

Codeposited Antimony-Bismuth Film Carbon Paste Electrodes for Electrochemical Stripping Determination of Trace Heavy Metals

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Applying synergic electroplating of antimony and bismuth at the carbon paste electrode substrates, new types of film electrodes were obtained allowing the determination of cadmium(II) and lead(II) ions at the microgram-per-liter concentration levels, when using square-wave anodic stripping voltammetric protocol. Compared with electrodes electroplated by individual metals, current responses obtained within reoxidation of both metal ions tested were favourably higher when related with measurements at codeposited films. In solutions of hydrochloric acid ($0.01 - 1.0 \text{ mol L}^{-1}$), an optimum concentration ratio $c(\text{Sb})/[c(\text{Sb})+c(\text{Bi})]$ was around 0.7 when *in situ* electrodeposition was applied and around 0.8 at *ex situ* plating. Formation of intermetallic compounds was confirmed by both microstructural and elemental analyses.

Keywords: film electrodes, synergic electroplating, carbon paste electrodes, stripping analysis, heavy metal ions

1. INTRODUCTION

Still, legislative and regulatory mandates continually push the threshold of chemical reagents to ever lower levels. One of the most successful electroanalytical techniques used to meet these demands has been stripping analysis [1,2]. In the past decades, mercury-based electrodes have proved themselves as inevitable detection tools in electroanalysis thanks to their simple renewability, high selectivity, reproducibility and mainly, reliability in stripping voltammetry [3,4]. Similarly, since its introduction [5], potentiometric stripping analysis was predominantly connected with the use of mercury-based electrodes and related sensors. Despite the dominant position of these electrodes in

stripping techniques and in electroanalysis as such, the toxicity of mercury and especially its compounds has led to search some alternative and more environmentally friendly materials.

In 2000, the first successful application of bismuth film electrodes (BiFEs) was reported [6]; since that time, the whole topic has already achieved a respectable position within the research activities devoted to the development of mercury-free electrodes. As shown in recent reviews [7,8], BiFEs have attracted the attention of several research groups interested in their applications in both stripping voltammetry and stripping chronopotentiometry of metal ions, especially cadmium, lead, zinc, indium and thallium. In our first contribution to the matter, we have shown that also carbon paste electrodes (CPEs) may successfully be applied to form bismuth-based sensors [9]. First, deposition of the Bi film onto the freshly renewed and polished CPE was performed by external preplating, in the second case, a carbon paste was mixed with Bi_2O_3 powder; more detailed studies were published elsewhere [10, 11]. Introduction of Bi(III) salts and BiFEs into electroanalysis has also brought a novel approach of the stripping chronopotentiometry based on total substitution of mercury by bismuth [12].

The first attempt to prepare an analogous antimony-based film electrode (SbFE) was not very successful because application of the same medium as originally suggested for determinations with BiFEs (pH 4.5 acetic buffer) appeared less suitable [13]. Subsequent investigations of antimony-based electrodes in more acidic solutions indicated their much wider utility. As reported, different supports were studied, first a glassy carbon and carbon fiber substrate electrodes [14] followed by antimony film carbon paste electrodes (SbF-CPEs) [15-17], sputtered antimony film electrode [18], antimony nanoparticles modified boron-doped diamond electrode [19], and antimony porous electrode [20]. Experiments with antimony powder-modified carbon paste electrodes have also been published [21]. It should be mentioned that similarly to Bi(III) salts, also Sb(III) may totally substitute Hg(II) salts in metal film formation as well as in its role as oxidant in stripping chronopotentiometry, giving even better results when compared with applications of Bi(III) salts [17].

