with a two-component epoxy resin glue (RS Components, UK). The assembly was polished of emery polishing paper to remove the excess glue from the tip and to reveal the microelectrode tip. The surface was inspected by SEM and optical microscopy.

Collection and Preparation of the Samples

Collection of the Sample. A tap water sample was collected from taps in our laboratory. For the determination of Cd(II) and Pb(II) in tap water, 0.90 mL of tap water was added to 0.10 mL of the 1 mol L⁻¹ acetate buffer (pH 4.5) and analyzed directly.

Analysis of Standard Solutions and Samples. The SWASV voltammogram was recorded by immersing the electrodes into the solution to be analyzed, spiking the solution with the required volume of the 1000 mg L⁻¹ solution of Bi(III) to achieve the desired Bi(III) concentration and carrying out preconcentration at the deposition potential, E_{DEP} , for a precisely defined deposition time, t_{DEP} , under stirring. After accumulation, the stirring was stopped and, after a 10 s rest period, an anodic square-wave scan was applied to the working electrode from a starting potential, E_{INIT} , to a final potential, E_{FIN} . Finally, a cleaning step was utilized at a cleaning potential, E_{CL} , for a cleaning time, t_{CL} , under stirring to oxidize and strip off any remaining bismuth and deposited target metals from the electrode. Appropriate additions of the stock metal (Cd(II), Pb(II), Zn(II), In(III), Tl(I)) solutions were made directly into the cell as required and the measurement procedure was repeated after each addition. The standard additions plot was used to calculate the native concentration of target metals in the sample.

Electroanalytical Measurements and Related Procedures

Air and Oxygen Removal. For the cyclic voltammetric experiments, the solution was deoxygenated by bubbling with N₂ (purity of 99.9%) for approx. 5 min. For the SWASV experiments, no deoxygenation was necessary.

Conditioning of the Iridium Microelectrode. The iridium microelectrode was electrochemically treated in 0.1 mol L⁻¹ acetate buffer (pH 4.5) by successive potential scans in the range ± 1.5 V until a stable baseline was obtained.

Voltammetric Measurements

Cyclic Voltammetry (CV). The iridium microdisc electrode was characterized in a 5 mmol L⁻¹ ferricyanide/0.1 mol L⁻¹ KCl solution by potential scanning from +0.5 V to -0.5 vs. Ag/AgCl and reversely with a scan rate of 5 mV·s⁻¹.

Square-Wave Anodic Stripping Voltammetry (SWASV). The detection was performed in the anodic direction after electrolytic accumulation at $E_{\text{DEP}} = -1.2$ V for at $t_{\text{DEP}} = 300$ s. If not stated otherwise, the scanning started at an initial potential, $E_{\text{INIT}} = -1.2$ V to a final potential, $E_{\text{FIN}} = +0.3$ V vs. ref. Ag/AgCl with square-wave conditions: frequency, 50 Hz; pulse height, 40 mV; step increment, 4 mV. Finally, cleaning was performed at $E_{\text{CL}} = +0.3$ V for $t_{\text{CL}} = 10$ s. For the analysis of the tap water sample, electrolytic accumulation was performed at $E_{\text{DEP}} = -1.0$ V the initial potential was set to, $E_{\text{INIT}} = -1.0$ V.

Processing and Evaluation of the Measurements. The individual analytical signals were evaluated as the peak heights calculated by a purpose-developed application programme developed in LabVIEW 7.1.

Results and Discussion

Electrochemical Characterization of the Iridium Microdisc Electrode

The CV scan of the iridium microdisc electrode in a 5 mmol L^{-1} ferricyanide/ 0.1 mol L^{-1} KCl solution in the potential range $+0.5$ V to -0.3 vs. Ag/AgCl is illustrated in Fig. 1. The current-potential plot is sigmoidal, indicating a near-steady state response characteristic of near-microelectrode behaviour.

