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Antimony Trifluoride-Modified Carbon Paste Electrode for Electrochemical Stripping Analysis of Selected Heavy Metals

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Abstract: In this article, a new typ of non-mercury metal-based electrode, antimony trifluoride-bulk-modified carbon paste electrode (SbF_3-CPE) is for the first time reported and examined for electrochemical stripping analysis of selected heavy metal ions at their trace concentration level. In the role of bulk modifier and a source of antimony film generated *in state nascenti*, SbF_3 in a content of 3% (w/w) in the carbon paste mixture was the ultimate choice. All important experimental parameters have been optimised by using Cd(II) and Pb(II) as the model ions and employing the square-wave anodic stripping voltammetry (SWASV) as the proper technique. As found out, the SbF_3-CPE has exhibited a finely linear response (with $R^2 = 0.999$) in the concentration range of 20–120 $\mu g \cdot L^{-1}$ Me(II), while the signal of interest could be reproduced with a relative error of ±6.5% for Cd and ±1.2% for Pb (n = 7).

Keywords: Antimony-modified electrode; Antimony trifluoride; Carbon paste; Electrochemical stripping analysis; Heavy metals; Cd(II) and Pb(II).

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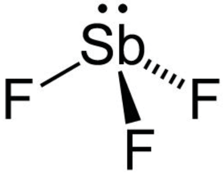
Introduction

Among momentarily popular non-mercury metallic electrodes [1], the antimony-based electrodes occupy the second position, just behind the far most abundant and still unrivalled bismuth film electrodes (BiFEs) and related bismuth-based configurations (BiEs).

Since the discovery of "bismuth-coated electrode" [2] for electrochemical stripping analysis (ESA), the individual variants of BiFEs and BiEs have been the central point of interest in nearly 200 scientific papers published within the period 2000-2009 [1], including further *ca.* 50 contributions appearing afterwards and up until now [3]. Compared to this, related *antimony film electrodes* (SbFEs) and other *antimony-based electrodes* (SbEs) have been reported in more than 30 papers and conference articles since their initial testing [4-6] and, then, already definitive introduction in ESA during 2007 (see refs. [7-34]). Besides both bismuth- and antimony-modified electrodes, there are some other non-mercury metal(loid) alternatives being also fairly applicable in ESA of heavy metals and consisting of lead films (PbFEs; *e.g.* [35,36]), gallium film (GaFE [37]), tin films (SnFEs; *e.g.* [38]), tantalum rod (TaE [39]), or thin layer of selenium (SeFE [40]).

Concerning BiFEs and SbFEs, these two most frequent configurations share very similar physicochemical and electrochemical characteristics. Certain nuances or even differences are in the degree of stability / resistivity of the corresponding films in solutions of acidic pH (due to hydrolysis). Also, somewhat different is the re-oxidation pathway for Bi- and Sb-films; the latter giving markedly smaller stripping signals. Otherwise, the overall electroanalytical performance of both Bi- and Sb-based electrodes is comparable and the same can be stated about their bulk-modified variants, containing either finely dispersed powders of the metal — in case of antimony, Sb-CPE [8,24] and nSb-BDDE [10] — or some Bi(III) and Sb(III) precipitates in the solid state. Again, concerning the latter in combination with antimony variants, the hitherto described configurations of these electrodes are: Sb_2O_3-CPE [4,33], Sb_2O_3-SPE [5], and SbOL-CPE [22]. Yet another type, SbF_3-CPE — the central subject of this article — has been elaborated as the direct successor and closely related arrangement of recently developed NH_4BiF_4-CPE [41] and, especially, BiF_3-CPE [42,43], both offering a very good electroanalytical performance thanks to insolubility of the native BiF_3 in aqueous solutions (see [32] and the table therein).

Although antimony trifluoride (Scheme 1) is highly soluble in water (385 g / 100 mL at 20 °C [44]), it may react with water [45] forming a polymer-like, water-resistant structure [46]. Due to this, SbF_3 could be used as bulk modifier and the respective combination first examined as a novel working electrode for ESA of selected metal ions. The results and observations obtained are summarised in the following sections.