Antimony, as an electrode material, has proved an attractive electroanalytical behaviour imposing the need for its further systematic investigation [22]; properties of its alloys forming capabilities have yet to be fully explored [23-25]. It was observed that in highly acidic solutions, the stripping peak corresponding to re-oxidation of antimony is very small, probably due to formation of insoluble compounds. This characteristic of the Sb-FEs allows measuring of other potentially interesting analytes with their stripping potentials close to the re-oxidation potential of the antimony itself, e.g. Cu(II) [26, 27]. Continuing in such step-by-step investigations, we also demonstrated recently that the presence of cadmium(II) ions during the accumulation step in solutions to be analyzed had an apparent catalytic effect in determinations of both mercury [28] and bismuth [29] because of the formation of CdSb intermetallic films. As documented by microstructural analysis (see Fig. 2 in [27]), the structure of the deposit in the presence of Cd(II) was completely different from that obtained from pure Sb(III) solution.

Surprisingly, qualitatively new and more sensitive film electrodes for voltammetric stripping analysis of some heavy metals can also be obtained when both bismuth and antimony are codeposited as alloys. Quite interesting results obtained in our recent investigation of these metal film electrodes are presented in this contribution.

2. EXPERIMENTAL

2.1. Chemicals, Solutions and Apparatus

All chemicals used in this work were of analytical grade. Atomic absorption standard stock solutions (1000 mg L^{-1} , Fluka) were used for antimony(III), bismuth(III), cadmium(II), and lead(II). A modular electrochemical analyzer AUTOLAB equipped with PGSTAT12 controlled by GPES software (EcoChemie, Utrecht, The Netherlands) was used for all voltammetric measurements. The conventional three-electrode configuration with various metal film-plated carbon paste electrode (SbF-CPE, BiF-CPE) was employed throughout the work. The Ag/AgCl/3M KCl and a Pt plate served as the reference and auxiliary electrodes.

All electrochemical experiments were carried out in one-compartment voltammetric cells (10-20 mL) at conditioned room temperature ($23 \pm 1 \text{ }^\circ\text{C}$). In voltammetric stripping measurements, a magnetic stirrer was employed during the electrochemical deposition step.

2.2. Carbon Paste Substrate Electrode

The carbon paste was prepared by intimately hand-mixing of graphite powder (0.5 g; CR-5, Maziva Týn nad Vltavou) with highly viscous silicone oil (0.3 mL; LUKOIL MV 8000, Lučební závody Kolín). Both components were homogenized to obtain a mixture that was subsequently packed into a piston-driven carbon paste holder [30], thus providing a carbon paste electrode support for plating with either antimony or bismuth or composited films.

3. RESULTS AND DISCUSSION

3.1. Optimization of the Sb/Bi Ratio for the Codeposited Film

First, an effect of the concentration Sb/Bi ratio of the deposited film on the magnitude of stripping peaks of cadmium and lead was studied. Electroplating *in situ* was realized in solutions containing either Sb(III) or Bi(III) (500 ppb) and Cd(II) and Pb(II) (both 50 ppb) salts at -1.2 V. Effect of the codeposition at different $x(\text{Sb}) = c(\text{Sb})/[c(\text{Sb}) + c(\text{Bi})]$ concentration ratios on the magnitude of the stripping peaks of both cadmium and lead was studied in corresponding HCl solutions (diluted with water to obtain $\text{pH} \cong 0 - 3$) or in an acetic buffer ($\text{pH} \cong 4$). Following the electrochemical deposition step and a short equilibration period ($t_{\text{ep}} 15 \text{ s}$), a square-wave (SW) voltammogram was recorded by applying a square-wave potential scan toward more positive potentials. Before each measurement, the "cleaning" step was performed by keeping the working electrode at +0.3 V for 30 s. In order to obtain signals at different $x(\text{Sb})$, stepwise 100 ppb injections of either Sb or Bi have been carried out to the plating solution of Bi or Sb, respectively, until the desired value (0.5) in both of the plating solutions. As shown in Fig. 1, an optimum value was around $x(\text{Sb}) = 0.714$. In its bottom section (1c), anodic stripping voltammograms recorded on such codeposited film are compared with those obtained with pure SbF-CPE or BiF-CPE ($\text{pH} \cong 2$).