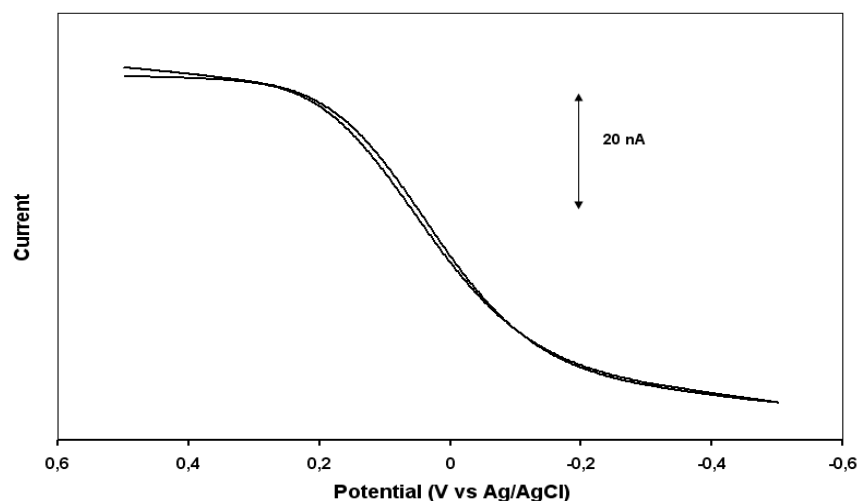


Fig. 1: Cyclic voltammetry at the iridium microdisc electrode ($75 \mu\text{m}$ in diameter) in 5 mmol L^{-1} ferricyanide/ 0.1 mol L^{-1} KCl. Experimental conditions: CV initial and final potential, E_{INIT} and $E_{\text{FIN}} = +0.5$ vs. Ag/AgCl, vertex potential, $E_{\text{VX}} = -0.5$ V vs. Ag/AgCl; $v = 5 \text{ mV s}^{-1}$.

The diffusion-limited current, I_L , associated with n -electron redox reaction at a microelectrode is given by:

$$I_L = 4nFCDr \quad (1)$$

where: " C " is the concentration of the redox species, " D " is the diffusion coefficient, " r " is the radius of the microelectrode, and " F " is the Faraday constant.

By substituting into the equation (1): $n = 1$; $C = 5 \times 10^{-3} \text{ mol L}^{-1}$; $D = 7.63 \times 10^{-6} \text{ cm}^2 \text{ s}^{-1}$; $I_L = 53 \text{ nA}$; and $F = 96\,485 \text{ C} \cdot \text{mol}^{-1}$, the diameter was calculated to be $72 \text{ }\mu\text{m}$ which corresponds to 96 % of the nominal value of $75 \text{ }\mu\text{m}$. During the course of this study, regular CV scans confirmed that the diameter was always within 5% of its nominal value.

Study of the Bi(III) Concentration, the Preconcentration Time and the Deposition Potential

The effect of the final Bi(III) concentration on the Pb and Cd stripping peak currents in a solution containing $20 \text{ }\mu\text{g l}^{-1}$ each of Cd(II) and Pb(II) in 0.1 mol l^{-1} acetate buffer (pH 4.5) is illustrated in Fig. 2A. At low Bi(III) concentrations (up to 0.5 mg l^{-1}), a sharp increase in both stripping peaks was observed with increasing Bi(III) concentration. In the higher Bi(III) concentration regime ($> 0.5 \text{ mg l}^{-1}$), as the Bi(III) concentration increased the Pb peak decreased as opposed to the Cd peak that increased. The results of the study of the effect of the deposition time on the Pb and Cd stripping peak currents in a solution containing $20 \text{ }\mu\text{g l}^{-1}$ each of Cd(II) and Pb(II) in 0.1 mol l^{-1} acetate buffer (pH 4.5) are illustrated in Fig. 2B. While both the Pb and Cd stripping peaks increased with increasing deposition time until eventual levelling-off, the rate of increase was markedly faster in the case of Cd. The results of these two experiments suggest that thicker films (due to higher Bi(III) concentration and/or higher deposition times) favour the deposition and stripping of Cd while thinner bismuth films favour the deposition and stripping of Pb. This trend has been observed previously with a bismuth-coated iridium wire electrode [5] but not with other types of supports.

The effect of the deposition potential on the stripping peaks of Pb and Cd in a solution containing $20 \text{ }\mu\text{g l}^{-1}$ each of Cd(II) and Pb(II) in 0.1 mol l^{-1} acetate buffer (pH 4.5) are illustrated in Fig. 2C. The stripping peaks increased as the deposition potential became more negative and achieved their maximum value at -1.2 V . At even more negative potentials, a drop was observed attributed to the evolution of hydrogen gas that mechanically prevented the deposition of the metals on the electrode surface.

