

Carbon Paste Electrodes Modified with a Reaction Product Obtained by Hydrolysis of an Antimony(III) Salt

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Abstract: In this article, a new type of antimony-modified electrode is described based on carbon-paste bulk dispersion of a precipitate obtained by hydrolysis of the respective Sb(III) salt. Subsequently, the resultant electrode (SbOL-CPE in two variants) — operated *via* the antimony film formed *in nascenti* at the electrode surface — was subjected to the basic characterisation with respect to its electroanalytical performance in the anodic stripping voltammetry of six heavy metal ions (Zn^{2+} , Cd^{2+} , Pb^{2+} , Sn^{2+} , In^{3+} , and Tl^+). As found out, the electrodes of interest have offered the behaviour and functioning comparable to the two related configurations of antimony film-plated (*in situ*) and antimony trioxide-modified carbon paste electrodes (SbF-CPE and Sb_2O_3 -CPE, respectively). Most importantly, the bulk modification with laboratory-prepared precipitate has been shown sufficiently reliable and the compound itself fairly reducible with stable behaviour; i.e., without need to refine or otherwise specially treat prior to use.

Keywords: Carbon paste electrode; Hydrolysed antimony salt; Bulk modification; Antimony film; Anodic stripping voltammetry; Electroanalytical characterisation, Heavy metals ions (Zn^{2+} , Cd^{2+} , Pb^{2+} , Sn^{2+} , In^{3+} , and Tl^+)

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Introduction

At present, antimony-modified electrodes represent the second largest group of non-mercury metallic electrodes popularised widely in the recent years as possible alternative to controversial mercury counterparts in modern electrochemical stripping analysis (ESA). Being inspired by the great success and unprecedented boom of bismuth-based electrodes [1,2], the related antimony electrodes (SbEs) had preliminarily been tested already in the early 2000s (see [3,4]); nevertheless, the real beginning of SbEs came some years later, after the respective report in a worldwide accessible literature had firstly introduced the standard film configuration [5]. Since then, a series of twelve contributions has appeared [6-17], together with three brand new items on the way [18-20]; all having concerned the characterisation and initial applications of various antimony-based electrodes in the individual variants of ESA. Among these papers, one can also find some sophisticated combinations, such as the use of the ASV-SIA tandem for measurements in flowing streams [17-19].

Concerning antimony film electrodes (SbFEs) and their comparison with the bismuth analogues, they offer some specifics with effective use. At first, it is a better performance of SbFEs in more acidic solutions [5,10], which can be appreciated in situations, when a wet acid-assisted digestion of the samples is required. (In these cases, the residua of mineral acids remaining present after the decomposition process do not need to be extensively buffered — or even removed by additional, usually complicated procedures — and the proper specimen for analysis can be obtained by sole diluting the post-digestion solutions [21].) Second, the base-lines of SbFEs practically do not suffer from the large dissolution ("stripping") signal of the Sb-film [5,6], which is quite advantageous for simultaneous co-deposition and the subsequent detection of some nobler metal ions, such as Cu(II), Hg(II), or even Bi(III) [15,19,22]. On the other hand, the individual variants of antimony-modified electrodes seem to be more sensitive towards the experimental conditions chosen — especially, the actual pH has to be adjusted carefully — and the use of antimony as such means the step backwards with respect to its less favourable toxicological classification [2].

In fact, there is a series of possible configurations of antimony-modified electrodes. The most frequent variants are represented by the metallic films deposited either *in situ* or pre-plated in an external ("plating") solution [5-7,9-11]. Both these electrodes of the "SbFE" type can be eventually substituted by a dispersion of fine antimony powder (see e.g. "Sb-CPE" in [6]). Also, a very thin metallic layer can be firmly deposited with the aid of photolithographic sputtering onto a silicon-chip substrate [11].

Finally, antimony film can be generated *in nascenti* by reducing the electroactive Sb^{III} compound (the use of an Sb^{V} -derivative has not yet been reported) being present in the solid state inside the electrode material, delivered *in via* the bulk modification. So far, the latter has been accomplished by admixing the antimony(III) oxide into the heterogeneous carbonaceous matrixes, when using ordinary carbon paste (" Sb_2O_3 -CPE" type; [3]) or a commercially marketed carbon ink, representing the starting substrate for manufacturing the so-called screen-printed electrodes (" Sb_2O_3 -SPE"; [4]). Certainly, there are other antimony compounds potentially applicable to this purpose; the use of self-polymerising and water-insoluble antimony(III) fluoride, SbF_3 , is currently being under investigation [23].

In this study, the compound of interest and a potentially applicable modifier of this kind was a product obtained by alkalic hydrolysis of antimony(III) chloride, SbCl_3 . The resultant white precipitate was filtered, decanted, and — without any other purification — left to dry to be immediately applied for the bulk modification. The new electrodes obtained in this way were then subjected to routine electrochemical examination by means of ESA, with a goal to evaluate the overall effectiveness and reliability of such a way of modifying. The principal results and observations from the respective electroanalytical characterisation are summarised and discussed below.