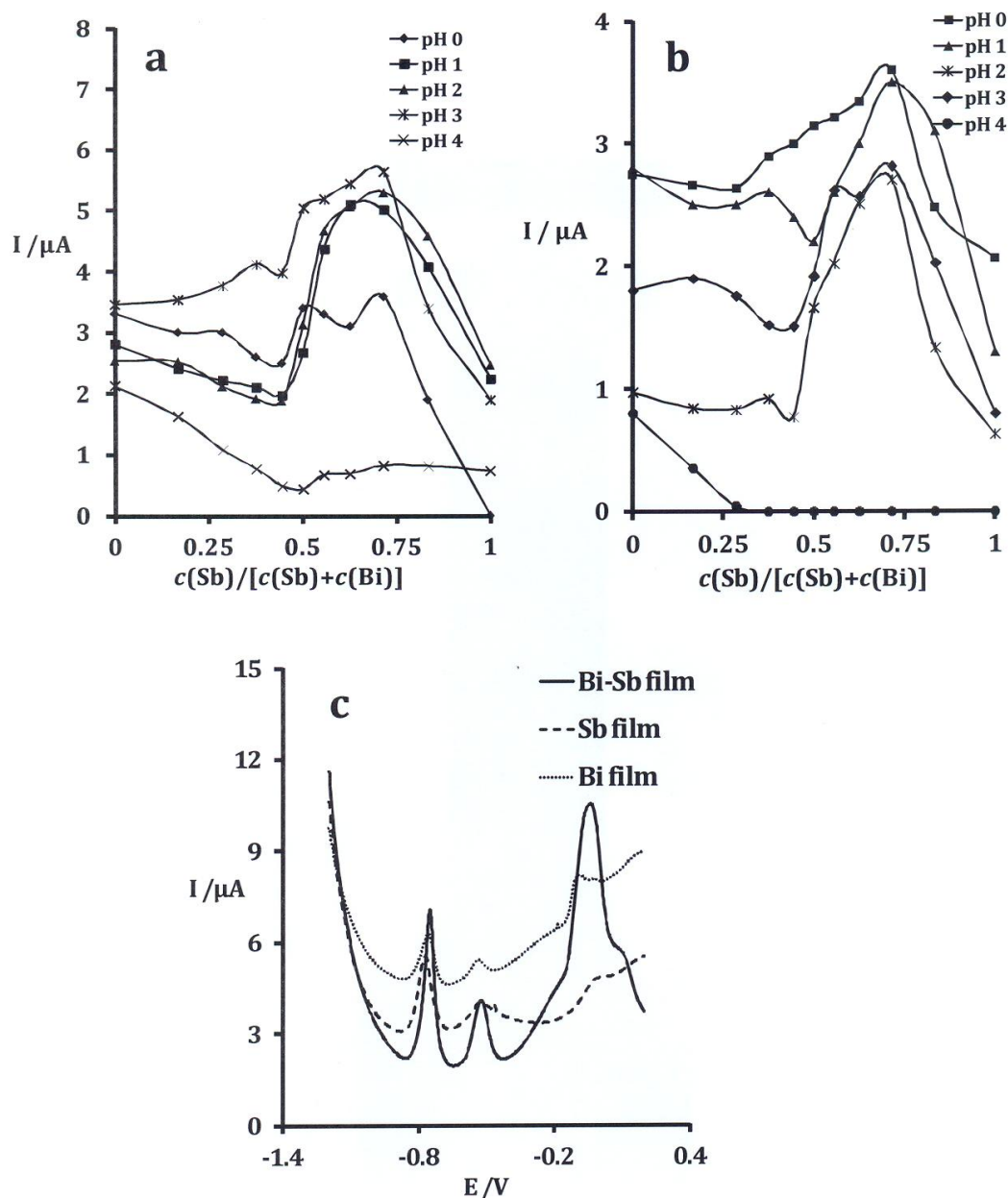


Figure 1. Effect of $c(\text{Sb})/[c(\text{Sb}) + c(\text{Bi})]$ ratio on (a) Cd(II) and (b) Pb(II) oxidation peaks at *in situ* film electrode in different pH solutions. Deposition potential -1.2 V, deposition time 60 s, equilibration time 15 s, square-wave voltammetric scan, frequency 25 Hz, potential step 4 mV, amplitude 25 mV. (c) Anodic stripping voltammograms of 50 ppb Cd(II) and Pb(II) at the *in situ* prepared SbFE, BiFE and codeposited Sb-BiFE at $c(\text{Sb})/[c(\text{Sb}) + c(\text{Bi})] = 0.714$, $\text{pH} \cong 2$ (0.01 M HCl).

Effect of the Bi(III) addition into the plating solution has been investigated when Sb *ex situ* electroplating was used, the higher starting concentration (10 ppm) of Sb(III) was used at -0.5 V. After rinsing, the electrode was placed into the analyte solution and potential of -1.0 V was applied for accumulation of both analytes. After each measurement, the electrode surface was polished to renew a new one. The concentration ratio was gradually varied in the Sb plating solution by stepwise injections (2 ppm) of Bi(III) until achieving to $x(\text{Sb}) = 0.5$. As shown (Fig. 2), an optimum value of $x(\text{Sb}) =$

0.830 was found in this case (left); stripping voltammograms recorded with the three electrodes are also compared (right).