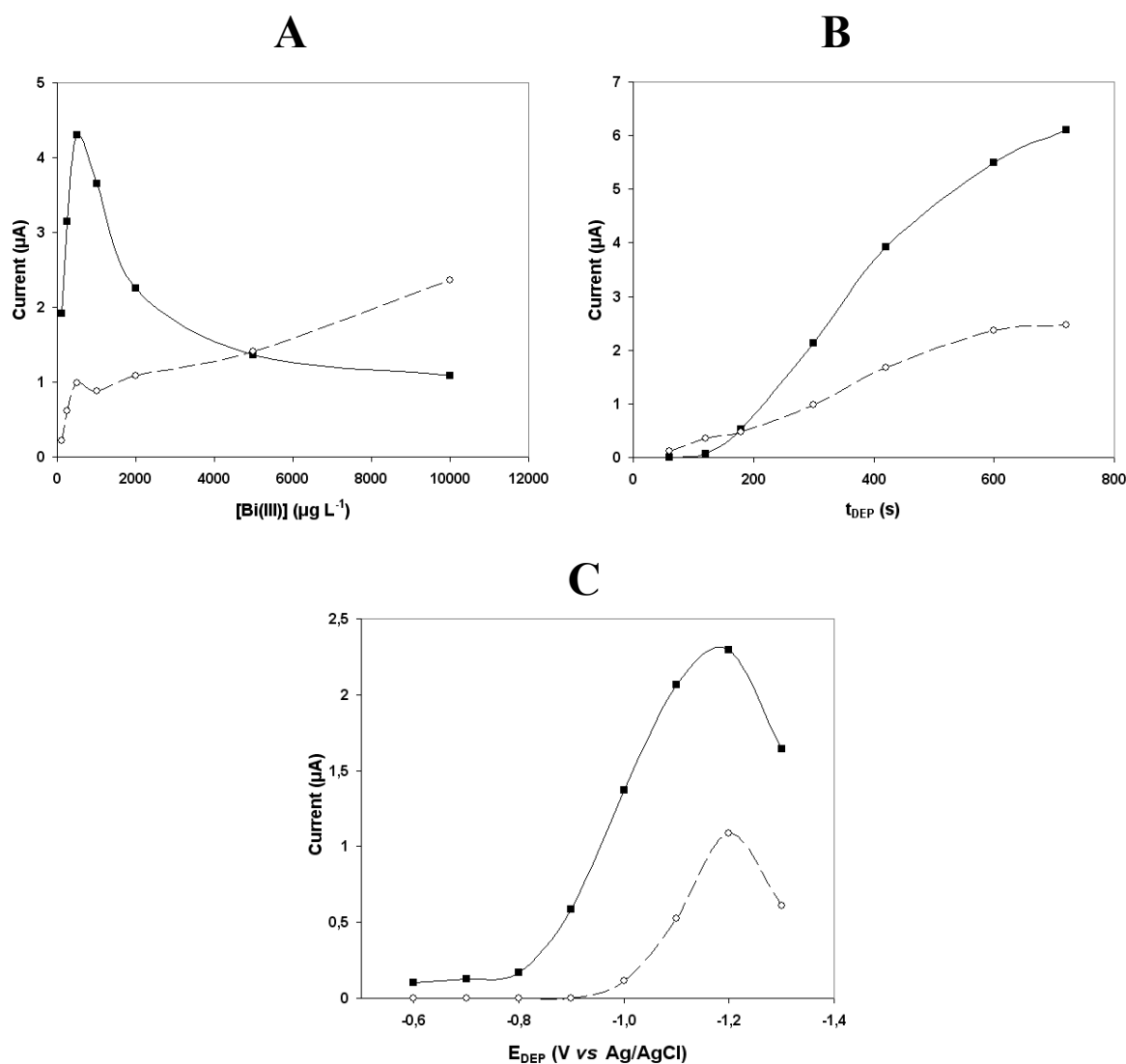


Fig. 2: The effect of the Bi(III) concentration, deposition time and deposition potential on the peak currents for Pb and Cd. Legend: **A)** Bi(III) concentration, **B)** deposition time, **C)** deposition potential. Experimental conditions: **A)** $t_{\text{DEP}}=300$ s; $E_{\text{DEP}} = -1.2$ V vs. ref.; **B)** $c(\text{Bi}^{\text{III}}) = 2$ mg L⁻¹, 300 s; $E_{\text{DEP}} = -1.2$ V vs. ref., **C)** $t_{\text{DEP}}=300$ s; $c(\text{Bi}^{\text{III}}) = 2$ mg L⁻¹; Pb (■—■), Cd (○—○); for other details, see *Experimental*.

