

Dual Approach to Amplify Anodic Stripping Voltammetric Signals Recorded Using Screen Printed Electrodes

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Received: 5 November 2016 /Accepted: 5 December 2016 /Published: 30 December 2016

Abstract: Screen printed electrodes plated with bismuth were used to record anodic stripping voltammograms of Pb(II), In(III) and Cd(II). Using two bismuth precursors: Bi₂O₃ dispersed in the electrode body and Bi(III) ions spiked into the tested solution it was possible to deposit bismuth layers, demonstrating exceptional ability to accumulate metals forming alloys with bismuth. The voltammetric signals were amplified by adjusting the electrode location with respect to rotating magnetic field. The electrode response was influenced by vertical and horizontal distance between the magnet center and the sensing area of screen printed electrode as well as the angle between the magnet surface and the electrode. When the electrode was moved away from the magnet center the recorded peaks were increasingly smaller and almost not affected by the presence of bismuth ions. It was shown that to obtain well-shaped signals a favourable morphology of bismuth deposits is of key importance. Hypotheses explaining processes responsible for the amplification of voltammetric signals were proposed.

Keywords: Screen printed electrodes, Anodic stripping voltammetry, Bismuth precursors, Bismuth film electrode.

1. Introduction

Anodic stripping voltammetry (ASV) is a proven electrochemical method for trace metal analysis, providing low detection limits (sub μgL^{-1} range) and the capability of multimetal analysis. All stripping techniques have two consecutive steps in common: preconcentration of analyte species and follow-up electrooxidation or electroreduction of accumulated analyte. After accumulation the recorded signals are several times higher than that not preceded by analyte accumulation and, in this way, the stripping

techniques have the lowest limits of detection of any of the commonly used electroanalytical techniques.

Historically, mercury was the electrode of choice for ASV. Recently, however, there has been much interest in developing substitute electrode materials because of mercury's toxicity and volatility. Bismuth is an alternate electrode material that possesses many of the same properties for metal ion analysis that mercury does, and is both non-toxic and non-volatile [1]. Some of the attractive properties of bismuth electrodes for electroanalysis are their wide negative potential window, large overpotential for hydrogen evolution, insensitivity to dissolved oxygen (an

essential feature for onsite applications) and simple preparation. Bismuth film electrodes (BiFEs) have been found to provide a sensitive, reproducible, and stable response for several metal ions [2] and other priority organic compounds [3] in different types of samples.

The unique capability of bismuth electrode to accumulate metals could be ascribed to the ability of bismuth to form 'fused' alloys, with a melting point below 100 °C [4]. Bismuth readily combines with many metals and forms with them binary and multimetal alloys: binary (e.g., Bi-Pb), ternary (e.g., Bi-Pb-Sn; Bi-Sn-In), quaternary (e.g., Bi-Pb-Sn-Cd) and even quinary (e.g., Bi-Pb-Sn-Cd-In) or senary (e.g., Bi-Pb-Sn-Cd-In-Tl). Electrodeposited alloys are similar to thermally prepared alloys in structure and they usually contain the same phases [5].

During co-deposition of bismuth and one or more metals non only an alloy can be deposited but also formation of individual crystals of each metal is possible. The formation of different deposits of zinc on both bismuth and carbon support, which exhibit different lattice energy, was responsible for peak splitting reported for screen printed and glassy carbon electrodes [6-7].

Unlike spectrometric methods, electrochemical techniques are suitable for miniaturization and on-site applications. Using microfabrication techniques (e.g. chemical or physical vapor deposition coupled with photolithography) or screen-printing techniques it is possible to produce small planar electrodes serving as electrochemical sensors.

The screen-printed electrodes (SPEs) have been attracting increasing interest in stripping voltammetry as an alternative substrate for metal film formation because of their numerous advantages, such as mass production, low cost, small size, lower susceptibility to oxygen interferences and the possibility of disposal after a single use [8-10]. Moreover, integrated screen-printed electrodes comprising 3-electrodes on one strip require smaller amounts of samples, which decreases the volume of the solutions used and waste generated. SPEs could be coupled with portable, battery-operated electrochemical analyzers making them a convenient tool for on-site analysis for the reasons of cost, simplicity, speed (analysis time shorter than 5 min), sensitivity (LOD's below $\mu\text{g/l}$) and portability. Before the application of the SPE's in voltammetric analysis its surface is frequently modified with additional layers which positively influence their voltammetric performance.