Scheme 1: *Antimony trifluoride and its chemical structure.* (from archives of the authors)

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, Sigma-Aldrich, and Lachema (Brno, Czech Republic). The stock solution of 1 M HCl was prepared from doubly distilled water. The AAS-standard solutions of Cd(II) and Pb(II) (1000 ± 0.1 mg·L^{-1}) were used and diluted as required. Water used throughout the experimental work was obtained by double distillation of deionised water through a laboratory made distillation unit. All the measurements were carried out at room temperature (23±1 °C).

Electrochemical Apparatus and Other Instrumentation

A modular electrochemical system AUTOLAB (model "PGSTAT-12" with ECD modules; EcoChemie, Utrecht, Holland) was used in combination with the NOVA software (up-grade "1.7"; the same manufacturer). This assembly was connected to an external electrode stand incorporating the three-electrode cell with the working electrode (see below), Ag/AgCl/3M KCl reference, and a Pt-plate auxiliary electrode. Stirring was devised with magnetic bar rotated at *ca.* 400 rpm.

Carbon Paste Electrode

Carbon Paste. The proper mixture was prepared by thoroughly hand-mixing of 0.5 g graphite powder ("CR-5", *Maziva Týn*, Czech Republic) with 0.2 ml of highly viscous silicone oil ("LUKOIL MV 8000"; *Lučební závody Kolín*, Czech Rep.) using a porcelain pestle and mortar and according to the recommended procedure [47].

***Modified Carbon Pastes*.** Into a 0.5 g portion of the bare carbon paste, the appropriate amounts of antimony trifluoride were added in order to obtain a series of modified carbon pastes containing from 1 to 10% (w/w) SbF_3. The individual mixtures were homogenized in the same way as above.

Carbon paste electrode (CPE). Freshly made bare and modified carbon paste mixtures were checked with respect to their ohmic resistance; all values were within an interval of 7–25 Ω [48]. After that, all the pastes were packed into piston-driven carbon paste holders of our own construction and production [49,50]. The carbon paste electrode surfaces were renewed by extruding *ca.* 0.5 mm of carbon paste out from the holder with subsequently smoothing with a wet filter paper. Typically, this mechanical renewal was made before starting a new set of experiments or prior to analysis of each sample.

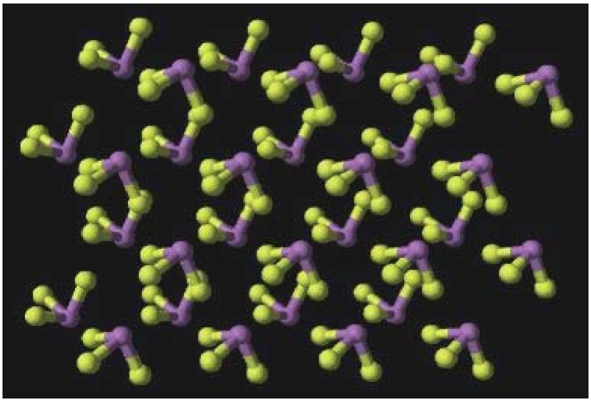
Voltammetric Measurements

Anodic stripping voltammetric measurements combined with the square-wave potential ramp as the modulation of choice [51] consisted of three conventional steps [52]: (i) time-controlled electrochemical deposition, (ii) the rest period, and a (iii) positive-going voltammetric stripping scan under conditions chosen. In some cases, the whole procedure was completed with an additional sequence: electrochemical conditioning / cleaning step. Due to a diversity of the individual experimental conditions and instrumental parameters used, the corresponding values are specified in further text; usually, in the legend of each figure.

Results and Discussion

Antimony Trifluoride: The Solubility *vs*. Insolubility Profile

As already mentioned, antimony trifluoride [*syn*. antimony(III) fluoride, SbF_3] is a salt well-soluble in aqueous solutions, but capable of rearranging into a special crystalline structure. According to roentgen-diffraction analysis [53], the SbF_3 compound may form a very tight microstructure, in which some molecules are aggregated into dimers and trimers (see the structural model in Scheme 2); higher polymers being also likely to occur [46].