Effect of the Square-Wave Parameters

The stripping step was performed using the square-wave modulation that enables high sensitivity and speed as well as tolerance to the presence of dissolved oxygen that allows the analysis to be carried out in the presence of oxygen thus avoiding the time-consuming deoxygenation step. The SW parameters affecting the response were the frequency, the scan increment and the pulse height and were investigated unvaried using a solution containing 20 μg l⁻¹ each of Cd(II) and Pb(II) in 0.1 mol l⁻¹ acetate buffer (pH 4.5).

The effect of frequency was studied in the range of 12.5-200 Hz (Fig. 3A) and the effect of step increment was investigated between 1 and 16 mV (3B); increasing either of these parameters results in an increase of the effective scan rate. The Pb and Cd peaks shifted to more positive values and their heights increased with the frequency or step increment. The anodic shift was attributed to the fact that oxidation of metals became less reversible at higher scan rates while the increase in the peak heights was a consequence of the higher scan rates. However, at higher scan rates, the peaks widened and the anodic background deteriorated. As a compromise, a frequency of 50 Hz and step increment of 4 mV were selected.

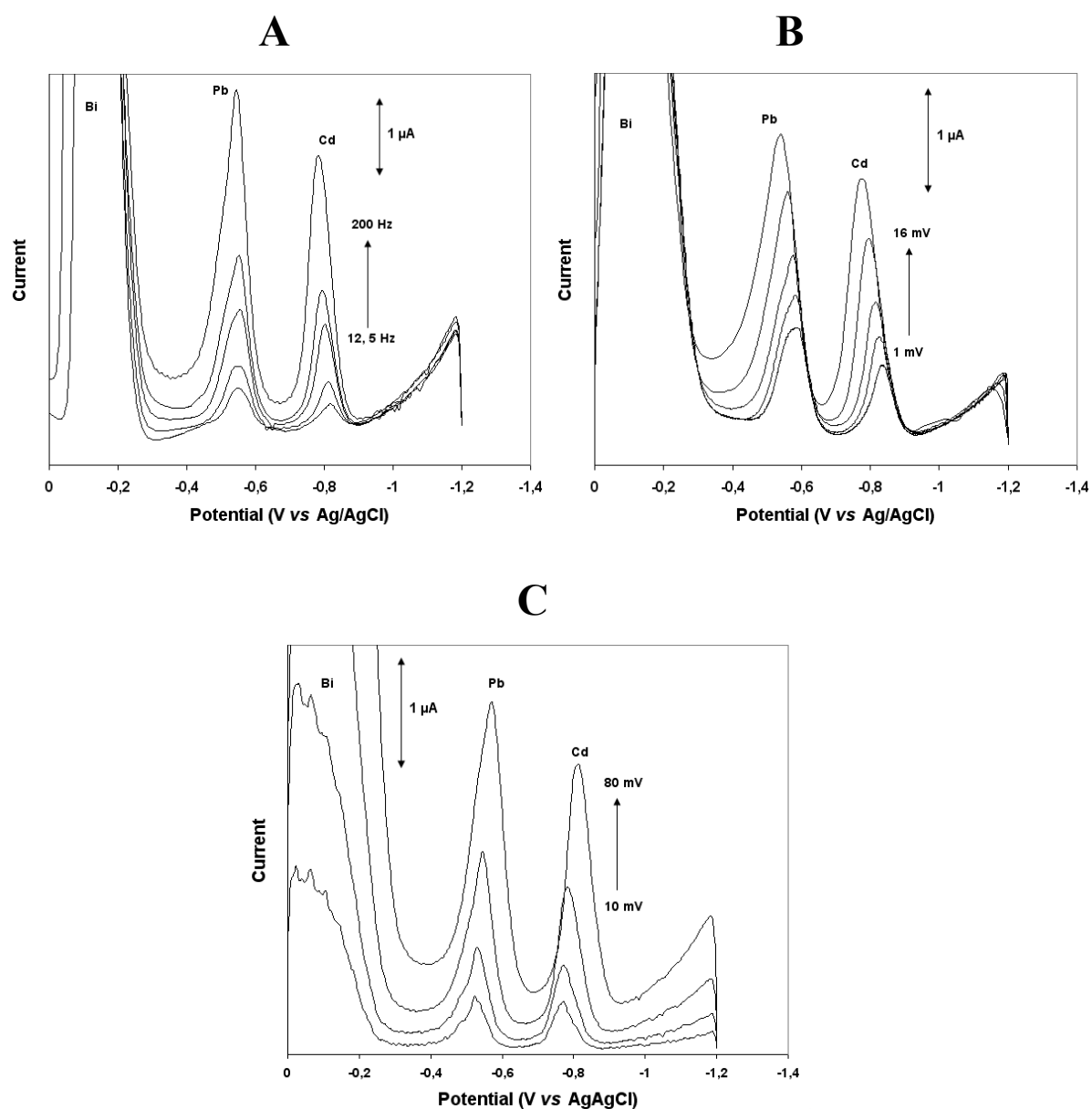