In this paper SPE's plated with bismuth film originating from two bismuth precursors: Bi_2O_3 dispersed in the electrode body and Bi(III) ions spiked into the tested solution were applied for the development of Pb(II), In(III) and Cd(II) voltammetric curves. The deposition of bismuth film was performed using different locations of SPE strips with the respect to magnetic field induced by the rotating permanent magnet. Eventually, the synergic effect of two bismuth precursors and the favorable location of SPE contributed to the amplification of target metals.

2. Experimental

2.1. Apparatus and Instrumentation

Electrochemical measurements were performed using an Autolab PGSTAT204 (Nova 1.10.1.9 software) potentiostat with a standard three-electrode configuration. The screen-printed electrodes (4 mm in diameter; bismuth-oxide-modified DRP 110BI) were provided by Dropsens, Spain. The magnetic stirrer (Metrohm 801) was controlled with NOVA software. The magnet built into the stirring device induced a magnetic field of up to 86 mT, while the field induced by the 7 mm long stirring flea was up to 3 mT. The voltammetric experiments were performed in the cuboid (50×50×29 mm) polystyrene vessel.

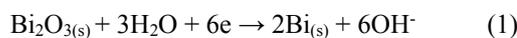
2.2. Procedure

Prior to the experiments, the SPE electrode was immersed in the tested solution for 1 minute. The supporting electrolyte contained 0.08 M $\text{CH}_3\text{COONH}_4$, $1.5 \text{ mg}\cdot\text{l}^{-1}$ Bi(III), $0.26 \text{ g}\cdot\text{l}^{-1}$ NaCl, and had a pH of 6.3. The accumulation potential of -1.5 V was then applied for 300 s and the DP-ASV curve was recorded within the range of -1.5 V to 0.3 V. During accumulation, the solution was stirred using a magnetic bar. The parameters of the DPV mode were as follows: $\Delta E = 25 \text{ mV}$, $E_s = 5 \text{ mV}$, $t_{\text{eq}} = 5 \text{ s}$.

3. Results and Discussion

3.1. The Selection of Bismuth Precursor

The SPEs modified with bismuth oxide were chosen as a sensor for anodic stripping voltammetric studies. Bismuth oxide may be electrochemically converted to metallic bismuth in both highly alkaline media (1) and acidic media (2) after the application of a negative potential.



When other metals are present in the solution they could be co-deposited with bismuth. During co-deposition alloys or deposits consisting of individual crystals of target metals and bismuth are formed. In the course of stripping the opposite process takes place, namely the target metal and bismuth are stripped off from the electrode surface by positive going potential scan.

In Fig. 1 the ASV voltammograms recorded using bismuth film deposited in 0.1 M KOH by electroreduction of Bi_2O_3 dispersed in SPE carbon ink are shown. The recorded signals of Zn(II) and Cd(II) did not stabilize and continued to drift downward starting from the forth curve. When the fifth

voltammogram is considered the zinc signal retained only 6 % of the current value measured on the first voltammogram.

Given that poor performance of bismuth films deposited in alkaline media the consecutive experiments involved bismuth films plated in acidic media only.

The first results obtained after deposition of bismuth layer from bismuth oxide dispersed in SPE's ink were still unsatisfactory. The ASV peaks recorded using such electrode (Fig. 2, curves 1-3) were rather low, wide and sometimes distorted by undesirable shoulders. The electrode response improved clearly only after Bi(III) ions were introduced into the tested solution (Fig. 2, curve 4). Using a combination of these two precursors i.e. Bi₂O₃ dispersed in carbon ink and Bi(III) present in the examined solution, it was possible to deposit bismuth layers demonstrating exceptional ability to accumulate metals forming alloys with bismuth [11]. The double-precursor-electrode was therefore selected as suitable for further experiments.

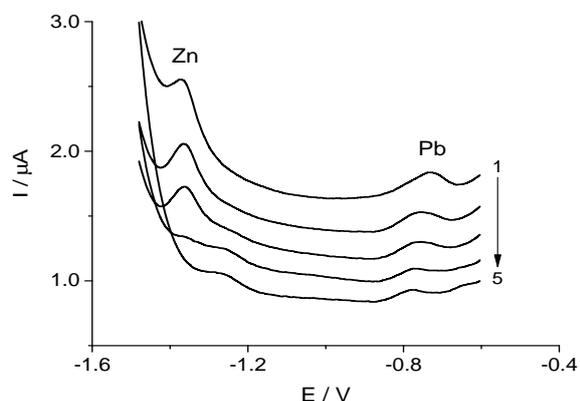


Fig. 1. DP-ASV curves of Zn(II) and Pb(II) obtained in mineral water. Composition of the examined solution: mineral water diluted 2 times, 0.08 M CH₃COONH₄, pH = 6.3. E_{acc} = -1.5 V, t_{acc} = 300 s. Plating procedure: 0.1 M KOH, E_{plat} = -1.2 V, t_{plat}: 600 s (ex-situ plating).

