SCIENTIFIC PAPERS
OF THE UNIVERSITY OF PARDUBICE
Series A
Faculty of Chemical Technology
**13** (2007)

# ANTIMONY-MODIFIED CARBON PASTE ELECTRODES: INITIAL STUDIES AND PROSPECTS

Ivan ŠVANCARA[a1], Samo B. HOČEVAR[b], Lucie BALDRIANOVÁ[a], Eva TESAŘOVÁ[a], Božidar OGOREVC[b] and Karel VYTŘAS[a]
[a]Department of Analytical Chemistry,
The University of Pardubice, CZ–532 10 Pardubice
[b]Analytical Chemistry Laboratory, National Institute of Chemistry,
SI–1001 Ljubljana

Received September 27, 2007

*Initial studies with antimony-modified carbon paste electrodes are presented focused on their performance in anodic stripping voltammetry. The investigations performed have comprised the first experiments with antimony film-plated and antimony powder-dispersed carbon paste electrodes (SbF-CPE and Sb-CPE, respectively), as well as the corresponding bismuth-based electrodes in selected measurements carried out in parallel. The respective experiments have dealt with the characterisation of electrochemical behaviour of antimony, the effect of pH, and the electrode substrate used. When using diluted solutions of HCl as the supporting electrolyte of choice together with $Pb^{2+}$ + $Cd^{2+}$ as model ions, the basic electroanalytical performance of both SbF-CPE and Sb-CPE in the square-wave anodic stripping voltammetric mode is outlined and some specifics found discussed with respect to possible applications in practical analysis.*

---

[1] To whom correspondence should be addressed.

## Introduction

In modern electrochemistry and electroanalysis, metals and metallised substrates still represent one of the most popular group of electrode materials used in detection systems for practical measurements [1]. This is the case of classical types of working electrodes made from noble metals (Pt, Au, or Ag), mercury (in a drop configuration as DME and HMDE; or in the form of a mercury film electrode, MFE), and recently also of bismuth. Whereas the latter has been introduced in potentiometry half a century ago [2], its voltammetric equivalent comes much later — at the dawn of a new millennium [3] — when a bismuth-coated electrode is introduced as environmentally friendly alternative to the preceding mercury electrodes. During a relatively short period since 2000, bismuth-based electrodes have undergone a very dynamic development, showing great potential in stripping voltammetry and related techniques, especially for the determination of various metal ions at the trace concentration level [4,5].

These achievements with bismuth electrodes have soon stimulated analysts to examine even other metals or metallic materials similar in nature to bismuth and mercury. Within such studies, electrodes based on Bi-Ag or Bi-Cu alloys [6,7] and Pb- [8,9], Ga- [10] or Sb- [11,12] thin layers were already of interest. In contrast to bismuth alloys and lead- or gallium films which have shown some promise for practical analysis, related antimony-modified substrates did not show satisfactory performances during initial tests with two different forms of antimony films — (i) after deposition *in situ* from solutions with $Sb^{3+}$ ions [11] or (ii) in the nascent state *via* reduction of $Sb_2O_3$ contained as a solid in heterogeneous carbon matrices [11,12]. Thus, despite very close physico-chemical and electrochemical properties of antimony and bismuth [13,14], a combination of antimony-based electrodes and a stripping analysis protocol had been considered as less attractive up until a year ago when our group elaborated a special study focused on both metals with direct comparison of their electrochemical behaviour.

A major part of these investigations was performed with the glassy carbon electrode (GCE) as a substrate for antimony- or bismuth films and the respective results have already been presented as the introductory report [15] on applicability of antimony electrodes in electrochemical stripping analysis (ESA). In this association, it should be noted that regarding antimony and its employment in electrochemistry as such, a metal–metal oxide electrode of the $Sb|Sb_2O_3$ type has been known for a long time as potentiometric sensor responding proportionally to pH changes; see Refs [16,17] and Refs therein.