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 Sigma-Aldrich or Merck. Of the same purity specification and from the formerly mentioned dealer were also antimony compounds used for the preparation of modifier; i.e., antimony trichloride (SbCl_3) or as the modifier itself (antimony trioxide, Sb_2O_3). Stock solutions of either hydrochloric acid or acetate buffer were made 1 mol L^{-1} in concentration; the latter being a mixture of $\text{CH}_3\text{COOH} + \text{CH}_3\text{COONa}$ (1:1).

Stock solution of Sb^{III} used for electrolytic deposition of the film and preparation of an antimony film electrode for some comparative measurements was the spectroscopic standard with a guaranteed content of $1000 \pm 1 \text{ mg L}^{-1} \text{ Sb}^{3+}$. To prevent hydrolysis in aqueous solutions after dilution, this standard had been strongly acidified (to pH ca. 1).

Finally, stock solutions of Pb^{2+} and Cd^{2+} , selected as two model ions for characterisation of the electrode of interest in the ESA regime and the SWASV mode (for further specification, see later), were prepared containing 1 mg L^{-1} Pb^{2+} or Cd^{2+} ; again, when stabilising the corresponding standards by acidifying with HCl (to pH 2).

Throughout the experimental work, all solutions were prepared from doubly deionised water obtained by passing through a laboratory cartridge purifier (system "Milli-Q"; Millipore, USA). The appropriate volumes of water and solutions used were dosed with a set of automatic adjustable pipettes (model "Finnpipette"; Labsystems, Finland).

Apparatus and Other Instrumentation

A modular electrochemical system AUTOLAB equipped with PGSTAT-12 and ECD modules (Eco Chemie, Utrecht, Holland) was used in combination with GPES software (*ibid.*). This assembly was connected to an external electrode stand incorporating the three-electrode cell with the working electrode (see below), $\text{Ag} | \text{AgCl} | 3 \text{ M KCl}$ reference, and Pt-plate (approx. 0.5 cm^2) serving as the counter. Stirring was devised with a magnetic bar ($10 \times 2 \text{ mm}$) agitated at 300 rpm.

The pH was measured using a portable pH-meter in conjunction with a combined glass sensor (both Metrohm, Switzerland). The ohmic resistance of newly made carbon pastes was checked with a Voltcraft® multimeter (model VC 404, Conrad Electronics, Germany).

Preparation of the Precipitate

The stock solution of SbCl_3 was prepared by careful dissolving 1.0 g of solid chemical in 1000 mL distilled water acidified with 10 mL 30% HCl (to avoid possible hydrolysis during preparation). Then, under stirring, 100 ml of this solution was mixed with 10 mL 0.1 M NaOH. A dense dispersion with white precipitate formed was filtered and repeatedly desalinated / washed out by decantation (until the negative reaction with the Cl^- ions). Then, without any further purification, the compound isolated was left to dry for 12 hours in a laboratory oven at $70 \text{ }^\circ\text{C}$ and, for 24 h., in a glass desiccator filled with drying agent (P_4O_{10}). Then, the fine powder was immediately used as the carbon paste modifier denoted as "SbOL" (see below).

Working Electrodes

Carbon Pastes. The bare (unmodified) mixture was prepared by thoroughly hand-mixing of 1.5 g graphite powder ("CR-5", Maziva Týn, Czech Republic) with 1.0 ml highly viscous silicone oil (LUKOIL MV 8000; Lučební závody Kolín, Czech Republic). Both components were manually homogenised using recommended procedure [24].

Afterwards, three equal portions of about 0.5 g of the bare carbon paste were modified with the appropriate amounts of solid antimony trioxide (*p.a.*, Merck) to contain 1 % Sb_2O_3 (w/w; a ratio according to [3,4]) or with laboratory-made precipitate; the latter in two mixtures with 1 and 10 % (w/w) SbOL. The additional homogenisation of these mixtures yielded the resultant modified pastes.

Carbon Paste Electrodes. The bare carbon paste and the individual modified mixtures were packed into four identical piston-driven holders (of our own design [25,26]) with the same surface diameter of 2 mm. All freshly prepared carbon paste electrodes were checked *via* the actual ohmic resistance, serving as indirect indicator of their homogeneity [24].

Antimony Film-Plated Carbon Paste Electrode. The electrode filled with the bare carbon paste was plated with antimony films *in situ*; i.e., by potentiostatic electrolysis performed directly in the sample solutions spiked with Sb^{3+} ions. Prior such a deposition, the CPE surface was renewed, which was accomplished mechanically by smoothing the soft carbon paste with a wet filter paper [24,25]. Typically, this quick and simple operation was done before a new set of measurements.