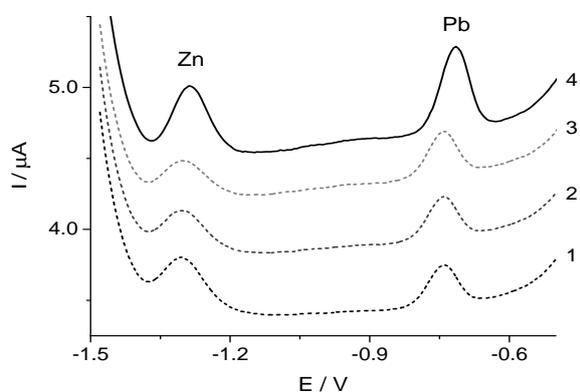


Fig. 2. DP-ASV curves of Zn(II) and Pb(II) obtained in mineral water. Composition of the examined solution: mineral water diluted 2 times, 0.08 M CH₃COONH₄ (curves 1 – 3), 1.5 mg×l⁻¹ Bi(III) (curve 4), pH = 6.3. E_{acc} = -1.5 V, t_{acc} = 300 s. Plating procedure: bismuth co-deposited with target ions (in-situ plating).

3.2. The Arrangement of SPE and Magnetic Stirrer

The ASV signal of examined metals could be amplified by another 200 %-600 % after adjusting the SPE location with respect to magnetic field [11-12]. Three factors were considered: (v) vertical and (h) horizontal distance between the magnet center and the sensing area of SPE and, finally, the angle (α) between the magnet surface and the SPE strip as shown in Fig. 3. Effect of different SPE arrangements on the geometry of voltammograms of lead, indium and cadmium is shown in Figs. 4–7.

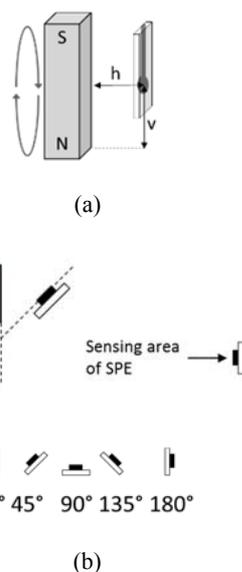


Fig. 3. (a) Side, and (b) top view of SPE arrangement. M – magnet.

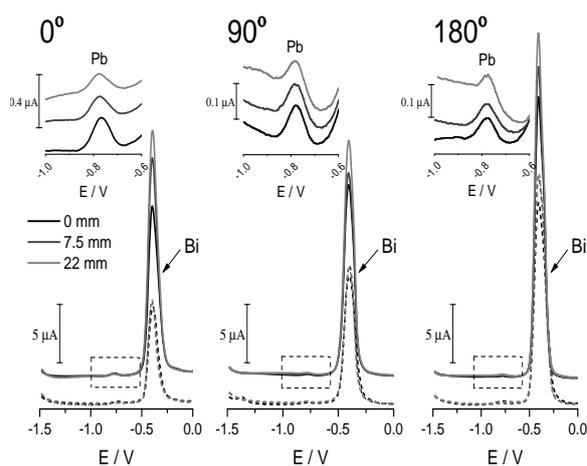


Fig. 4. DP-ASV curves of Pb(II) obtained in the absence (dash line) in the presence (solid line) of Bi(III) ions at different vertical (v) SPE's location. Composition of the examined solution: 10 μg×l⁻¹ Pb(II), 0.08 M CH₃COONH₄, 1.5 mg×l⁻¹ Bi(III) (solid lines only), pH = 6.3, 0.26 g×l⁻¹ NaCl. E_{acc} = -1.5 V, t_{acc} = 300 s. h = 8 mm. Insets: magnified fragment of voltammograms showing lead signals.