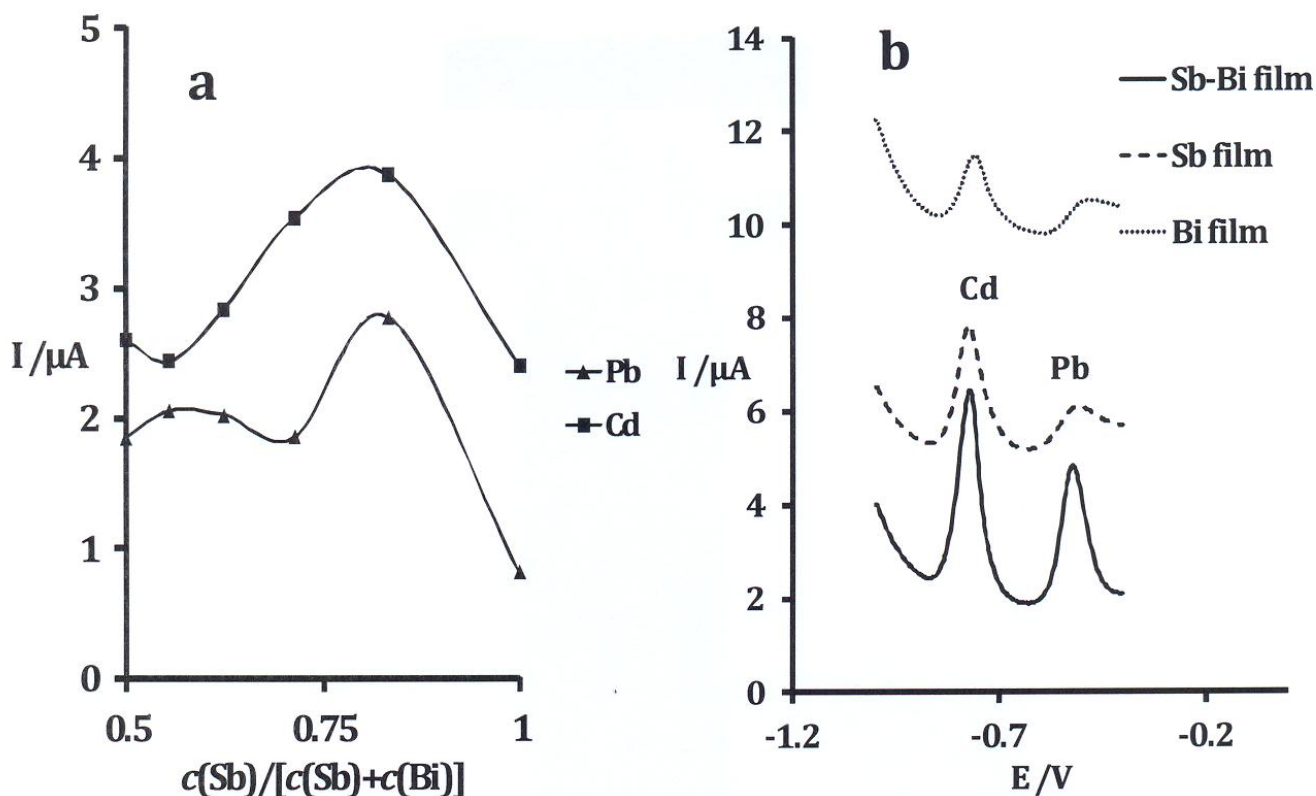


Figure 2. (a) Effect of $c(\text{Sb})/[c(\text{Sb}) + c(\text{Bi})]$ ratio on Pb(II) and Cd(II) peaks. (b) Anodic stripping voltammograms of 50 ppb Cd(II) and Pb(II) at the *ex situ* prepared SbFE, BiFE and Sb-BiFE at $c(\text{Sb})/[c(\text{Sb}) + c(\text{Bi})] = 0.83$, $\text{pH} \approx 2$ (0.01 M HCl). Deposition potential -1.0 V, other parameters as mentioned under Fig. 1.

3.2. Microstructural Analysis

Corresponding SEM images were taken under conditions described in the caption of Fig. 3 for electroplating *in situ* (left) or *ex situ* (right). Evidently, while the Sb “film” contains separated agglomerates of the metal and the Bi “film” more crystalline particles, morphology of codeposits obtained at optimized $x(\text{Sb})$ ratios looks quite different and more compact. The content of both antimony and bismuth in the codeposite obtained in *ex situ* plating was determined also by SEM-EDX technique; the found values (82% Sb, 18% Bi) agreed very well with the optimum $x(\text{Sb})$ one mentioned above. To obtain a clear image, concentration of both bismuth and antimony had to be increased; in the case of *ex situ* plating, deposition time was also prolonged.

