Electrochemical Stripping Analysis of Selected Heavy Metals at Antimony Trioxide-Modified Carbon Paste Electrode

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Antimony trioxide-modified carbon paste electrode (Sb_2O_3-CPE) was developed and tested in combination with square-wave anodic stripping voltammetry as a new "mercury-free" sensor for the determination of selected heavy metal ions at the low $\mu g\ L^{-1}$ concentration level. Measurements were carried out using non-deaerated solutions of 0.01 M HCl (pH 2) with Cd(II) + Pb(II) as model ions. Several important experimental parameters, e.g. deposition potential, deposition time, and the concentration of hydrochloric acid were studied and optimized, when the electroanalytical performance of the Sb_2O_3-CPE was critically compared with bismuth trioxide-modified carbon paste electrode (Bi_2O_3-CPE), and with the *in-situ* prepared antimony film carbon paste electrode (SbF-CPE) using either 0.01 M HCl (pH 2.0) or 0.1 M CH_3COOH + CH_3COONa (pH 4.4) as the supporting media. In contrast to other configurations of antimony film-operated electrodes, the Sb_2O_3-CPE has exhibited well-defined anodic stripping signals also in acetate buffer, proving thus itself to be generally applicable in both mild and more acidic supporting media. The sensor of interest showed a fairly linear behaviour in the concentration range of 10-100 $\mu g\ L^{-1}$, offering good reproducibility and favourable detection limits of about 1 $\mu g\ L^{-1}$ for Cd(II) and of 0.7 $\mu g\ L^{-1}$ Pb(II) in combination with 90 s accumulation. The practical applicability of the Sb_2O_3-CPE, when the electrode could also be applied in the stripping chronopotentiometric operating mode (with chemical oxidation), was demonstrated on the voltammetric determination of Cd(II) and Pb(II) in sample of tap water.

1. INTRODUCTION

Heterogeneous carbon materials have for long time been used in preparation of electrochemical sensors and biosensors because of their variability, chemical inertness, low cost, widely exploitable potential window, and — in particular — the possibility of modification [1].

Among the carbon-based electrodes that can be modified not only on the surface but also in bulk during their preparation, carbon paste electrodes (CPE) and screen-printed carbon electrodes (SPCE) belong to the most frequent choice. For modifications, various organic and inorganic compounds can be employed, including metal oxides that are preferably used as bulk modifiers and mediators in the configurations of biosensors.

Particularly popular oxides, used mainly in biosensors for hydrogen peroxide, glucose or amino acids are Cu_2O [2-4], CuO [5,6], MnO_2 [7-9], NiO [10-12], RuO_2 [13-16] and Fe_2O_3 or Fe_3O_4 [17,18], but experimental testing has involved also further oxides, such as SnO_2 [18,19], CoO/Co_2O_3 [20], RhO_2 [21,22], platinum metals (PdO, IrO_2, PtO_2) [23], Nb_2O_5 [24,25], Al_2O_3 [26], PbO_2 [27], CeO_2 [27], CdO [28], and TiO_2 [29,30].

In electrochemical stripping analysis (ESA), there is yet another group of metal oxides, HgO [31-33], Bi_2O_3 [35-37], and Sb_2O_3 that are generally employable as inner source of the metal deposited in the form of very thin films onto the surface of a carbonaceous substrate during accumulation step. Regarding the latter, this substance had already been of interest as a modifier for carbon paste or carbon ink almost ten years ago [38,39]; however, the respective configurations with Sb_2O_3 were found — despite some promising results — less effective compared to the parent Bi_2O_3-CPE or $B_{i2}O_3$-SPCE and further investigations were discontinued [40]. Nevertheless, few years later, antimony film-plated electrodes [41-47] and, recently, also other antimony-based sensors [48-52] were successfully introduced to the contemporary electroanalysis as another type of non-mercury sensor and a perspective alternative to still more widespread bismuth-based electrodes; especially, for some special measurements in more acidic media.

In this work, a study with the above-mentioned configuration of antimony trioxide-modified carbon paste electrode is reprised having revealed — after a systematic optimization — that also this variant of antimony-based electrodes is useful in ESA for determination of selected heavy metals. Moreover, compared to all of its antimony predecessors, the Sb_2O_3-CPE variant seems to be more versatile for practical analysis as reported in the following sections.

2. EXPERIMENTAL

2.1. Instrumentation

A modular electrochemical system AUTOLAB equipped with PGSTAT12 (Eco Chemie, Utrecht, Netherlands) was used in combination with GPES software (Eco Chemie).

All electrochemical experiments were carried out in a one-compartment 20 mL voltammetric cell at room temperature.

A three-electrode cell compartment with the working antimony trioxide-modified carbon paste electrode (d = 2 mm), the Ag/AgCl/3M KCl reference electrode, and a Pt-wire as the auxiliary electrode were employed together with a PC-controlled magnetic stirrer accomplishing the inevitable convective transport at approximately 300 rpm (IKA) during the electrochemical deposition and cleaning step.