Fig. 3: The effect of the SW parameters upon the voltammetric peaks for Pb and Cd. Legend: A) SW frequency, B) SW scan increment, C) SW pulse height. Experimental conditions: $t_{\text{DEP}}=300$ s; $E_{\text{DEP}}=-1.2$ V vs. ref., $c(\text{Bi}^{\text{III}})=4$ mg L⁻¹; for other details, see *Experimental*.

The effect of the SW pulse height was studied in the range from 10 to 80 mV (Fig. 3C). The peak potentials were shifted to the cathodic direction and the peak heights increased upon increase of the pulse height. However, the background deteriorated at both the anodic and cathodic sides and the peak widths increased at higher pulse heights. Therefore, a pulse height of 40 mV was finally used.

Calibration Parameters for Pb(II) and Cd(II) Determination

The previous experiments have demonstrated that maximal sensitivity for Cd(II) was achieved at high Bi(III) concentrations while for Pb at low Bi(III) concentrations. Therefore, calibration graphs for the determination of Pb(II) and Cd(II) were constructed for depositions for 300 s at two Bi(III) concentrations: 0.5 and 8 mg L⁻¹; series of voltammograms for increasing target metal concentrations being illustrated in Fig. 4A and 4B (with calibration plots as insets).

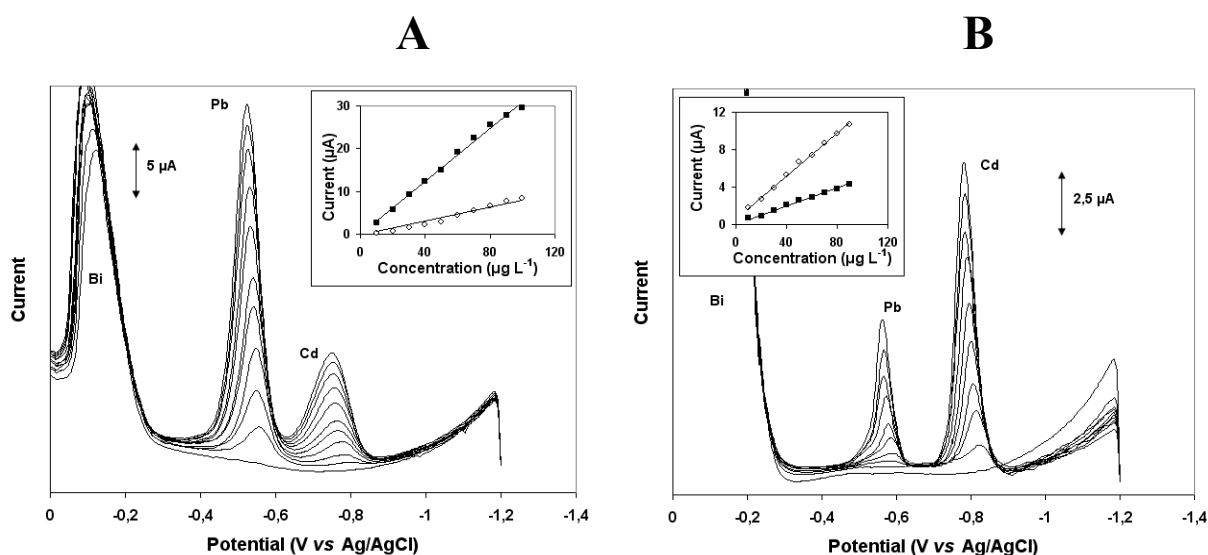


Fig. 4: Voltammograms for increasing Cd(II) and Pb(II) concentrations in steps of 10 g L⁻¹ and respective calibration plots (insets). Legend: **A**) c(Bi^{III}) = 0.5 mg L⁻¹, **B**) c(Bi^{III}) = 8 mg L⁻¹. Experimental conditions: t_{DEP}=300 s; E_{DEP} = -1.2 V vs. ref.; Pb (■ —■), Cd (○ —○); for other details, see *Experimental*.