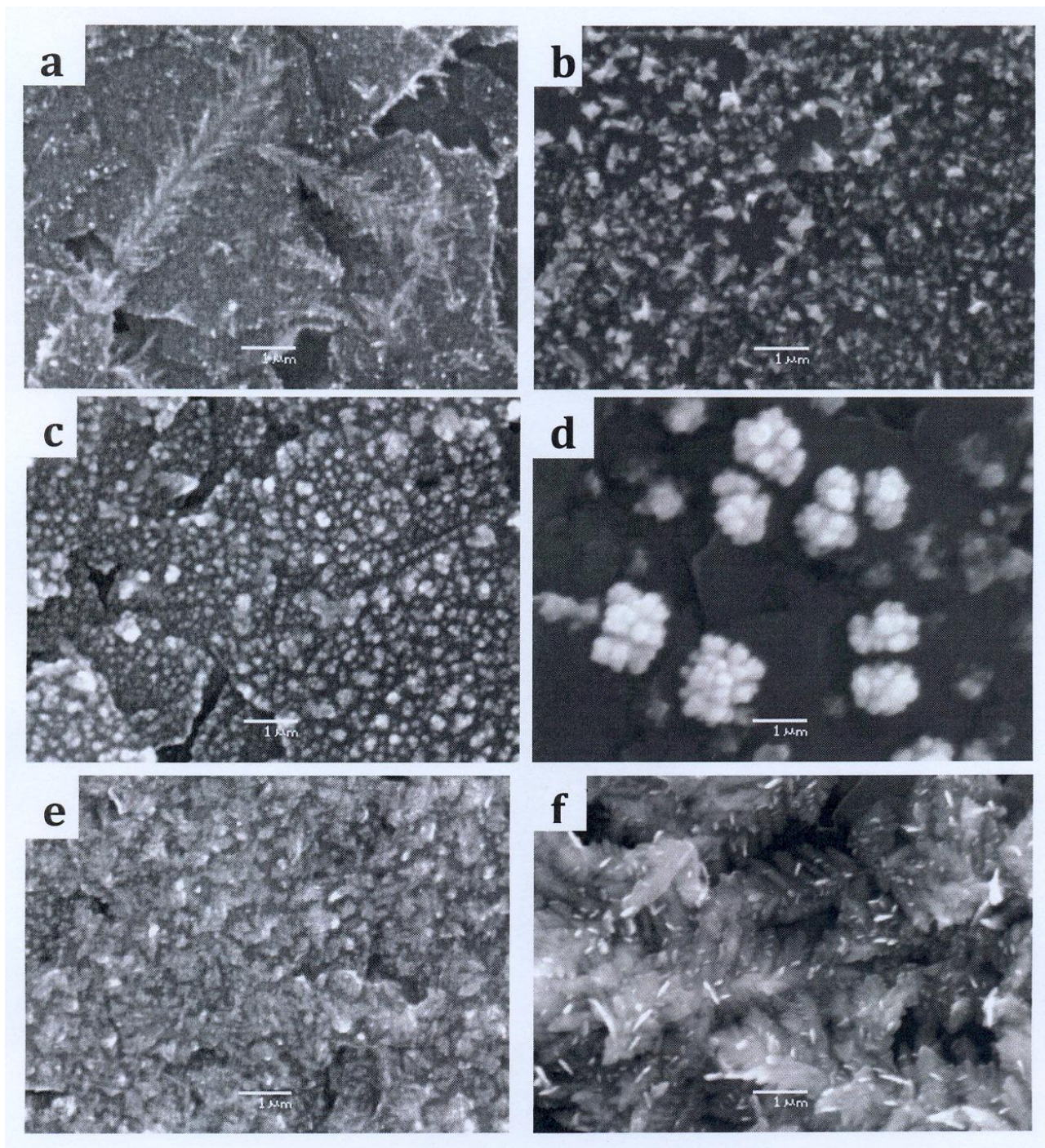


Figure 3. SEM images of (a) *in situ* BiFE, (b) *ex situ* BiFE, (c) *in situ* SbFE, (d) *ex situ* SbFE, (e) *in situ* Sb-BiFE, (f) *ex situ* Sb-BiFE. *Ex situ* plating with 100 ppm Bi or Sb, in the case of Sb-Bi film with 100 ppm Sb and 20 ppm Bi, deposition potential -0.5 V, deposition time 300 s. *In situ* plating with 100 ppm Bi or Sb, in the case of Sb-Bi film with 100 ppm Sb and 40 ppm of Bi, deposition potential -1.2 V, deposition time 120 s.

3.4. Stripping Voltammetric Determination of Heavy Metals

As mentioned above, both bismuth- and antimony-based electrodes were successfully applied to determine heavy metal ions. Here, Fig. 4a illustrates a series of voltammograms for an electrode

with a film codeposited *in situ* for successive additions of both Cd(II) and Pb(II) in 10 ppb steps in the concentration range of 10-70 ppb. The characteristic peaks of Cd(II) and Pb(II) were observed at -0.88 and -0.61 V, respectively.