2.2. Reagents and Solutions

All chemicals used for the preparation of stock and standard solutions were of analytical reagent grade purity and were purchased from Aldrich. 1000 mg L^{-1} atomic absorption standard solutions of antimony(III), cadmium(II) and lead(II) were diluted as required. Antimony trioxide (99.999%) and bismuth(III) oxide (99.9%) used for the modification of carbon paste were provided by Aldrich too. Hydrochloric acid (pH 0 - 4) and in some experiments also 0.1 M acetate buffer (pH 4.4) were used as supporting electrolytes. Water used throughout the work was first deionized and then further purified via Elix 10/Milli-Q Gradient unit (Millipore, Bedford, USA).

2.3. Fabrication of working electrodes

The carbon paste mixture was prepared by thoroughly hand-mixing of 0.5 g spectroscopic graphite powder (CR-5, Maziva Tyn nad Vltavou, Czech Republic) with approximately 0.3 mL of highly viscous silicone oil (LUKOIL MV 8000, Lucebni zavody Kolin, Czech Republic). Both components were homogenized to obtain a mixture which was either used as a carbon paste substrate for in-situ plating with the antimony film or was subsequently mixed with 3% (w/w) of Sb$_2$O$_3$ powder, or with 3% (w/w) of Bi$_2$O$_3$ powder, respectively. The so prepared carbon paste mixture was packed into a specially designed electrode holder [53] equipped with a piston for extruding out the used paste and its subsequent renewal.

The electrode surface was renewed mechanically by extruding approximately 0.5 mm of carbon paste out from the holder with subsequent smoothing on wet filter paper before starting a new set of experiments. The antimony film plated carbon paste electrode used in some comparative tests was prepared according to our previous report [43].

2.4. Procedures

Electrochemical Stripping Analysis. The measurements in the anodic stripping voltammetric mode were carried out using the square-wave potential ramp with a frequency of 25 Hz, a potential step of 4 mV, and an amplitude of 50 mV; all in non-deaerated solutions. In contrast to this, experimentation with stripping chronopotentiometry (SCP) with chemical oxidation required the removal of oxygen from the solutions to be analyzed.

Otherwise, all experiments comprised an electrochemical accumulation step usually at -1.0 V for 90 s, an equilibration period of 10 s, and a stripping scan (voltammetric or chronopotentiometric) usually from -1.0 V to +0.2 V or -1.0 V to -0.15 V vs. ref., depending on the measurement mode used. Before each measurement, a pre-conditioning "cleaning" step at potential of +0.2 V was applied taking place for 60 s.

Sample Preparation. The tap water sample was collected after 10 minutes of running the water out from the water-supply and immediately acidified to pH 2 with the addition of adequate amount of hydrochloric acid.

3. RESULTS AND DISCUSSION

3.1. Fundamental characterization of antimony trioxide-modified carbon paste electrode

The proper electrode material, as well as the appropriate amount of antimony trioxide in the role of modifier were chosen based on our previous experience (see *e.g.* [38,40]). Thus, a mixture of graphite powder and a highly viscous silicon oil was modified with 3 % (w/w) Sb_2O_3 powder.

A comparison in the stripping voltammetric performance of the Sb_2O_3-CPE with that of its bismuth analogue, i.e. bismuth(III) oxide-modified carbon paste electrode (Bi_2O_3-CPE) and together with the antimony film-plated carbon paste electrode (SbF-CPE) is illustrated in Figs. 1 and 2 (due to different electrode surface area, the corresponding signals are presented as current densities). Fig. 1 displays the comparison of stripping voltammetric responses in a non-deareated solution of 0.01 M HCl (pH 2), a suitable supporting media for the antimony film electrodes. All electrodes exhibited well-defined stripping signals for Cd(II) and Pb(II) together with relatively low background currents contribution. While SbF-CPE (dashed line) and Bi_2O_3-CPE (dotted line) revealed slightly higher signal for Cd(II), Sb_2O_3-CPE (solid line) exhibited higher and narrower signal for Pb(II). The difference between the peak potentials of the tested metal ions is similar using all three electrodes varying from 243 mV at Sb_2O_3-CPE to 263 mV at SbF-CPE. Note also a strongly suppressed re-oxidation signal for antimony at the SbF-CPE (at ca. 0.0 V) as a specific feature of the anodically dissolved film which has not been yet fully explained [42,43] and the corresponding, well-visible signal for Sb_2O_3-CPE.
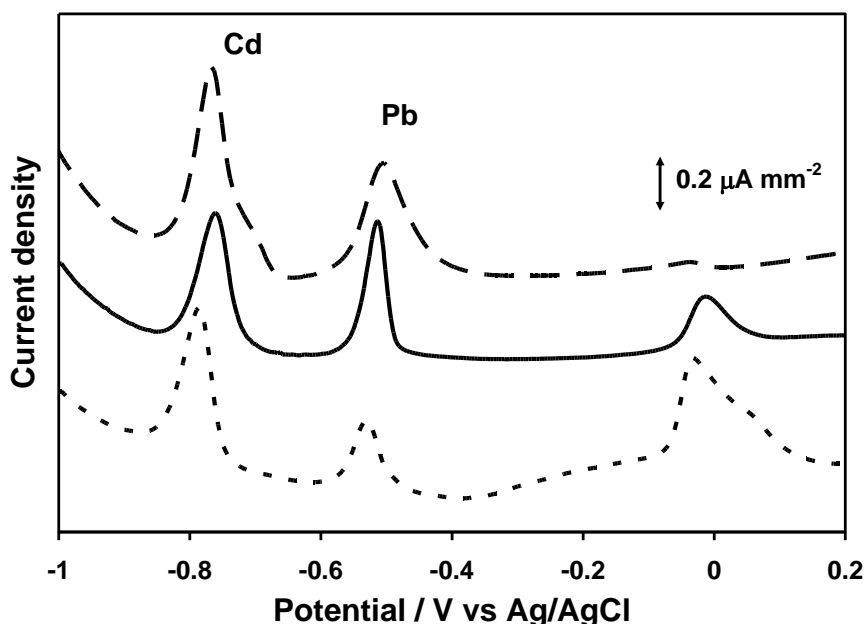