The LODs for Pb(II) and Cd(II) achieved using 0.5 and 8 mg L⁻¹ Bi(III), respectively, were both 1 μg L⁻¹ at the 3σ level. The reproducibility of the electrodes was investigated by 10 repetitive measurements in a solution containing 20 μg L⁻¹ of Pb(II) and Cd(II) at the two Bi(III) concentrations (0.5 and 8 mg L⁻¹); the coefficient of variation were lower than 4.2 % for Pb(II) and 5.1 % for Cd(II) in all cases.

Scope for the Determination of Other Metals

The bismuth-coated iridium microdisc electrode was applied to the determination of other trace metals normally detected by stripping voltammetry. Voltammograms and calibration plots for the determination of Tl(I) and In(III) and are illustrated in Fig. 5A and 5B, respectively (the small peak at -0.53 V in Fig. 5B was attributed to the presence of Pb(II) as contamination). Linear calibration plots were obtained in a wide concentration range. These initial experiments suggest that the proposed sensors could be applied to the determination of other metal cations provided that their peaks potentials are sufficiently separated. Therefore, In(III) could be determined in the presence of Pb(II) but not Cd(II) while the Tl peak overlaps with both the Cd and Pb peaks and requires the use of EDTA to achieve effective separation.

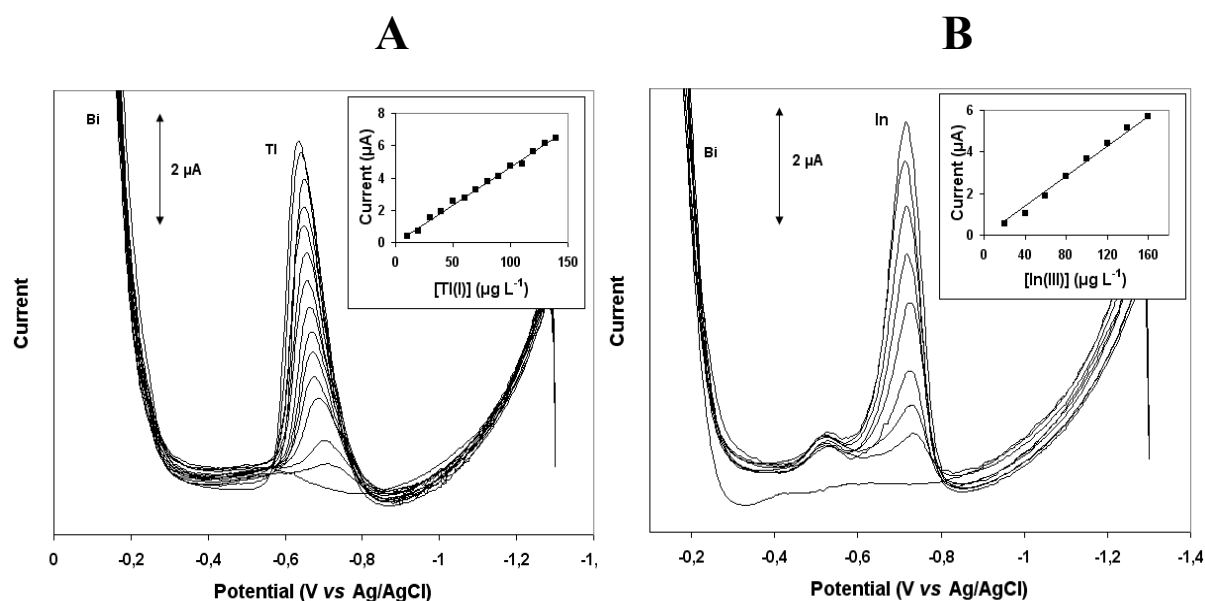


Fig. 5: Voltammograms for increasing Tl(I) and In(III) concentrations in steps of 10 g L^{-1} and respective calibration plots (insets). Legend: **A)** Tl(I), **B)** In(III). Experimental conditions: $c(\text{Bi}^{\text{III}}) = 2 \text{ mg L}^{-1}$; $t_{\text{DEP}} = 300 \text{ s}$; $E_{\text{DEP}} = -1.2 \text{ V vs. ref.}$; for other details, see *Experimental*.