In order to distinguish among the individual types of CPEs prepared, the already adopted denotation (see e.g. [2,6]) is used throughout the text; namely, (i) "CPE" for the bare (unmodified) carbon paste, (ii) "SbF-CPE" for the standard antimony film-plated configuration, (iii) " Sb_2O_3 -CPE" for the variant modified with antimony oxide, and (iv) "SbOL_(1%)-CPE" or "SbOL_(10%)-CPE" for the electrodes containing the precipitate at two different percentages.

Electroanalytical Measurements and Related Procedures

Square-Wave Anodic Stripping Voltammetry (SWASV). All the experiments consisted of three conventional steps: (1) time- and potential-controlled pre-concentration (accumulation or deposition, resp.), (2) the equilibrium period, and (3) the stripping step applied in the positive scan direction. Because the individual experimental conditions and instrumental parameters varied from case to case, the respective set is always specified directly within the "Results & Discussion" part; usually, in the legend of the corresponding figure.

Oxygen Removal. Due to the potential ramp used [27], as well as according to the previous experience [5,6], no purification of the solutions from the dissolved air oxygen was necessary and therefore, the corresponding procedure — bubbling with inert gas — had not been included in any experiment performed within the study.

Processing and Evaluation of the Measurements. Finally, the individual analytical signals were evaluated as the peak areas using manual base-line setting by the analyser software. Where applicable, the results of measurements were evaluated statistically, when using the standardised procedures and commonly used criteria.

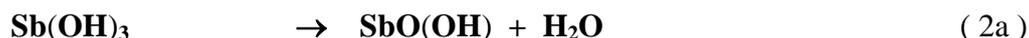
Results and Discussion

Characterisation of the Precipitate Prepared

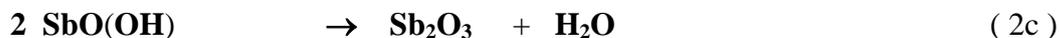
During the alkalic hydrolysis of the SbCl_3 solution, one can anticipate the following reactions:



With respect to the individual antimony precipitates [28], they frequently contain antimonyl ion, SbO^+ , possible is also the formation of hydroxides, SbO(OH) and Sb(OH)_3 , or hydrated trioxide, $\text{Sb}_2\text{O}_3 \times \text{H}_2\text{O}$, respectively. Regarding the latter two, it can be expected that the intensive drying will result in the deliberation of water according to the schemes,



including the subsequent dehydration of the monohydroxide:



A set of schemes (1a-d) and (2a-c) suggests one that the final product of hydrolysis is either SbOCl , related SbO(OH) , or Sb_2O_3 , and eventually mixture of some of these forms. In any case, it is anticipated that the resultant product will enable the instantaneous generating of the antimony film during electrolytic deposition in the ASV regime, according to the scheme:



Then, the above-proposed abbreviation "SbOL" (where "L" is the ligand; i.e., Cl^- or OH^-) fits to the denotation system adopted [5,6] regardless of which compound forms the precipitate.

It is evident that the exact chemical composition should be defined with the aid of physicochemical identification, when using the proper instrumental techniques, such as thermogravimetry (TG), infrared spectrometry (IR- and FTIR), roentgen analysis of solids (XRF and XRD), mass spectrometry (MS), or even some isotope-variants of NMR (see e.g. [29]). However, due to a preliminary character of this study, such an analysis — similar to that in our previous work [30] — has not been performed.

Initial Electroanalytical Measurements

Effect of the Modifier Quantity. Two electrodes of the SbOL-CPE type, differing from the content of the modifier added, were first examined in 0.1 M HCl, when using a model mixture of Cd^{2+} and Pb^{2+} ions. The result of the corresponding assay is shown in Fig.1.