Figure 1. Comparison of voltammetric responses of 100 μg L^{-1} Cd(II) and Pb(II) at Sb_2O_3(3%)-CPE (solid line), Bi_2O_3(3%)-CPE (dotted line) and in-situ prepared SbF-CPE (dashed line) in 0.01 M HCl. Experimental conditions: conditioning potential of +0.2 V, conditioning time of 60 s, deposition potential of -1 V (-1.2 V for SbF-CPE), deposition time of 90 s, equilibration time of 10 s, frequency of 25 Hz, amplitude of 50 mV, potential step of 4 mV, Sb(III) concentration for the in-situ plating of the Sb-film of 500 μg L^{-1}.

In addition, Fig. 2 demonstrates the comparison of stripping voltammetric responses in a non-dearated solution of 0.1 M acetate buffer (pH 4.4), a suitable supporting media for bismuth-based electrodes. As seen, there were almost no signals for Cd(II) and Pb(II) at the SbF-CPE (dashed line), which could be expected and according to our knowledge about the necessity of using acidic supporting solutions for good performance of this electrode. On the other hand, the signals obtained at the Sb_2O_3-CPE (solid line) were surprisingly well-developed and comparable in both height and shape to those obtained at the Bi_2O_3-CPE (see dotted line and slightly narrower separation between the signals for Cd(II) and Pb(II) vs. Bi_2O_3-CPE. This observation is different from those by Pauliukaitė et al. [38,39], who has detected only Cd(II) at the Sb_2O_3-SPCE, explaining also that the Sb_2O_3-CPE would not be able to determine Cd and Pb due to the mutual formation of intermetallic compounds at the electrode surface.
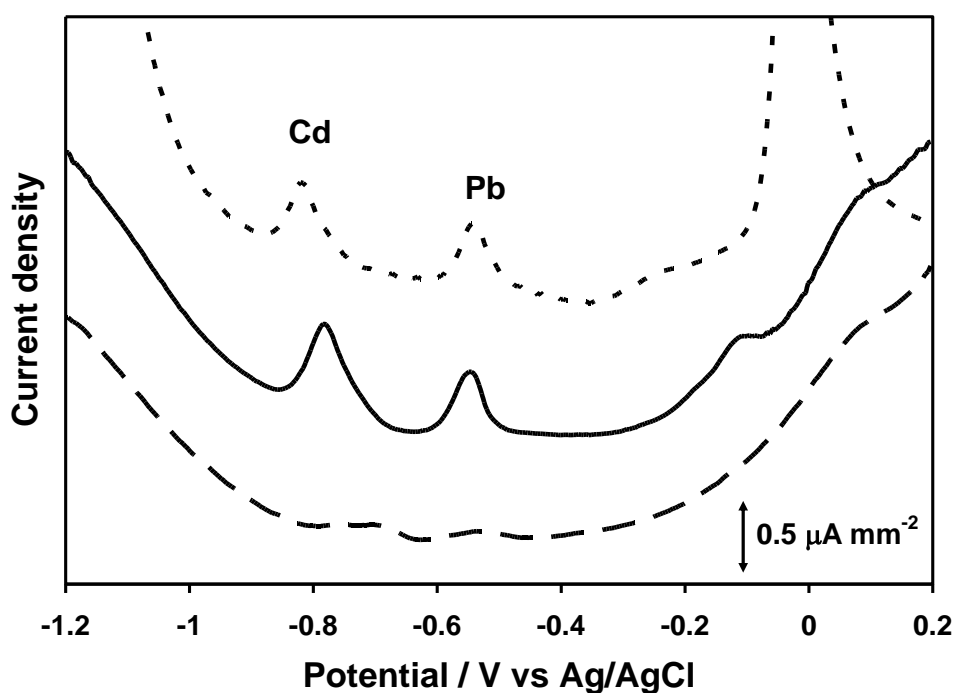

Figure 2. Comparison of voltammetric responses of 80 μg L^{-1} Cd(II) and Pb(II) at Sb_2O_3(3%)-CPE (solid line), Bi_2O_3(3%)-CPE (dotted line) and in-situ prepared SbF-CPE (dashed line) in 0.1 M acetate buffer solution. Experimental conditions: deposition potential of -1.2 V for all electrodes, other conditions, as in Fig. 1.