Analysis of Tap Water

The bismuth-coated iridium microelectrode was applied to the determination of Pb(II) and Cd(II) in tap water. In this case, the electrolytic accumulation was performed at $E_{\text{DEP}} = -1.0 \text{ V}$ to avoid the co-deposition of Zn that exists in a large excess in this type of sample.

The concentration of Cd(II) was lower than the LOD of the methods while the Pb(II) was determined as $(6.8 \pm 0.08) \mu\text{g L}^{-1}$ ($n=3$) using the method of standard additions. Stripping voltammograms and the respective standard additions plot for the tap water sample are illustrated in Fig. 6 below.

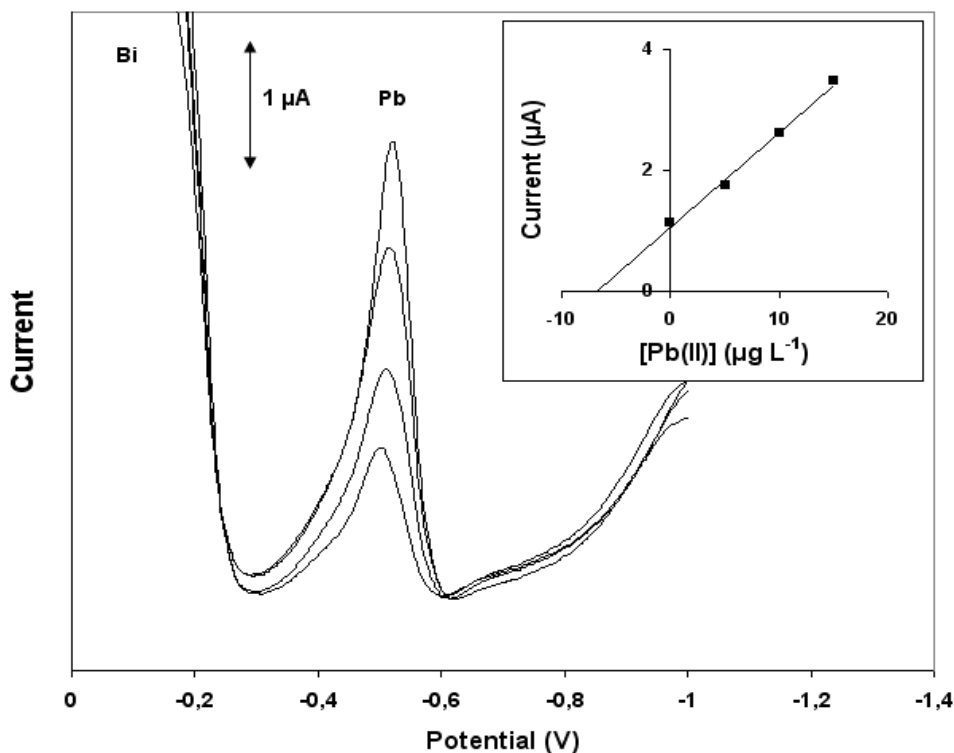


Fig. 6: Voltammograms and standard additions plot for the determination of Pb(II) in tap water. Experimental conditions: $c(\text{Bi}^{\text{III}}) = 8 \text{ mg L}^{-1}$; $t_{\text{DEP}}=300 \text{ s}$; $E_{\text{DEP}} = -1.0 \text{ V}$ vs. ref. ; traces (from below): sample and 3 successive additions of $5 \mu\text{g L}^{-1}$ Pb(II); for other details, see *Experimental*.

Conclusions

In this article, an iridium disk microelectrode was proposed as a support for *in situ* plating of bismuth films. The resulting BiFE was used for the determination of trace metals by square-wave anodic stripping voltammetry. The sensor was investigated in terms of the deposition time, deposition potential, the Bi(III) concentration and the square-wave modulation ramp and was successfully applied to the trace determination of Cd(II) and Pb(II). The electrode exhibited favourable analytical performance and could be potentially applied to determine some less common but important toxic metals, such as Tl(I) or In(III), respectively [30].

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