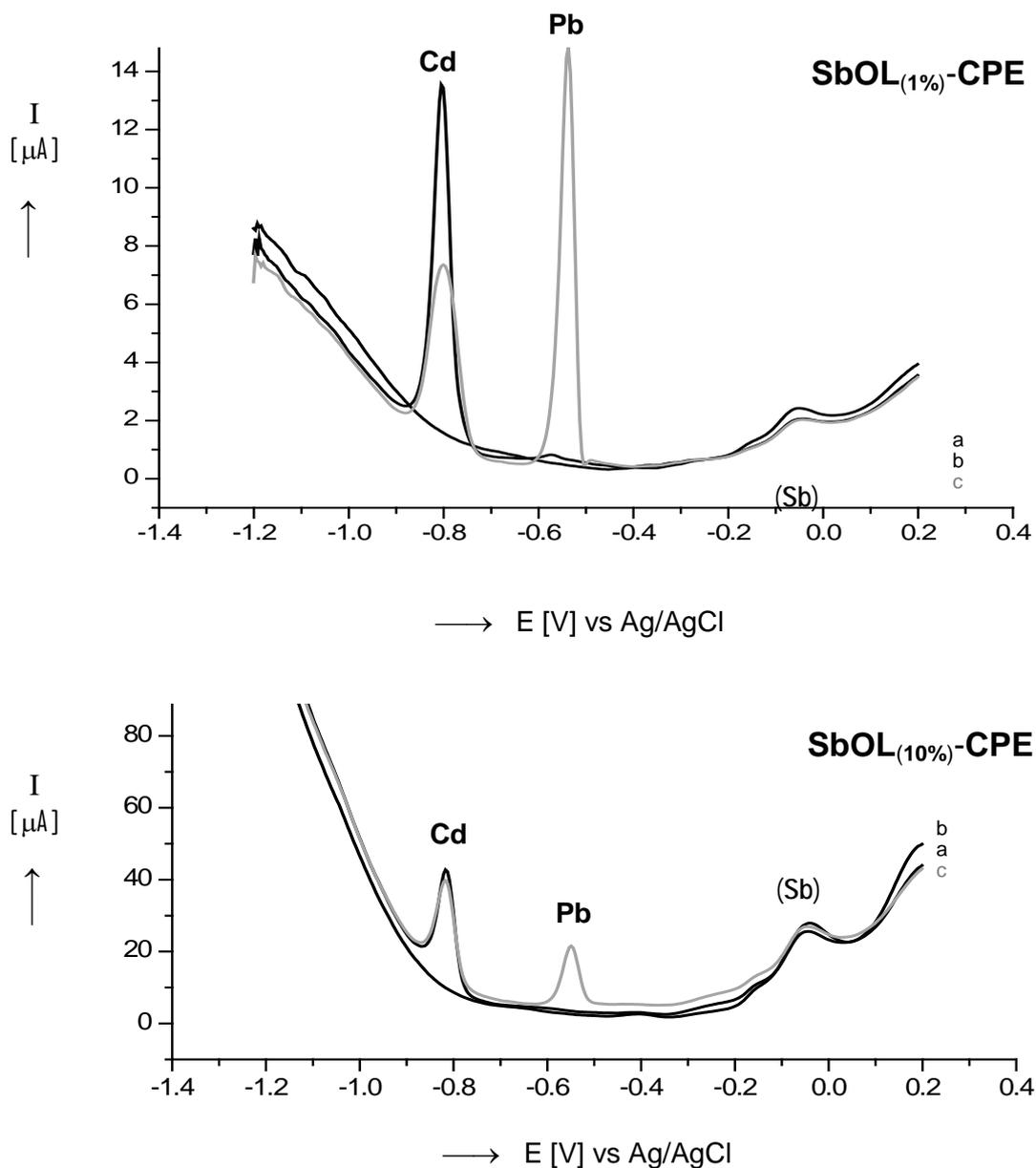


Figure 1. Effect of the modifier content on the overall performance of the SbOL-CPEs. Legend: a) base-line, b) $+50 \mu\text{g}\cdot\text{L}^{-1} \text{Cd}^{2+}$, c) $+50 \mu\text{g}\cdot\text{L}^{-1} \text{Cd}^{2+} + 100 \mu\text{g}\cdot\text{L}^{-1} \text{Pb}^{2+}$. Experimental conditions: silicone oil-based carbon paste; SWASV; 0.1 M HCl (pH 1); $c(\text{Me}) = 100 \mu\text{g}\cdot\text{L}^{-1}$; deposition conditions: potential, $E_{\text{DEP}} = -1.2$ V vs. ref., time, $t_{\text{DEP}} = 60$ s; equilibrium period, $t_{\text{EQ}} = 15$ s; scan range (stripping step), from -1.2 V to $+0.2$ V vs. ref.; square-wave ramp: frequency, $f_{\text{SW}} = 25$ Hz; pulse amplitude, $\Delta E = 20$ mV; step increment, $v_{\text{SW}} = 4$ mV.

Two sets of voltammograms depict that the lower percentage of the SbOL precipitate had resulted in more favourable signal-to-noise ratio due to the somewhat lower background of the SbOL_(1%)-CPE. Due to this, the electrode with lower content of modifier was evaluated as superior and employed for further measurements.

Otherwise, however, the performance of both chemically modified electrodes was satisfactory (notice the different current intensity for both sets of voltammograms), confirming our previous observations [31-33] that the bulk modification of the carbon paste material does not require so strictly adjusted ratio “modifier vs. carbon paste”.

Finally, it is interesting to see that, despite relatively high content of the modifier in the carbon paste bulk, the dissolution peak of antimony (at about 0.0 V vs. Ag/AgCl) has been found fairly small for both electrodes, which is a typical feature of each antimony film-based electrode [5,6] compared to its bismuth counterparts [31,32].

Effect of Supporting Electrolyte. Similarly as the standard SbFE, also both SbOL-CPEs tested had exhibited a very poor behaviour in acetate buffer-based solutions (not shown), whereas optimal functioning could be attained in more acidic solutions of mineral acids. A trio of voltammograms, depicted in Fig. 2, offers a comparison of the SbOL(1%)-CPE for decimolar solutions of HCl, HClO₄, and HNO₃.