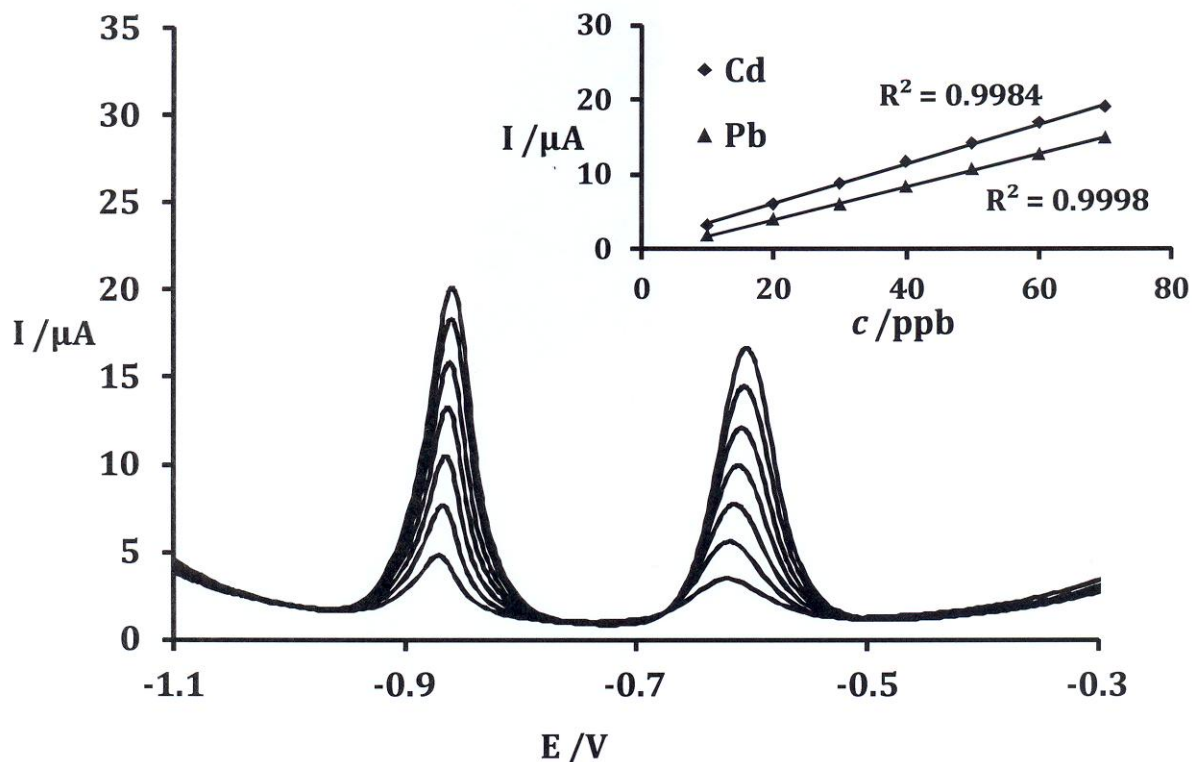


Figure 4. Anodic stripping voltammograms of Cd(II) and Pb(II) at *in situ* prepared Sb-BiFE from a solution of 500 ppb Sb(III) and 200 ppb Bi(III). Deposition potential -1.2 V, deposition time 120 s, equilibration time 15 s, square-wave voltammetric scan, frequency 25 Hz, potential step 4 mV, amplitude 25 mV. Inset, corresponding calibration curves.

As seen, corresponding calibration plots are linear for both metal ions under investigation. For *in situ* plating, 15 ppb Cd(II) or Pb(II) and deposition time 300 s, detection limits (DLs, 3σ) for 8 replications were 0.8 ppb for Cd(II) or 0.9 ppb for Pb(II), resp., and RSD 4.7% for Cd(II) or 2.0% for Pb(II). For the same concentrations of both metal ions and *ex situ* plating, we obtained DLs 1.1 ppb for Cd(II) or 1.4 ppb for Pb(II), and RSD 8.1% for Cd(II) or 5.2% for Pb(II), respectively. It should be mentioned that within preparation of this contribution, similar paper using a Bi-Sb film electrode was simultaneously published [31] in which determination of Cd(II) was studied with similar results.

4. CONCLUSION

The novel Sb-Bi codeposited film electrodes show well-defined stripping signals for both cadmium(II) and lead(II) and thus present another interesting alternative to mercury electrodes in

electrochemical stripping analysis with a sensitivity that is significantly higher than those observed for single (pure) Sb or Bi films-based electrodes. Further work is under way to study their application for determination of other metal ions.

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