Scheme 2:
Antimony trifluoride, SbF_3
Ball-and-stick model of its
tight crystalline structure

(according to ref. [53])

The fluoride anion with the electron octet appearing in $(SbF_3)_n$ aggregates

Note: It can be assumed that his phenomenon is associated with the extremely high electronegativity of the fluoride ion, released in contact with water, and its tendency to be obscured by the maximal numbers of electrons (see the insert beneath the legend). Thus, the electron-deficient fluorine species, $\cdot\overline{\underline{\mathrm{F}}}|$, tend to be somehow aggregated – either between themselves or with electron-pair donating Sb(III) atoms (see, again, Schemes 1 & 2).

Thus, the prediction on possible transformation of antimony trifluoride into its pseudo-polymeric form — *i.e.*, the existence in $(SbF_3)_n$ aggregates — allowed us to test this salt as the bulk modifier of carbon paste in the same way as previously used antimony trioxide, Sb_2O_3 [4,33], or precipitated and subsequently dried antimonyl hydroxide / chloride, SbOL (where "L" is OH and/or Cl [22]), including similar percentage in the carbon paste mixture.

In this study, the initial experiments had shown clearly that all three carbon paste mixtures tested (with 1, 3, and 5 % (w/w) solid SbF_3) exhibited a sufficient stability in aqueous media and there was no evidence for "carbon paste bleeding"; *i.e.*, a spontaneous release of the modifier out of the paste due to its solubility in water [54,55]. This has confirmed that antimony trifluoride can, indeed, be used as the bulk modifier despite the fact that its common form is highly soluble in water.

Choice of the Amount of Antimony Trifluoride in the Carbon Paste Mixture as a Source (of Trivalent Antimony) for *In- State-Nascenti* Generating the Metallic Film

Analogically to similarly operated Sb_2O_3-CPE, SbOL-CPE, or even Bi_2O_3-, NH_4BiF_4-, and BiF_4-bulk-modified CPEs, it can be deemed that the electrode proper (*i.e.*, the thin metallic layer) is being formed according to the following reaction,

$$Sb^{III}F_3 + 3\ e^- \longrightarrow Sb^0 + 3\ F^- \qquad (\mathbf{1})$$

during the preconcentration step in the ESA regime, when the resultant quality and electro-analytical performance of the film would depend on the actual selection of experimental conditions (the composition of the supporting electrolyte, the actual pH), as well as upon some instrumental parameters (deposition potential and time, intensity of stirring).

Regarding our study, Fig. 1 shows the relationship between the amount of SbF_3 (added in to the paste) and the corresponding response(s) for both model metal ions chosen. As seen, the best developed and highest signals were obtained with bulk-modified CPE containing 3 % SbF_3 , further denoted as the $_{(3\%)}SbF_3$-CPE type; whereas the increasing amount of SbF_3 in the CP-mixture had already resulted in a decrease of the responses; particularly, that one for Pb. Moreover, the experimentation with the carbon paste composition has also revealed that this novel electrode may offer a higher sensitivity towards lead compared to that for cadmium, which cannot be said about each antimony-based configuration [7-9,12,23,24,42].