In this assay, performed here with all model ions (i.e., Zn²⁺, Cd²⁺, Pb²⁺, In³⁺, Sn²⁺, and Tl⁺; the latter two being depicted in the figure), when hydrochloric acid and perchloric acid had represented more or less optimal acidic media with and without complex-forming capabilities [28], while nitric acid was selected due to its frequent use for wet decompositions of the samples [21], as well as for potentially electrocatalytic properties [34]. As can be seen, distinct responses for thallium could be obtained in all electrolytes examined, while the signal for tin appeared in 0.1 M HCl only. Regarding the remaining metals, reoxidation of cadmium and lead gave rise to well-developed responses in all acid solutions, the signal for zinc deposited at -1.3 V did not develop in 0.1 M HNO₃ (being seen as negligible wave obscured by high background), and the stripping peak of indium was not registered at all for the concentration chosen.

Due to the sensitivity to a SbFE to the actual pH [5,6], the proper acidity of HCl solutions was investigated *extra* for each element, having resulted in the following relations: Zn / pH 2.5, Cd & Pb / pH 2.0, In & Tl / pH 1.5, Sn / 1.0. (In the case of indium, the concentration of In³⁺ ions had to be additionally increased up to 1000 µg·L⁻¹.)

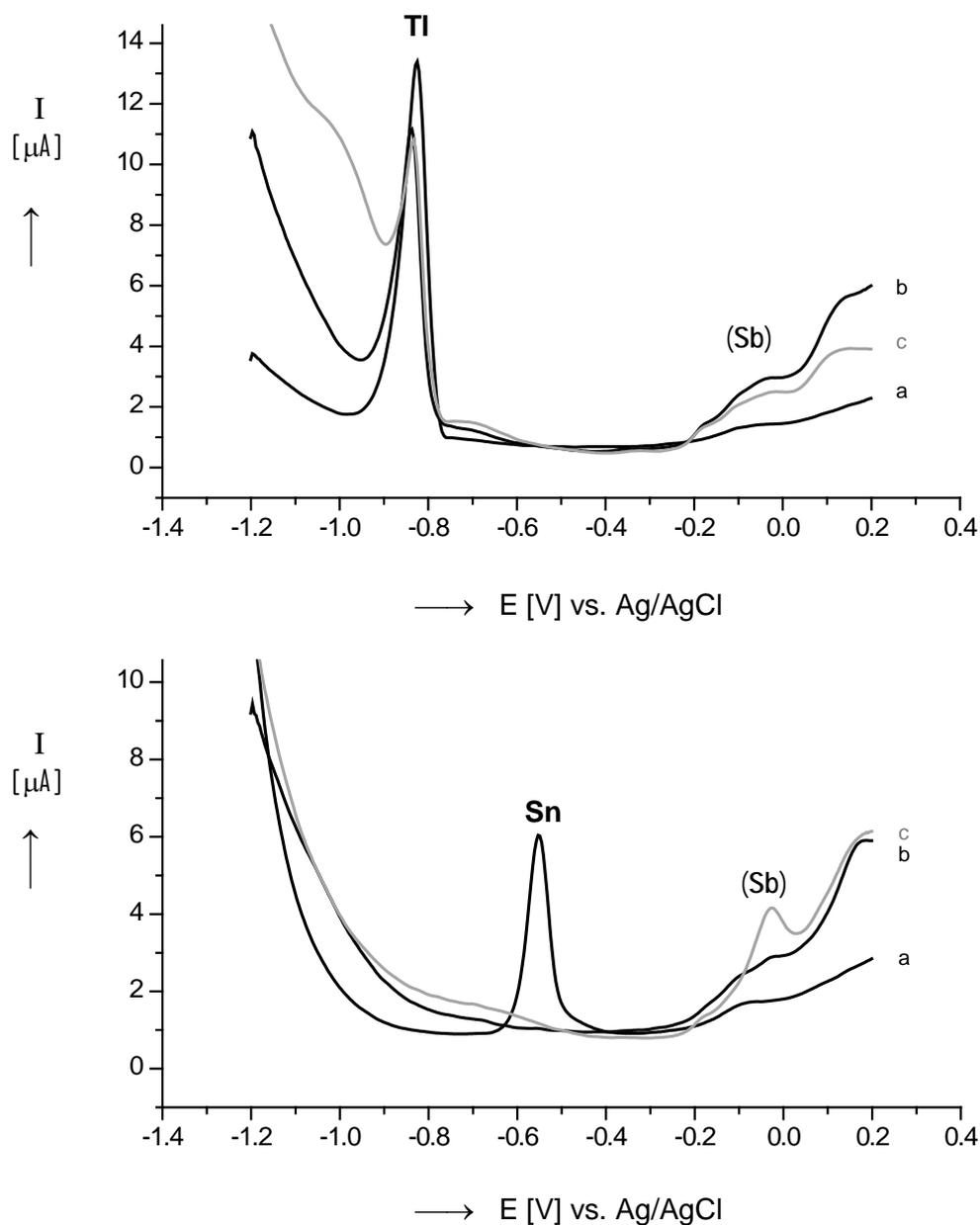


Figure 2. Effect of mineral acid in the supporting electrolyte upon the SWASV detection of thallium (left) and tin (right) with SbOL-modified electrode. Legend: a) 0.1 M HCl (pH 1.0), b) 0.1 M HClO₄ (pH 0.9), and c) 0.1 M HNO₃ (pH 1.2). Experimental conditions: SbOL_(1%)-CPE; c(Me) = 500 μg·L⁻¹. For other conditions and parameters, see Fig.1

Comparison of Three Antimony-Modified Carbon Paste Electrodes. Interesting observations were made during an assay, when the SWASV performance of the SbOL_(1%)-CPE had been mutually compared with those of Sb₂O₃-CPE and SbF-CPE (operated *in-situ*). Regarding very similar configurations of the first two electrodes, the respective results are illustrated in Fig. 3, making comparison in-between for two different measurements.