3.2. Effect of pH, deposition potential and deposition time

Some fundamental operation parameters affecting the stripping performance, such as composition of the supporting electrolyte and its pH or the deposition conditions were of interest in the continuing investigation. Although acetate buffer could be also used as the supporting medium of choice, which is documented in Fig. 2, it was decided to use diluted hydrochloric acid because of better signal-to-noise characteristics, as well as improved reproducibility. The dependence of the peak

heights for Cd and Pb upon the pH of the supporting electrolyte with HCl is shown in Fig. 3A. For both model ions, it is evident that the maximal peak height has been obtained at pH 2, and furthermore, that the signal for Pb(II) was higher than the response for Cd(II) up to pH 2, whereas at higher pH values the signal for Pb(II) was notably lower.
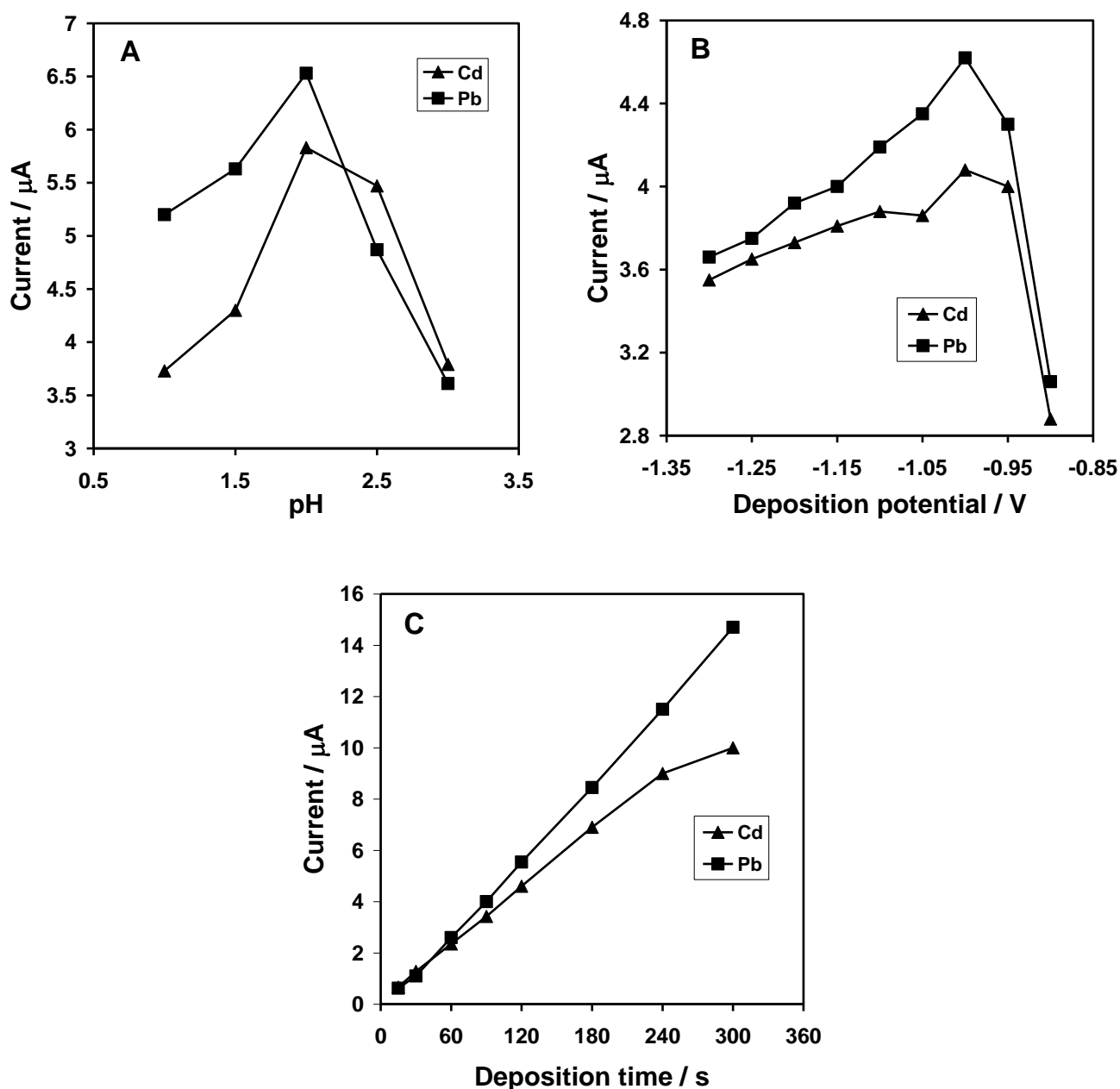

Figure 3. Effect of pH of HCl as a supporting electrolyte upon the stripping voltammetric response of 100 µg L^{-1} Cd(II) and Pb(II) (A), deposition potential upon the stripping voltammetric response of 60 µg L^{-1} Cd(II) and Pb(II) (B), and deposition time upon the stripping voltammetric response of 40 µg L^{-1} Cd(II) and Pb(II) (C) at Sb$_2$O$_3$(3%)-CPE. Experimental conditions: deposition potential in (A) of -1.2 V, deposition time in (A) and (B) of 60 s. Other conditions are as in Fig. 1.