The remaining measurements with antimony film electrode, hitherto only briefly mentioned in a tutorial review article [18], are gathered in this contribution together with some brand new experiments. Both these unpublished series have had two connecting points: (i) an approach when all the studies were performed in parallel with bismuth counterparts and (ii) the use of a carbon paste electrode

as alternative substrate [19], offering quicker and simpler surface renewal (prior to plating) compared to the originally employed GCE [15]. Last but not least, there is also another specific feature of carbon paste — its ability of being bulk-modified with a metal powder [20] — and thus, it has also been tested whether or not carbon paste mixtures containing pulverised antimony can be operated in ASV in the same way as the recently proposed carbon pastes with finely dispersed bismuth powder [21,22].

## Experimental

### Chemicals and Reagents

All chemicals used for the preparation of stock and standard solutions were of analytical reagent grade and purchased from Sigma-Aldrich or Merck. Antimony powder used for preparation of modified carbon paste was a commercial product (Merck, cat. Nº 1-07832; with particle size < 150 μm); similarly as the bismuth powder (Sigma-Aldrich, cat. Nº 00914 HQ; 99.99+ %, 100 mesh) for a carbon paste mixture used in comparative tests. Stock solutions of either hydrochloric acid or acetate buffer were made 1 mol $l^{-1}$ in concentration; the latter being a mixture of $CH_3COOH + CH_3COONa$ (1:1). The stock solutions of $Sb^{III}$ and $Bi^{III}$, used for electrolytic deposition of the films, were spectroscopic standards with a guaranteed content of 1000 ± 1 mg $l^{-1}$ $Sb^{3+}$ or $Bi^{3+}$, respectively; both being strongly acidified to prevent hydrolysis in aqueous solutions. 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, were prepared containing 1 mg $l^{-1}$ $Pb^{2+}$ or $Cd^{2+}$; again, with stabilization of 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 Milli-Q Millipore laboratory purification system. The appropriate volumes of water and solutions used were dosed with a set of automatic adjustable pipettes.

### Apparatus and Instrumentation

A modular electrochemical system AUTOLAB equipped with PGSTAT-12 and ECD modules (Eco Chemie, Utrecht, The Netherlands) was used in combination with GPES software (from 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 | 3 M KCl reference, and Pt-plate (*ca.* 0.5 $cm^2$) auxiliary electrodes. Stirring was devised with a magnetic bar (10×2 mm) rotated at approx. 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 measured with a Voltcraft® multimeter (model VC 404, Conrad Electronics, Germany).

## Working Electrodes

*Carbon Pastes.* The bare (unmodified) mixture was prepared by thoroughly hand-mixing of 0.5 g spectroscopic graphite powder (RW-B, Ringsdorff, Germany) with 0.3 ml highly viscous silicone oil (LUKOIL MV 8000; Lučební závody Kolín, the Czech Republic). Both components were homogenised using a recommended procedure [20,23]. Afterwards, into 0.5 g portions of the bare carbon paste ("C/SO" type), the appropriate amount of either antimony or bismuth powder was added to form mixtures with 17 % (w/w) Sb or Bi, respectively. Additional homogenisation then yielded the resultant modified pastes.
*Carbon Paste Electrodes.* The bare carbon paste and both modified mixtures were packed into three piston-driven holders (designed in our laboratory [24]) with identical surface diameter, $\varnothing$ = 2 mm. Such freshly prepared carbon paste electrodes were checked with respect to ohmic resistance; the values of about 10 $\Omega$ indicating a sufficient homogeneity [20,23].
*Glassy Carbon Electrode (GCE).* This electrode (from Metrohm) as the most common substrate for deposition of metallic films [1-5] served for comparison purposes, having approx. the same surface diameter as CPEs.
*Preparation of the Electrodes for Measurements.* Both antimony- and bismuth films were deposited *in situ*; i.e., by potentiostatic electrolysis performed directly in sample solutions containing $Sb^{3+}$ or $Bi^{3+}$ ions. This was the case of the bare CPE or GCE, whereas the metal-modified pastes did not require such film-plating. If needed, the carbon paste surface was renewed mechanically by its smoothing against a wet filter paper [20,23]. Typically, this operation was done prior to starting a new set of experiments. Regarding the GCE surface, it was polished in an ordinary way on a small pad with alumina slurry.

In accordance with our previous contributions [19,21,22], the film-plated carbon paste electrodes are further denoted as SbF-CPE and BiF-CPE, whereas the two metal-modified variants can be distinguished under abbreviations of Sb-CPE or Bi-CPE, respectively.