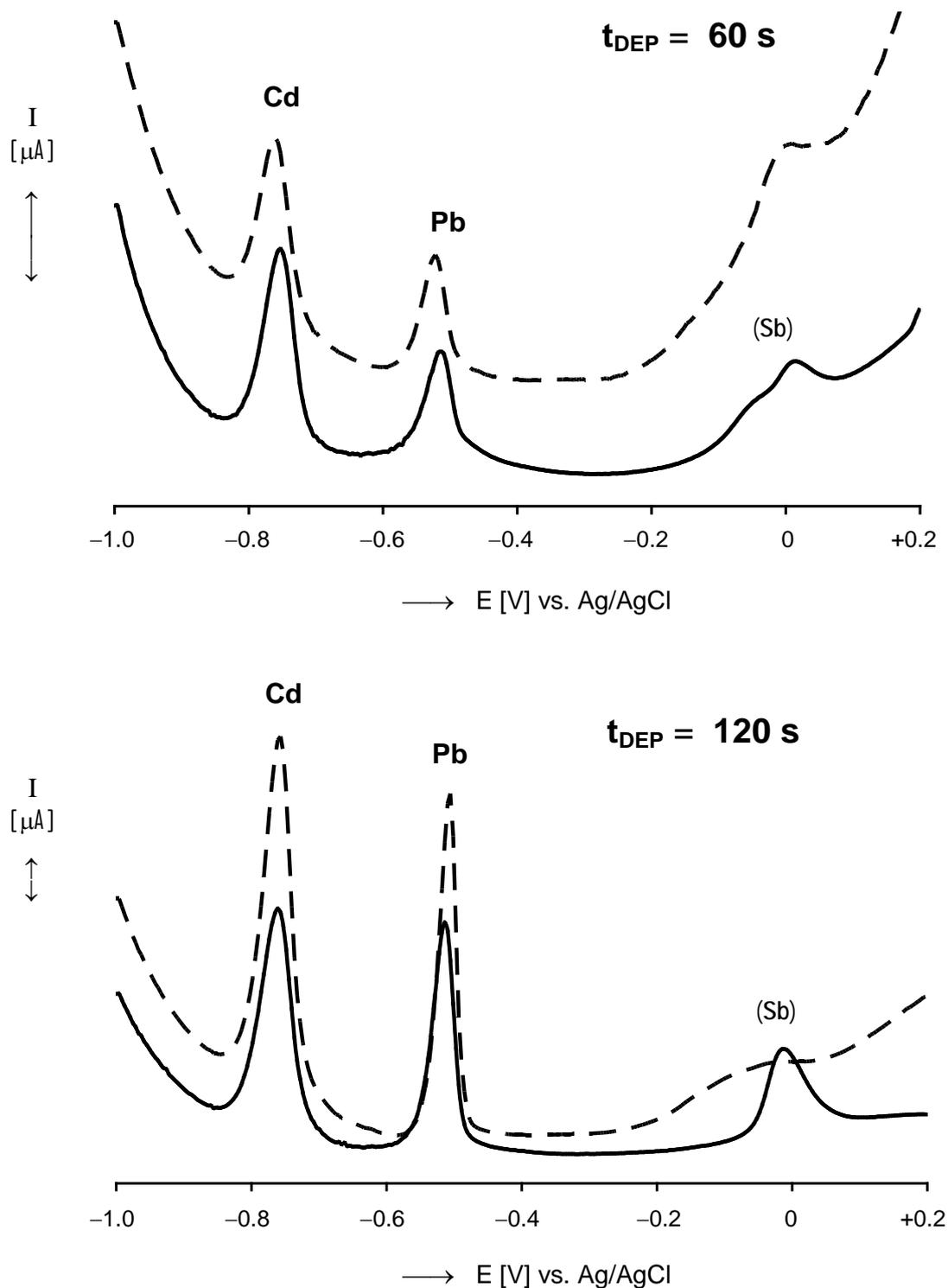


Figure 3. Comparison of two antimony(III) compound-modified carbon paste electrodes via their SWASV performance for a model mixture of Cd^{2+} and Pb^{2+} at two different deposition periods. Legend: full line ... $\text{Sb}_2\text{O}_3(1\%)\text{-CPE}$, broken line ... $\text{SbOL}(1\%)\text{-CPE}$. Experimental conditions: 0.01 M HCl (pH 2); $c(\text{Me}) = 50 \mu\text{g}\cdot\text{L}^{-1}$; $E_{DEP} = -1.0 \text{ V}$ vs. ref. For other conditions and parameters, see Fig.1. Note: Two-sided arrow corresponds to a current intensity of $1 \mu\text{A}$.

Namely, the second analysis was carried out with two-fold deposition, revealing unexpectedly significant difference in the overall electroanalytical performance of both electrodes with respect to the model analytes used. Moreover, as can be seen, the prolonged deposition had led to a further suppression of undersized dissolution signal for antimony, whereas one would have expected rather opposite trend. However, the same experiment confronting the SbOL-CPE with standard film variant of SbF-CPE has already shown almost comparable responses for both deposition times applied, including similar size of the corresponding antimony peaks (not shown). Thus, it can only be speculated about the reason behind the behaviour of the SbOL(1%)-CPE after more intensive accumulation and the proper interpretation will have to be given later – after additional and more detailed investigations.

The stability of analytical signals at both precipitate-modified CPEs was investigated next, when using the detection of lead as the model system. By analysing the solution of 0.01 M HCl with $50 \mu\text{g}\cdot\text{L}^{-1} \text{Pb}^{2+}$ in eight successive replicates and with deposition for 60 s, the reoxidation peak current could be reproduced within an interval of 1.55-1.60 μA ; i.e., with a relative error of about 3.3 %. Such a value was very satisfying and even better than the reproducibility commonly reported for the (bare) carbon paste electrodes themselves [24]. Moreover, in all cases, the SWASV responses had been well-developed and the overall background / noise over the potential range of interest fairly low, without evidence of any electroactive impurities; e.g., residual moisture in the precipitate.