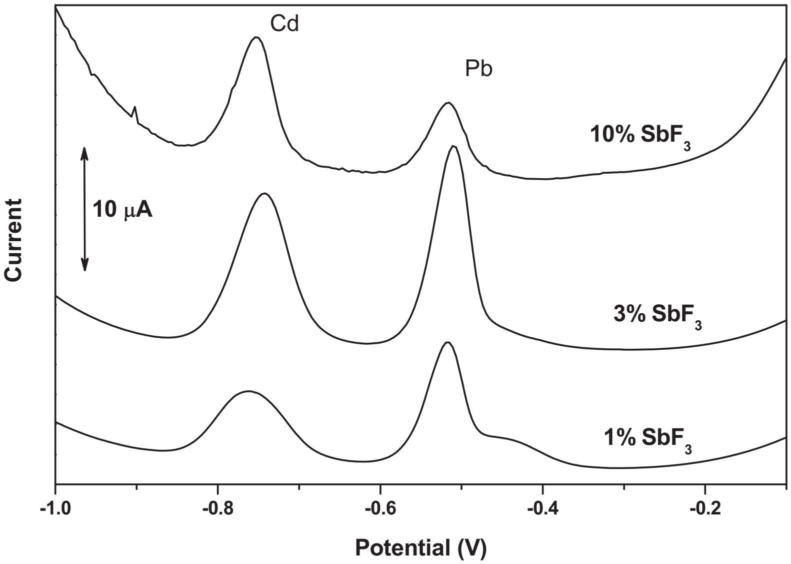


Fig. 1: *Effect of the amount of* SbF_3 *in the CPE-mixture upon the response for Cd and Pb.* Legend: as inscribed. Experimental conditions: Supporting electrolyte: 0.1 M HCl, $c_{(cd)} \equiv c_{(pb)} = 100\ \mu g \cdot L^{-1}$; deposition step: potential, $E_{dep} = -1.1$ V vs. ref., time, $t_{dep} = 120$ s; Equilibrium period, $t_{eq} = 10$ s; Stripping step: initial potential, $E_{init} \equiv E_{dep}$, final potential, $E_{fin} = -0.1$ V; Conditioning potential, $E_{cond} = + 0.3$ V; SWASV ramp: frequency, $f_{sw} = 25$ Hz; pulse height, $\Delta E_{sw} = 50$ mV; step increment, $s_i = 2$ mV.

Optimization of the Deposition Conditions and pH with Respect to Their Effect on the Responses for Cadmium and Lead

As can be seen in Fig. 2, the deposition potential had a significant influence on the current response of cadmium and lead; the optimal value for the deposition and the determination of both Cd(II) and Pb(II) being –1.2 V vs. ref. Further, it was interesting to notice that the peak height for Cd was less affected by the deposition potential chosen compared to the parent signal for the reoxidation of Pb. For this metal, the value of the peak height at –1.2 V was 32.1 μA, which was more than twice compared to the signal obtained at –1.1 V (with 12.9 μA). Within this test, cadmium did not show such difference in the peak heights (being 17.3 μA for a deposition at –1.2 V and 12.7 μA for –1.1 V vs. ref.).

The effect of pH in the sample solution (herein, modelled *via* the appropriate additions of HCl) can be seen in Fig. 3. With the weakened acidity, a noticeable decrease of the respective current response for both Cd and Pb can be observed for the optimal supporting electrolyte, for 0.1 M HCl (with the acidity corresponding to pH ≈ 1).