As observed in our earlier studies [43,52], such behavior and a dependence on pH might be due to the different oxidation rates for the metal ions tested and due to different interaction between the Sb-Pb and Sb-Cd adducts, when taking into account the reversible pathway of the respective processes.

Fig. 3B relates the effect of the varying deposition potential on the stripping voltammetric signals of both metal ions investigated. By applying more positive potentials than -0.9 V vs. ref., the signals obtained for the two metal ions were negligible; however, with the increase of negative potential from -0.9 to -1.3 V. (The signal firstly increased up to *ca.* -1.0 V and then started to gradually attenuate.) Based on this study, the deposition potential of -1.0 V vs. ref. was selected as optimum for all further measurements.

The effect of deposition time upon the stripping signals for Cd(II) and Pb(II) is illustrated in Fig. 3C, revealing slightly different behavior for each metal ion investigated when using deposition times higher then 240 s. While Pb(II)-peak current increased linearly in the whole range of interest (30-300 s), the peak current for Cd(II) increased linearly up to 240 s; with higher deposition times having started to deviate from linearity (due to saturation). Similar phenomenon — but with earlier tendency to saturation — was observed already before when using other types of antimony-based electrodes [43,52]. With respect to these observations, the deposition time of choice was $t_{DEP} = 90$ s.

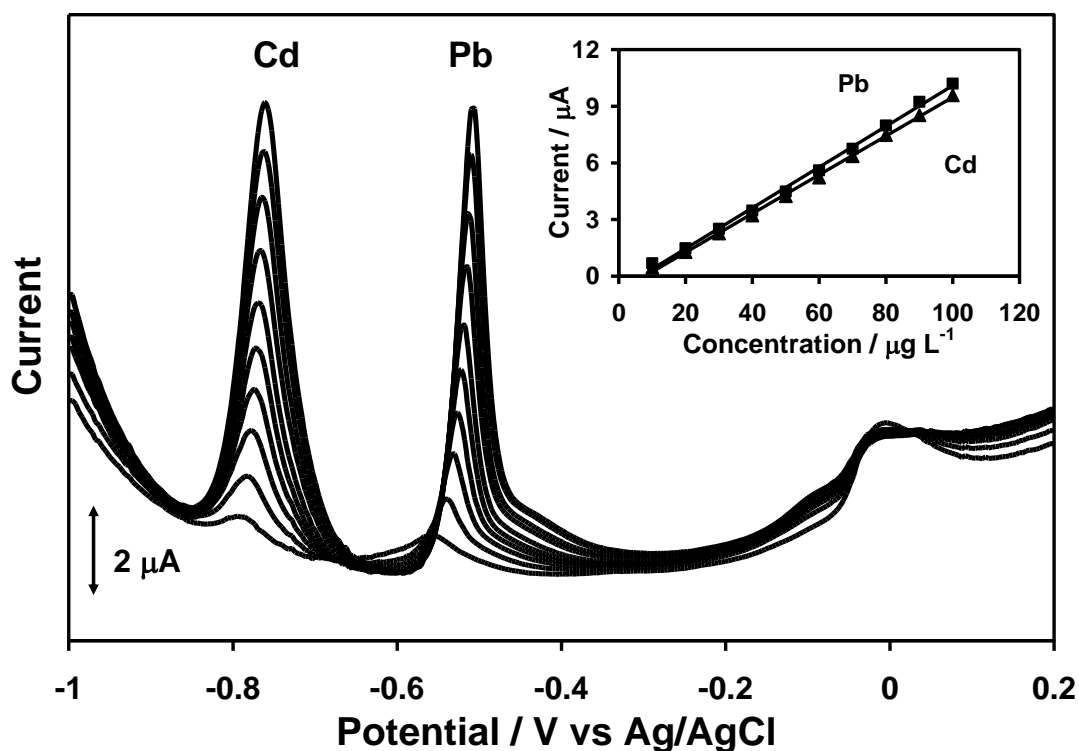### 3.3. Analytical parameters of the Sb$_2$O$_3$-CPE

Figure 4. ASVs for successive additions of Cd(II) and Pb(II) in 10 μg L^{-1} steps obtained at Sb$_2$O$_3$(3%)-CPE. The inset shows the corresponding calibration plot. Other conditions are as those given in Fig.1.

Typical electroanalytical performance of the Sb_2O_3-CPE at the low concentration level of Cd(II) and Pb(II) was tested under previously optimized parameters. The linear dependence of stripping voltammetric response of Sb_2O_3-CPE on increasing concentration levels of both tested metal ions in the range of 10–100 μg L^{-1} is shown in Fig. 4. The inset displays the corresponding calibration plots, with favourable correlation coefficients (R^2) of 0.998 and 0.997 for Cd(II) and Pb(II), respectively. The limits of detection (LODs) were estimated from experiments with 90s accumulation when using the 3σ criterion; the respective values being 1.0 μg L^{-1} Cd(II) and 0.7 μg L^{-1} Pb(II). Finally, model measurements with 40 μg L^{-1} Cd(II) and 40 μg L^{-1} Pb(II) could be reproduced in ten replicates with the relative standard deviation (RSD) of ±3.4% and ±1.4%, respectively.