## Electroanalytical Techniques and the Respective Procedures

*Anodic Stripping Voltammetry.* All the measurements were carried out in the anodic stripping voltammetric (ASV) mode with either linear scan (LS) or square-

wave (SW) modulation ramp. These experiments consisted of three conventional steps: (i) time- and potential controlled accumulation (deposition), (ii) the rest period, and (iii) the stripping step applied in the positive direction. The individual conditions and parameters used are specified below, usually in the legends of the corresponding figure.

## Results and Discussion

### Reoxidation of Antimony and Bismuth at the Carbon Paste Electrode Substrate after Deposition in the Regime of Anodic Stripping Voltammetry

Some preliminary assays with antimony(III) and its behaviour in ASV were already carried out with the bare carbon paste or mercury- and bismuth-film plated CPEs tested within the early era of experimenting with BiF-CPEs [25]. As found out, the detection of $Sb^{III}$ was almost irreproducible due to problems with stability in aqueous solutions and tendencies to hydrolysis, which had been observed in most supporting media tested, including diluted mineral acids. Regarding the deposition and the subsequent stripping in anodic direction, these processes in case of antimony had resulted in the formation of two or even three peaks; the highest signal at approx. –0.2 V *vs.* Ag/AgCl being a response corresponding to the oxidation $Sb^0 \rightarrow Sb^{III}$. Another response at about –0.5 V, in some cases being split into two small peaks, was of a plateau-like character and its / their origin has been attributed to the above-mentioned hydrolysis [25].

In order to minimise these hydrolytic effects, investigations on the reoxidation of antimony within this work were performed in highly acidic media and with higher contents of $Sb^{3+}$ ions. Nevertheless, even such precautions did not ensure a smooth anodic oxidation of antimony and its pathway again exhibited a series of consecutive steps. This can be seen in Fig. 1, illustrating the overall reoxidation of the deposited antimony over a wide potential range from –0.8 V up to +1.2 V (full-line curve); analogous experiment with bismuth performed under identical conditions is shown as well (dashed line). At first sight, the two voltammograms are significantly different.

Apart from dominant peaks corresponding to the processes $Sb^0 \rightarrow Sb^{III}$ and $Bi^0 \rightarrow Bi^{III}$, the oxidation of antimony has revealed other two signals which do not have equivalents in similar experiments with bismuth deposition and stripping. The second additional peak (in Fig.1, denoted as "Sb-3"), can be attributed to the process $Sb^{III} \rightarrow Sb^{V}$ because, in highly acidic solutions, such oxidation is normally attainable [13,14]. In contrast to that, the absence of the corresponding peak for bismuth indicates that there is no comparable oxidation $Bi^{III} \rightarrow Bi^{V}$, which is in accordance with literature admitting that the formation of pentavalent bismuth re-

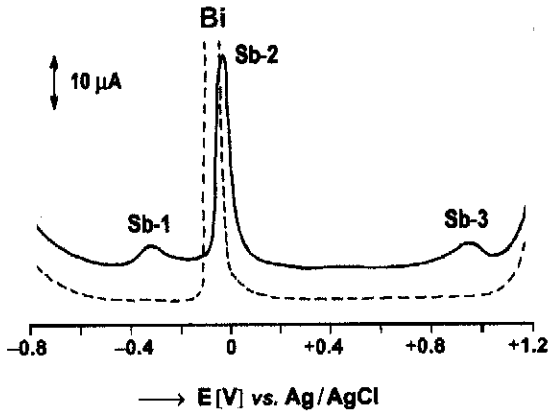


Fig. 1 Reoxidation of antimony ( —— ) and bismuth ( – – – ) at the CPE substrate. Experimental conditions: linear scan anodic stripping voltammetry (LSASV); silicone-oil based carbon paste, C/SO; supporting electrolyte: 0.5 M HCl (pH ~ 0); $c$(Sb,Bi) = 5 mg $l^{-1}$; accumulation (deposition) time, $t_{ACC}$ = 30 s; the rest period (equilibrium time), $t_R$ = 10 s; accumulation potential, $E_{ACC}$ = –0.8 V vs. Ag/AgCl; potential scan, $E_R$ = –1.6 V → +1.2 V; scan rate, $v$ = 50 mV $s^{-1}$. *Note*: A value specifying the arrow size is the peak current, $I_P$, and its actual intensity.