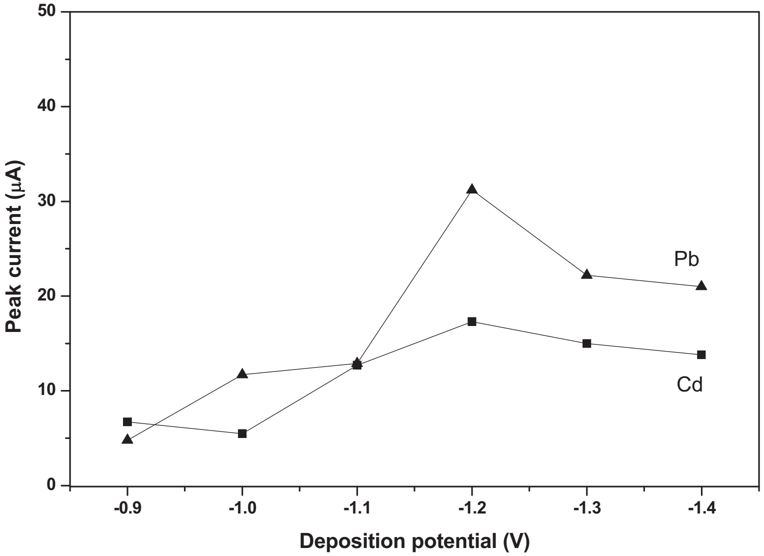


Fig. 2: *Effect of deposition potential upon the SWASV responses for Cd and Pb.* Experimental conditions: 0.1 M HCl, $c_{(cd)} \equiv c_{(pb)} = 100\ \mu g \cdot L^{-1}$. Deposition: E_{dep} from –0.9 to –1.4 V vs. ref., $t_{dep} = 120$ s; $t_{eq} = 10$ s; Stripping: $E_{init} \equiv E_{dep}$, $E_{fin} = -0.1$ V; $E_{cond} = +0.3$ V; SWV-ramp: $f_{sw} = 25$ Hz, $\Delta E_{sw} = 50$ mV, $s_i = 2$ mV.

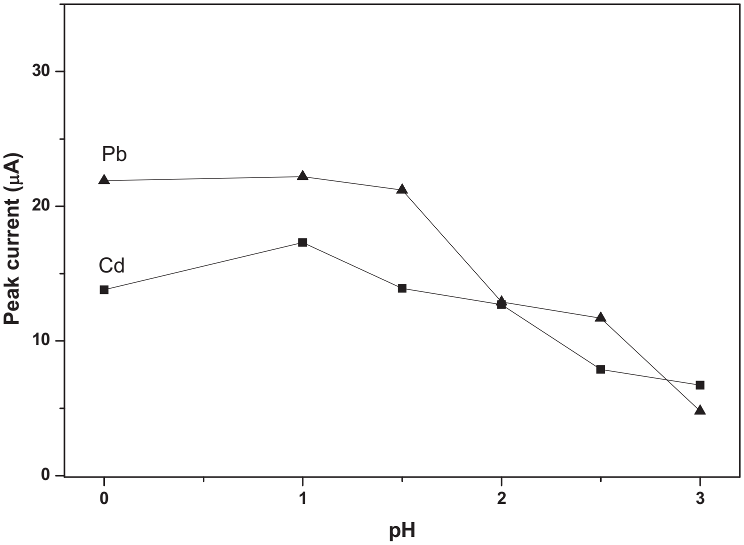


Fig. 3: *Effect of pH upon the SWASV responses for Cd and Pb.* Experimental conditions: 0.001–1.0 M HCl (in the plot, seen *via* the actual pH), $c_{(cd)} \equiv c_{(pb)} = 100\ \mu g \cdot L^{-1}$. Deposition: $E_{dep} = -1.2$ V vs. ref., $t_{dep} = 120$ s; $t_{eq} = 10$ s; Stripping: $E_{init} \equiv E_{dep}$, $E_{fin} = -0.1$ V; $E_{cond} = +0.3$ V; SWV-ramp: $f_{sw} = 25$ Hz, $\Delta E_{sw} = 50$ mV, $s_i = 2$ mV.

Fig. 4 presents the dependence of peak current on the deposition time (period). It is well-known that longer deposition times result in higher current responses due to the reduction of larger amount of the species deposited onto the electrode surface [52,54]. Of course, the respective pathway is limited by the actual character of the electrode surface and its tendency to be saturated by the increasing amount / layer of the deposit.

As found out, for $_{(3\%)}SbF_3$-CPE, even a very long deposition time of 900 s (≈ 15 min) used did not result in any more pronounced saturation — viewable *via* the increasing curvature of the corresponding "I_P-vs-t" plots —; especially, the response for lead exhibited a remarkable linearity over the entire time-span examined (see inset in Fig. 4).

Also, it is interesting to notice a marked shift of both peaks towards more negative potentials for shorter deposition times (30–60s). This is an effect being typical for the film-configured electrodes and, in some special cases, exploitable finely also for quantitative calibrations by means of the respective E_P shifts (see *e.g.* [55] and a commentary of such determination of gold at a CPE).