Thus, these observations have indirectly confirmed the fine quality of the modifier used, when the same conclusion could also be deduced from negligible and nearly constant ohmic resistance of the resultant carbon pastes. (Both modified variants with 1% and 10% precipitate plus the original native mixture were measured immediately after the preparation of all three electrodes; the complete assemblies in manually filled piston-driven holders exhibiting the resistance within 3.5-4.7 Ω only.)

Calibration Measurements

The individual calibrations were measured and plotted for all six metal elements studied, when using the diluted solutions of HCl with the concentration and pH chosen accordingly to the above-described supporting electrolyte composition. Except the deposition potential, all the experiments were carried out under the same conditions, providing the results summarised in Table I and given together with the relevant statistical data – see overleaf.

Table I: Calibration measurements. The results and statistical data

Metal ion	pH^A (23°C)	E_{DEP}^B [V]	t_{DEP}^C [s]	E_P^{B,D} [V]	Sensitivity [$\mu\text{A}\cdot\mu\text{g}^{-1}\cdot\text{L}$]	CC^E (R ²)	RSD^F [%]
Zn²⁺	2.45	-1.3	60 s	-1.09	0.019	0.998	± 4.2
			300 s	-1.10	0.056	0.997	± 3.6
Cd²⁺ ^(a)	2.05	-1.2	60 s	-0.80	0.065	0.999	± 4.9
			300 s	--	--	--	--
Pb²⁺ ^(a)	2.05	-1.2	60 s	-0.55	0.043	0.999	± 2.8
			300 s	--	--	--	--
In³⁺ ^(b)	1.60	-1.3	60 s	--	--	--	--
			300 s	1) -0.70 2) -0.55	0.086 0.006	0.998 0.999	± 3.2 ± 1.0
Sn²⁺	0.95	-1.2	60 s	-0.56	0.013	0.998	± 2.8
			300 s	-0.46	0.007	0.987	± 1.2
Tl⁺	1.60	-1.2	60 s	-0.83	0.027	0.999	± 4.7
			300 s	-0.83	0.073	0.998	± 2.9

Legend: A) Actual experimental value; B) vs. Ag/AgCl, C) Deposition time (period), D) Peak potential, E) Correlation coefficient, F) Relative standard deviation for three replicates (n = 3); (a) deposition for 300 s not studied, (b) two peaks observed.