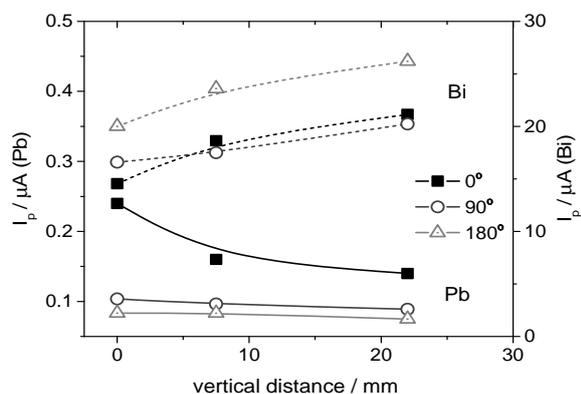


Fig. 5. The influence of vertical location and of the angle (α) between the magnet surface and the SPE strip on the lead (solid line) and bismuth (dash line) signal. $h = 0.8$ cm, $c_{Pb(II)} = 10 \mu g \times l^{-1}$. Other parameters as in Fig. 3.

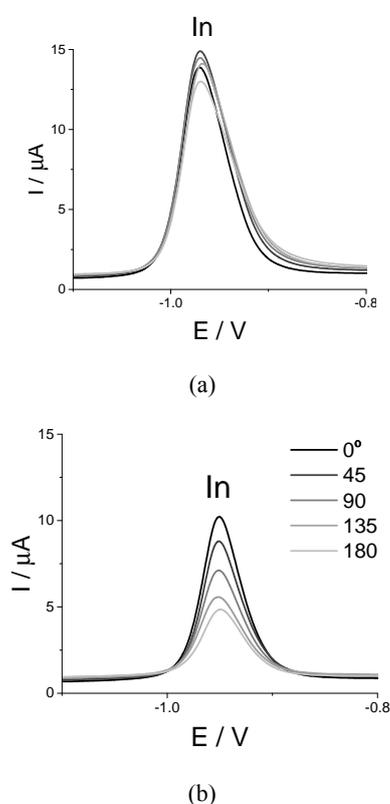


Fig. 6. DP-ASV curves recorded in two horizontal locations of SPE: (a) $h = 0.8$ cm, (B) $h = 1.6$ cm (b) and different α values. $v = 0$ cm, $c_{In(III)} = 50 \mu g \times l^{-1}$.

In the absence of Bi(III) ions in the examined solution the influence of SPE location on both lead (analyte) and bismuth (film material) signals is minimal (Fig. 4, dash line). When examined solution was spiked with Bi(III) ions the lead signal exhibited clear dependence on the location and SPE's angle. The highest lead signals were observed when the electrode was parallel to the stirring plane and the distance from magnet center was minimal. The opposite trend was observed for bismuth signal (Fig. 5). As far as indium and cadmium signals go, increasing of the distance between the magnet and the SPEs' surface both in

horizontal (Fig. 6) and vertical directions (Fig. 7) caused a decrease in their peak currents.

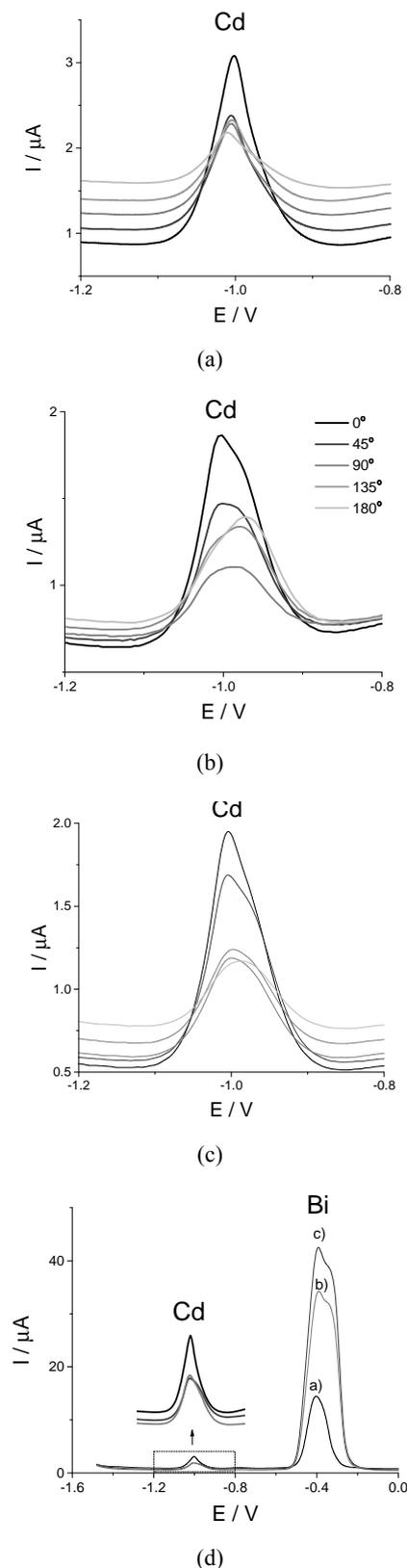


Fig. 7. DP-ASV curves recorded in three SPE positions: (a) $h = 0.8$ cm, $v = 0.75$ cm, (b) $h = 0.8$ cm, $v = 1.5$, (c) $h = 1.6$ cm, $v = 2.2$ cm and different α values. (d) voltammograms for $\alpha = 0^\circ$, $c_{Cd(II)} = 50 \mu g \times l^{-1}$.