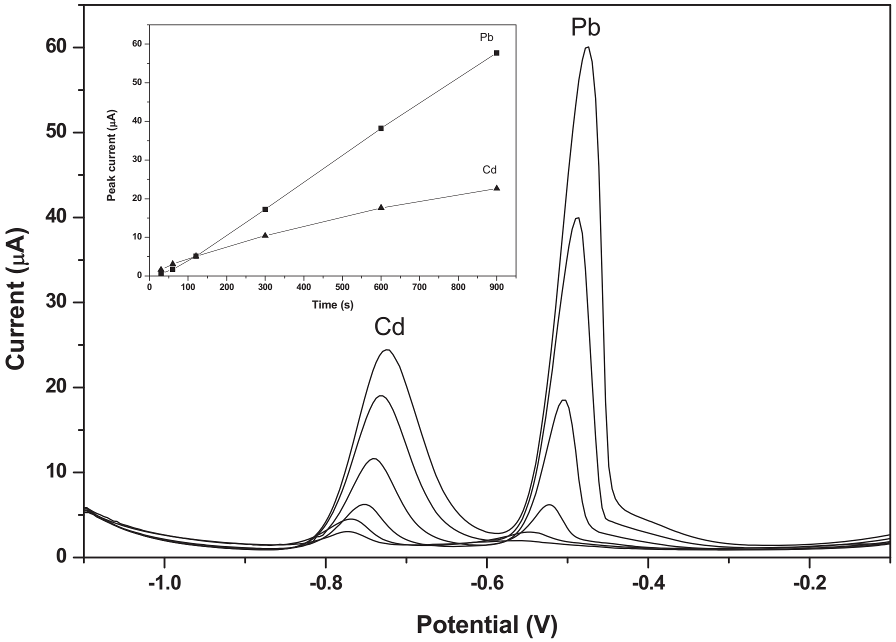


Fig. 4: *Effect of deposition time upon the SWASV responses for Cd and Pb.* Experimental conditions: 0.1 M HCl, $c_{(cd)} \equiv c_{(pb)} = 100\ \mu g \cdot L^{-1}$. Deposition: $E_{dep} = -1.2$ V vs. ref., $t_{dep} = 10$-900 s; $t_{eq} = 10$ s; Stripping: $E_{init} \equiv E_{dep}$, $E_{fin} = -0.1$ V; $E_{cond} = +0.3$ V; SWV-ramp: $f_{sw} = 25$ Hz, $\Delta E_{sw} = 50$ mV, $s_i = 2$ mV.

Model Calibrations of Cd(II) and Pb(II) and the Reproducibility at $_{(3\%)}$SbF$_3$-CPE

Fig. 5 illustrates a very nice linearity of the signals of interest at $_{(3\%)}$SbF$_3$-CPE calibrated over the concentration range of 20–120 μg·L^{-1} Cd(II) or Pb(II); *i.e.*, at the low-to-mid μg.L^{-1} level. (In the insert, the respective correlation coefficients are: $r^2_{(Cd)} = 0.999$ and $r^2_{(Pb)} = 0.993$.) With the electrode of choice, the reproducibility of Cd- and Pb-signals (seven replicates, n=7) was found to be ±6.47 % for Cd(II) and ±1.15 % for Pb(II).

The same studies had also been performed with the remaining two electrodes, $_{(1\%)}$SbF$_3$-CPE and $_{(10\%)}$SbF$_3$-CPE, respectively, confirming that the performance of the electrode containing 3 % (w/w) SbF$_3$ in the CP-mixture has remained unrivalled. (When using $_{(10\%)}$SbF$_3$-CPE, the reproducibility of the Cd-signal was better (R_{Cd} = ±1.70 %), while the same parameter for Pb(II) slightly higher (R_{Pb} = ±4.29 %). In both cases, however, these two SbF3-CPEs exhibited much more pronounced deviations from linearity.)

Note: Also during examining the above-described electroanalytical performance of $_{(3\%)}$SbF$_3$-CPE, all the measurements were of preliminary character and neither interference studies nor recovery and model-sample analyses have been carried out.