3.4. Interference studies

Herein, our attention was focused on the effect of various interfering ions present in the sample solutions with 50 μg L^{-1} Cd(II) + 50 μg L^{-1} Pb(II). In addition, the influence of some surface-active compounds was also observed. Regarding the metal ions, the following species were taken for investigation: Zn(II), Cu(II), Tl(I), In(III), Sn(II), Bi(III) and Hg(II).

As expected, the re-oxidation of Tl(0) → Tl(I) had completely overlapped the signal for Cd(II), giving rise to a slight shift to more negative potentials with respect to the peak for the related process Cd(0) → Cd(II). Also, if being added at a 10-fold excess in concentration, the stripping signal for In(III) at about -0.7 V somewhat affected the peak of Cd, but negligibly with respect to its peak height. However, even slight changes in the deposition conditions — *e.g.* the deposition potential set to -1.1 V vs. ref. — had resulted in a ten-fold increase of the In(III)-peak, overlapping both Cd(II)- and Pb(II) peaks almost totally.

Bivalent tin, Sn(II), showed the stripping signal at ca. -0.5 V; nevertheless, the sensitivity of these measurements was rather poor under the experimental conditions chosen (as confirmed recently in special studies [54,55], the Sn(II) species tend to self-oxidation to Sn(IV) with subsequent hydrolysis.) In this study, in more acidic solutions, the addition of Sn(II) at a 20-fold excess over Cd(II) and Pb(II) resulted in totally overlapped signal with Pb(II), shifted for 15 mV towards less negative potentials with similar peak height and a typical broadening. As experimentally proved, a 100-fold excess already resulted in the increase of the overlapped signal for about 70% compared to the original Pb-peak.

With Zn(II) and Cu(II) as the metal species readily forming intermetallic compounds, the interference studies were carfried out in more detail. While Zn(II) had almost no effect upon Cd(II) and Pb(II) response at even a 100-fold excess in concentration, the Cu(II) ions already interfered with the responses of both model ions at the comparable concentration level. The resultant undesirable effect is well-known from the detection of Cd(II) and/or Pb(II) at both BiFE and SbFE [56-59] and can be more or less suppressed by adding a suitable complexing agent; for instance, ferro- or ferricyanide (see refs. [57,58,60]).

The remaining metal ions tested — i.e., Bi(III) and Hg(II) — had unveiled a similar ascending effect on both responses for Cd(II) and Pb(II). Namely, addition of 50 μg L^{-1} Bi(III) or Hg(II) caused

approx. 50 % increase of Cd(II) and Pb(II) signals and a 5-fold concentration excess led to the increase of both up to 120 %. The observed increase in the signal(s) can be attributed to the parallel formation of mercury and bismuth films that behaves as concurrent electroactive sites [61,62].
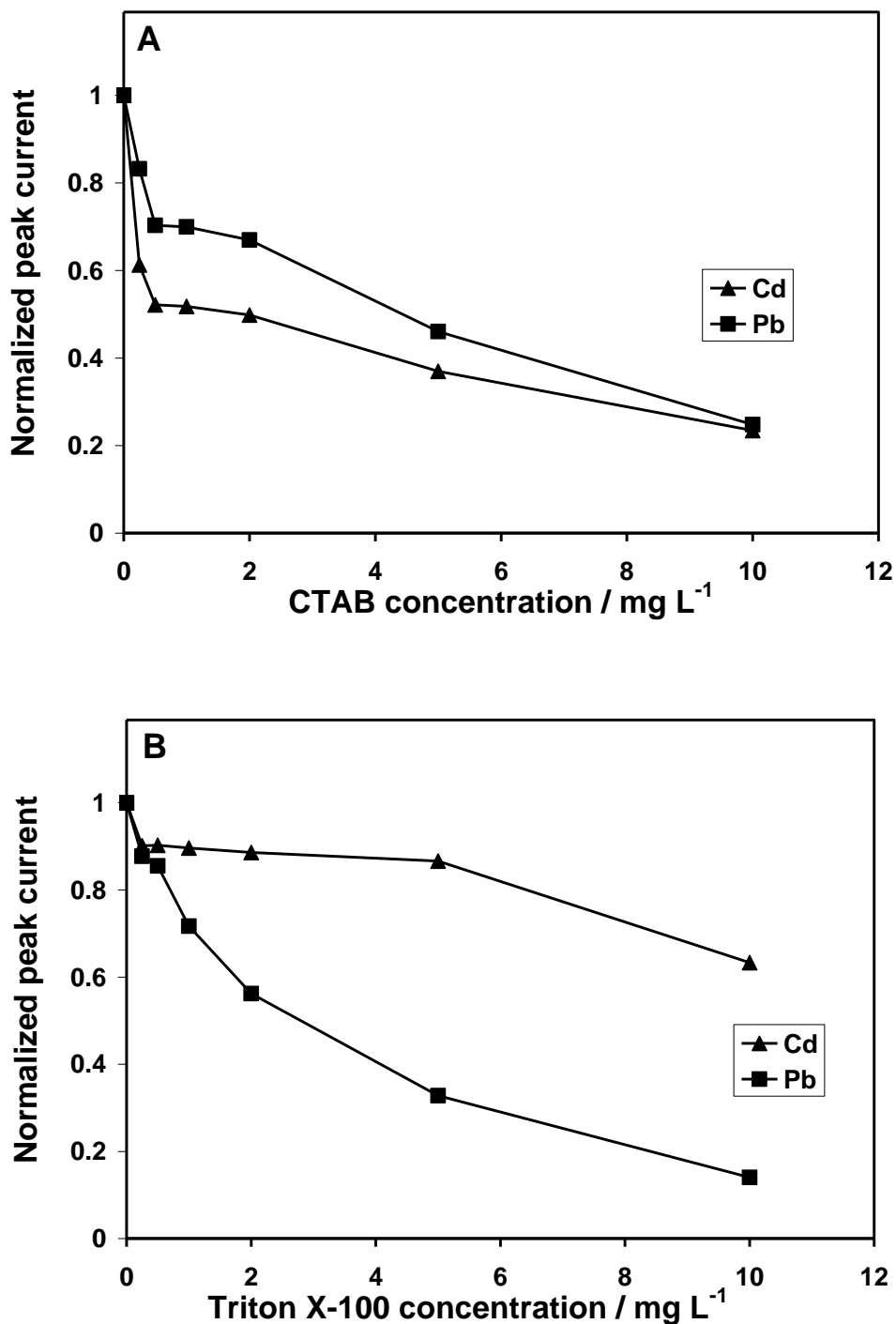