The influence of the angle α was more complex and depended on SPE localization and the type of target element. In the case of indium, when the SPE was immersed in the location expressed by $v = 0$ cm and $h = 0.8$ cm, α did influence the In signal intensity but only to a small degree (up to about 15 %). If the location of the SPE was more distant ($h = 1.6$ cm) the 180 degrees rotation of the SPE produced a large, 60 % drop in the signal intensity (Fig. 6).

Additionally, the SPE rotation angle α influenced not only the signal intensity but also its symmetry. The SPE's performance in terms of cadmium signal symmetry is highest at central locations. At farther, more peripheral locations the SPE's performance decreased and cadmium signals were wide and distorted by shoulders (Fig. 7(b), Fig. 7(c)). Not only cadmium signals but also bismuth peaks became considerably wider at peripheral locations of SPE (Fig. 7(d)). The signal splitting indicates that crystallites formed at the peripheral SPEs locations during accumulation are non-identical and, therefore, different energy must be delivered to oxidize them.

Furthermore, a comparison of oxidation signals shown in Fig. 4 and Fig. 7(d) (representing lead, cadmium and bismuth oxidation) reveals that it is not the amount of bismuth which is crucial to obtain well-shaped signals of cadmium but, instead, a favourable morphology of bismuth deposits is of key importance. As shown in Fig. 4 and Fig. 7(d), when the oxidation signal of bismuth is at minimum the cadmium signal reaches its highest value.

4. Conclusions

It was shown that using two bismuth precursors and a favorable location of SPE with respect to magnetic stirrer it is possible to greatly amplify ASV signal of lead, cadmium and indium.

To explain the role of two precursors and the influence of the location of SPEs in the magnetic field on the quality of the signals recorded using anodic stripping voltammetry several factors should be taken into consideration.

The electrochemical reduction of Bi_2O_3 solid particles was considered by Hwong [13]. The obtained results indicated that bismuth oxide could be successfully reduced to metallic bismuth during the electrochemical reduction step. However, it was observed that bismuth particles were highly agglomerated after the electrochemical reduction. The deposited crystals were non-identical and required different energy for the oxidation process to occur. When the bismuth film was deposited by reducing Bi_2O_3 the stripping peaks of deposited metals were wide and distorted by shoulders, which in turn indicates that they probably resulted from the stripping of metal layers with slightly different lattice energy [6, 14]. According to voltammetric results reflecting the structure of these deposited metals, the metal layers deposited using two precursors – Bi_2O_3 and Bi(III) – were more homogenous because signals

delivered by that electrodes were narrow and symmetrical.

By changing the location of SPE with respect to the stirring plane the transport of electroactive substances may be affected, especially Bi(III) ions. In the absence of Bi(III) ions the dependence of the anodic stripping signals on the location of SPE was barely discernible.

The results of studies investigating the effect of the magnetic field on the electrodeposition of bismuth [15-17] show that it is a very complex process. It is also reported that the magnetic field has no influence on the structure of Bi deposited from electrolytes containing diamagnetic Bi(III) ions [16]; however, when electrochemically inert paramagnetic ions are added to the electrolyte [16] the bismuth films were thinner in regions with a high magnetic gradient.

The electrodeposition at relatively negative potentials in acidic media leads to the reduction of protons and evolution of hydrogen bubbles, an increase in the pH value and subsequent hydroxide formation. The convection induced locally, occurring in inhomogeneous magnetic fields, can remove the hydrogen bubbles and hydroxide particles, which might block the electrode surface and favor the deposition of analyte, bismuth or their alloys.

In summary, it is evident that the external magnetic field applied to the electrochemical cell is an extra variable which influences processes taking place in it. It is difficult though to unambiguously indicate which processes are responsible for the observed amplification of voltammetric signals.

Acknowledgements

Financial support from the Polish National Science Centre (Project 2014/15/B/ST8/03921) is gratefully acknowledged.

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Published by International Frequency Sensor Association (IFSA) Publishing, S. L., 2016 (<http://www.sensorsportal.com>).

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