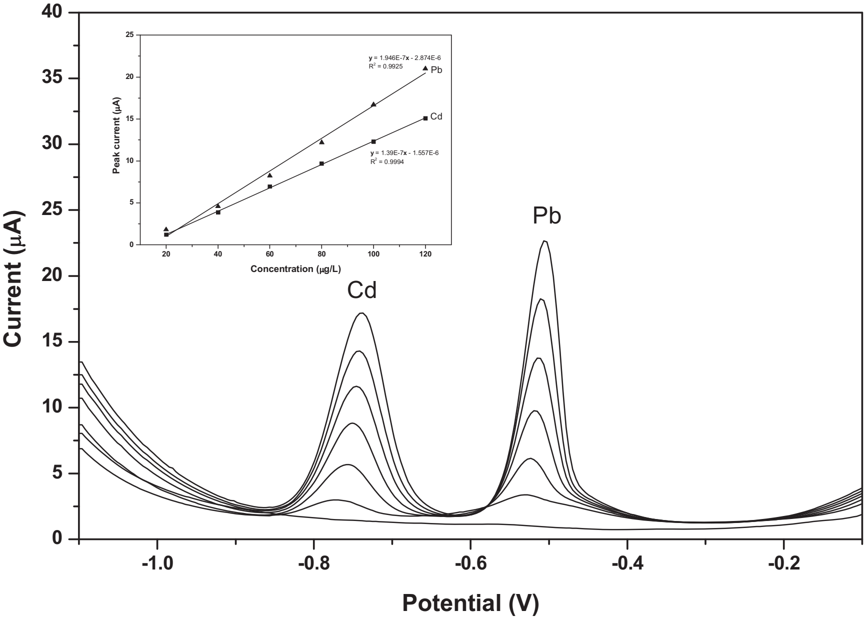


Fig. 5: *Calibration of both Cd(II) and Pb(II) at the μg.L^{-1} concentration level (for t_{dep} = 120 s)*
Legend: typical voltammograms (in main picture), the respective calibration plots (as inset)
Experimental conditions: see Fig. 4 (except the deposition time, specified in the title)

Conclusions

In this article, a novel type of an antimony film electrode has been introduced based on antimony trifluoride-bulk-modified carbon paste electrode, SbF_3-CPE and tested and SWASV of Cd(II) and Pb(II). All the key parameters have been optimized, finding that:

(i) the most suitable content of solid SbF_3 is 3 % (w/w) in the carbon paste mixture;
(ii) optimal acidity of the HCl-based supporting medium is about pH 1;
(iii) optimal deposition conditions are: $E_{dep} = -1.2$ V vs. ref. and $t_{dep} = 120$ s;
(iv) measurements are properly performed in the SWASV regime, when using common instrumental parameters.

Then, the $_{(3\%)}SbF_3$-CPE could be used to determine of both Cd(II) and Pb(II) ions over the examined concentration range of 20–120 $\mu g \cdot L^{-1}$ with good reproducibility of the respective signals; namely, ±6.5 % for Pb(II) and ±1.2% for Cd(II).

Among particular or even specific observations with the SbF_3-CPE can be highlighted:

(1) reliable function of the modifier used (despite its atypical solubility in water);
(2) fairly enhanced sensitivity towards lead at appropriately selected conditions;
(3) notably less sensitivity to saturation effect (being pretty low mainly for lead)

Regarding the first point, however, it should be admitted that the choice of antimony trifluoride means a certain step backwards compared to previously used highly insoluble precipitates; namely, this drawback is a considerably higher toxicity of SbF_3 compared to both Sb_2O_3 and SbOL (see discussion in [32,33] *vs.* specification in [44,45]).

Otherwise, the initial study presented in the above sections requires further continuation. Some second-phase investigations are already in progress, being focused on the advanced optimisation, unavoidable interference studies with other heavy metals (*e.g.* Zn, Tl, In, Sn, and Cu) or even other potentially disturbing species (*e.g.*, other co-alloying metals, complex-forming agents, or common surfactants). Finally, the SbF_3-CPE has to be thoroughly examined in quantitative analysis – from the orientation recovery measurements, via analyses of model solutions (*e.g.* spiked with heavy metals), up to the validated determinations in real environmental samples.

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