Figure 5. Effect of increasing concentrations of CTAB (A) and Triton X-100 (B) upon the normalized stripping voltammetric response of 50 μg L^{-1} Cd(II) and Pb(II). Other conditions as in Fig. 1.

To investigate the effect of surfactants which usually coat the surface of the electrode causing thus its total fouling [63], two compounds were used: (i) cetyltrimethylammonium bromide (CTAB) as the cationic type and (ii) *Triton X-100*® as a non-ionic compound. As depicted in Fig. 5, the dependence of the normalized peak currents (I with surfactant / I_0 without surfactant) on the increasing concentration of surfactants is illustrated. As can be seen, CTAB had similar influence on both metal ions, whereas Triton X-100 manifested completely different behavior, when the response for Cd had remained almost unaffected up to 5 mg L^{-1} Triton X-100 in the sample, which was in contrast to the signal of Pb(II), having decreased down to 30 % of its initial height.

3.5. Testing in the stripping chronopotentiometric mode

Similarly to Hg(II) and Bi(III) species, Sb(III) was proved to act as a weak ("gentle") oxidant and therefore advantageously applicable in stripping chronopotentiometry with chemical oxidation [64,65]. In this study, the stripping chronopotentiometric performance of the Sb$_2$O$_3$-CPE was tested in the deareated solution of 0.01 M HCl.

As seen in Fig. 6, the electrode exhibited well-developed, sharp stripping signals for both Cd(II) and Pb(II) with a linear dependence of the respective stripping chronopotentiometric response on the increasing concentration of Cd(II) and Pb(II) in an interval of 10-100 μg L^{-1} in a series of consecutive steps (for n = 10 with an increment of 10 μg L^{-1}), thus giving two fine calibration plots with R^2 = 0.997 for Cd(II) and R^2 = 0.996 for Pb(II). The LODs (3σ) were estimated to be about 1.0 μg L^{-1} for both ions, whereas ten replicate measurements with 30 μg L^{-1} Cd(II) and Pb(II) revealed a reproducibility with RSD of ±3.2 % for Cd(II) and ± 5.7% for Pb(II).
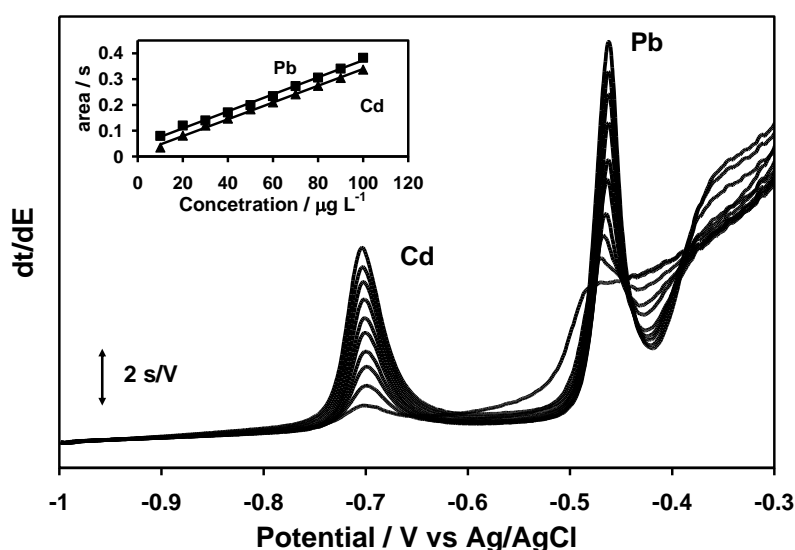

Figure 6. Stripping chronopotentiograms for successive additions of Cd(II) and Pb(II) in 10 μg L^{-1} steps obtained at Sb$_2$O$_3$(3%)-CPE. The inset shows the corresponding calibration plot. Experimental conditions: conditioning potential of +0.2 V, conditioning time of 60 s, deposition potential of -1 V, deposition time of 90 s, equilibration time of 10 s, potential limit of -0.15 mV.