As expected from joint comparison, the highest sensitivities were found for both Cd and Pb, for which the accumulation for 60 s was sufficient. On the contrary, a longer deposition had to be used to obtain an evident response for indium, appearing as a couple of closely positioned peaks, which could indicate either a consecutive reoxidation process $\text{In}^0 \rightarrow \text{In}^+ \rightarrow \text{In}^{3+}$ or a complex intermediate formed under conditions chosen.

Otherwise, all calibrations plotted have exhibited a linear increase with concentration (see again Table I and the column “r²”), when the corresponding limits of detections (LODs, 3σ) for 300s-deposition could be estimated to be: $19 \mu\text{g}\cdot\text{L}^{-1}$ Zn, $72 \mu\text{g}\cdot\text{L}^{-1}$ In, $53 \mu\text{g}\cdot\text{L}^{-1}$ Sn, $35 \mu\text{g}\cdot\text{L}^{-1}$ Tl, and approx. $5 \mu\text{g}\cdot\text{L}^{-1}$ for both Cd and Pb (the latter as a very rough estimate from measurements with $t_{\text{DEP}} = 60$ s).

Finally, selected metal ions have also been examined in model mixtures, finding that the supporting media containing solely diluted HCl do not allow us to distinguish between the stripping signals of Cd and Tl, Cd and Sn, as well as Cd with In, when the respective separation would require additional complex-forming constituent(s), such as halides (F^- , Br^- , and I^-), pseudohalides (SCN^-) or tartaric acid [19,35-38].

Conclusions

A new antimony-modified electrode has been introduced, containing the precipitate prepared by alkalic hydrolysis of SbCl_3 . The resultant electrode, the SbOL-CPE, completes the hitherto existing family of antimony-based electrodes that are being represented — as documented in Table II — by surprisingly diverse configurations if one considers a relatively narrow collection of the corresponding reports and a sole half a decade of the renaissance of antimony in electroanalytical measurements [2,5], after the classical era of potentiometric pH-sensors of the Sb / Sb_2O_3 type (see [39] and [40] with refs. therein).

Table II: *Types of antimony-based electrodes. A survey of configurations*

Type of electrode [abbreviation]	Specification of Preparation / Construction: Form of antimony, way of attachment, substrate (further characterisation)	Reference(s) [№] (note)
SbF-GCE	glassy carbon electrode plated with antimony film (electrolytic deposition <i>in situ</i> / <i>ex situ</i>)	5, 9, 12, 13 17-19
SbF-CPE	carbon paste electrode plated with antimony film (electrolytic deposition <i>in situ</i>)	6, 7, 10, 16, 20
Sb-CPE	carbon paste with admixed and finely dispersed antimony powder (by manually homogenising)	6, 20
nSb / BDDE	boron-doped diamond whose surface is coated with antimony nanoparticles	8
sSb / (Si-O-Si) _x	silicon-chip substrate with antimony thin layer deposited with the aid of lithographic sputtering	11
SbF-ME	Antimony film deposited onto and inside of a macroporous template (as electrode substrate)	14
SbF-CFi μ E	carbon fibre microelectrode plated with Sb-film (electrolytic deposition <i>in situ</i> / <i>ex situ</i>)	15
Sb ₂ O ₃ -CPE	carbon paste bulk-modified with solid oxide (by means of manual mixing and homogenisation)	3, 20
Sb ₂ O ₃ -SPE	carbon ink modified by admixing the solid oxide (subsequently used as the final electrode material)	4
SbOL-CPE	carbon paste bulk-modified with a precipitate obtained by hydrolysis of SbCl_3 solution	this report
Sb / Sb ₂ O ₃	antimony (metal rod) coated with antimony oxide (as indicatory electrodes for pH-sensing)	39

Other abbreviations used: n ... nano, s ... sputtered, L ... ligand (Cl^- or OH^-); SPE ... screen-printed electrode (manufactured by solidifying and machine-processing of special carbon ink)

As shown above, the performance of the SbOL-CPE in anodic stripping voltammetry was satisfactory and fully comparable with that of Sb₂O₃-CPE, being the closest configuration with respect to the electrode material composition, the way of preparation, as well as proper functioning during the measurements. In addition, compared to the antimony oxide-modified variant, the SbOL-CPE has exhibited markedly higher sensitivity in the regime of prolonged accumulation (in order of minutes), which may be a starting point for further improvements of the overall analytical performance. In introductory measurements presented herein, the SbOL-CPE could be reliably operated within the mid microgram-per-litre concentration level for the sextet of typical heavy metals ions. Nevertheless, as shown by some experiments with Cd²⁺ and Pb²⁺, the antimony(III) precipitate-modified electrode seems to be capable of their detecting at significantly lower concentrations, including the ultratrace (sub-ppb) level.

Last but not least, satisfactory function of the SbOL-CPE and no impurities identified in the precipitate used have demonstrated that a suitable modifier — herein, the alternate source of antimony film — can also be prepared in laboratory from accessible chemicals and without any other treatment(s), including additional purification. In other words, it is not always necessary to use the commercially marketed products with guaranteed quality.

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