3.6. Model application

Possible applicability of the Sb_2O_3-CPE was demonstrated on voltammetric analysis of a tap water sample prepared as specified in *Experimental.* In such a sample, Cd(II) ions had not been found and the lone Pb(II) corresponded to a concentration of 7.7 ±0.3 μg L^{-1} (obtained from three replicates), which was still under the limit of an EU standard for drinking water (No. 98/83/EU [66]).

Typical stripping voltammograms obtained by analyzing the tap water at the Sb_2O_3-CPE and with the aid of the standard addition method is illustrated in Fig. 7; in this case, with three standard aliquots of 3 μg L^{-1} Pb(II).
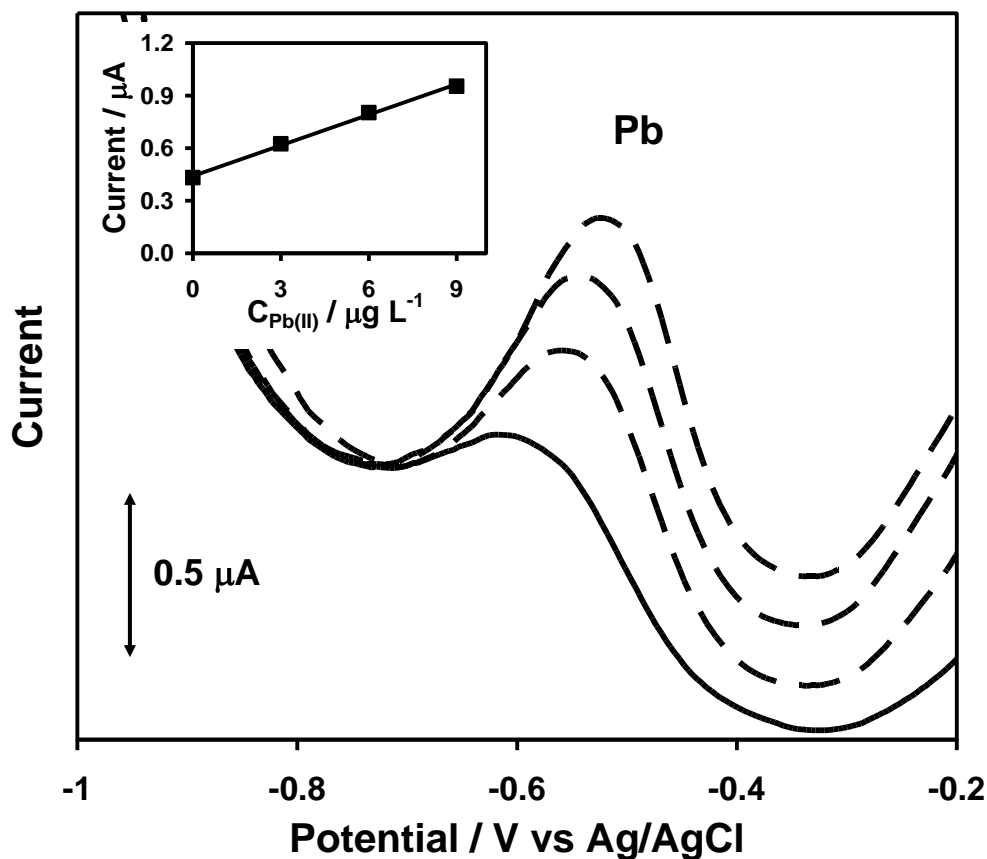

Figure 7. ASVs of tap water sample (solid line) together with three successive standard additions of 3 μg L^{-1} Pb(II) (dashed lines) using Sb_2O_3(3%)-CPE. The inset shows the corresponding standard addition plot. Other conditions are as in Fig. 1.

4. CONCLUSIONS

In this work, the preparation and characterization of the antimony trioxide bulk-modified carbon paste electrode (Sb_2O_3-CPE) is reported. As found out, the electrode has exhibited promising electroanalytical performance with reproducible and well-defined stripping signals for both tested model ions, Cd(II) and Pb(II). In contrast to all previously reported antimony-film operated electrodes,

the newly tested Sb$_2$O$_3$-CPE configuration performed well in mild acidic media (with pH about 4.5), as well as in more acidic solutions of diluted HCl (with pH 1-2).

In our opinion, this unique feature makes the Sb$_2$O$_3$-CPE yet more universal as initially expected. Moreover, the presence of antimony trioxide in the bulk of the electrode, as the source of ions for the nascent generation of the film, predestines the prospects of this electrode to be applicable in analyses, where the addition of Sb(III) ions into the sample solutions (inevitably needed for *in-situ* operated SbFEs) is undesirable or even impossible.

Finally, solid Sb$_2$O$_3$ is very stable and belongs amongst the least soluble inorganic compounds (with solubility product, $K_S(Sb_2O_3 . n H_2O) \approx 1 \times 10^{-42}$ [67]), which minimizes its toxicity towards living organisms compared to the above-mentioned single Sb(III) ions, representing highly toxic species whose use for *in-situ* prepared SbFEs is often being criticized [52,68].

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