quires extreme conditions whose realisation in common measurements is almost impossible [13]. In contrast to quite probable explanation on the rise of the third peak during anodic oxidation of antimony, the origin of the smallest signal, "Sb-1" (noticed also in some earlier studies [26]), is still rather unclear. There are two different hypotheses which can be assumed. First, this response could correspond to a reoxidation of $Sb^0$ *via* the $SbO^+$ species formed by hydrolysis in aqueous solutions and being present — at a certain concentration — even in highly acidic media. If so, the antimonyl, $SbO^+$, is an ion whose reduction in ASV and subsequent oxidation might proceed at slightly different potentials compared to those in a transformation scheme with the single ions: $Sb^{3+} \rightarrow Sb^0 \rightarrow Sb^{3+}$. Alternative interpretation follows the recent achievements in inorganic synthesis of new organometallic compounds where some complex structures with the homocyclic "metal-metal" bonds contain antimony atoms in atypical valencies — as $Sb^{I}$ or $Sb^{II}$, respectively [27]. And because the electrode processes may occasionally give rise to similar unusual intermediates [1,20], the occurrence of such low-valent antimony adducts cannot be completely omitted. Nevertheless, both hypotheses based on analogy with previous results need to be verified yet; maybe, in new special studies.

Regardless of exact explanation, it is worth mentioning that the signal for antimony, appearing at a potential from –0.5 to –0.4 vs. Ag/AgCl, was found to be analytically useful when using bismuth electrodes instead of inert carbonaceous

electrodes like CPE or GCE. If one takes into account very similar electrochemical properties of both antimony and bismuth, quite curious combination of "determination of antimony at a bismuth electrode" has attracted our attention and some preliminary measurements on possible analytical applications are also discussed at the end of the Results and Discussion section.

When going back to the main goal of this work, i.e. the investigations on basic behaviour of antimony in ASV, it can be stated that initial studies have resulted in a key conclusion — the deposition of this metal in acidic media has been found comparably effective as that for bismuth, as revealed by similar peak characteristics of both main stripping signals.

## Basic Characterisation of Antimony Film Carbon Paste Electrode (SbF-CPE) and Optimal Conditions for Its Operability in Anodic Stripping Voltammetry

*Supporting Electrolyte Composition and Effect of pH.* The next step was to ascertain if the antimony-plated carbon paste is capable of acting as a film electrode; in other words, whether its properties and interactions with other species correspond to those typical of bismuth- and mercury film electrodes. Initial tests were performed in 0.5 M HCl with $Pb^{2+}$ + $Cd^{2+}$ ions as a model pair of typical heavy metals with well-known behaviour in ASV [28]. However, experiments in highly acidic solution had led to very poor results as depicted in Fig. 2 (see curve a, full-line curve), being notably worse than the parallel measurement with the BiF-CPE (dashed line). Thus, it was necessary to lower the content of HCl in the electrolyte to ensure a better function of the antimony film as documented in the figure by voltammogram (b).

The following optimisation of the overall acidity in the supporting medium resulted in a concentration between 0.01-0.05 M HCl (with pH ~ 2); the lower limit being chosen due to the most favourable relation between the resultant shape of stripping peaks for both Pb and Cd and satisfactorily low residual currents in the potential range studied (curves b-d). Figure 2 does not include the curves obtained in more diluted solutions of 0.001-0.005 M HCl where the corresponding signals were less-developed; evidently, due to starting hydrolysis.

In order to complete the studies focused on definition of acidic pH-interval and its limiting values, within which the $Sb^{III}$ species are stable (and the respective antimony films can then be operated in ASV [5,25]), the performance of SbF-CPE was also examined in mild acidic solutions of acetate buffers, representing the most suitable supporting media for measurements with BiFEs and other bismuth-based electrodes [3-5]. By using a series of buffers, varying in concentrations from 0.50 down to 0.01 mol $l^{-1}$ (pH 3.5-5.0), it was found that the antimony film electrode was inapplicable in all the media tested. This finding as a major diffe-

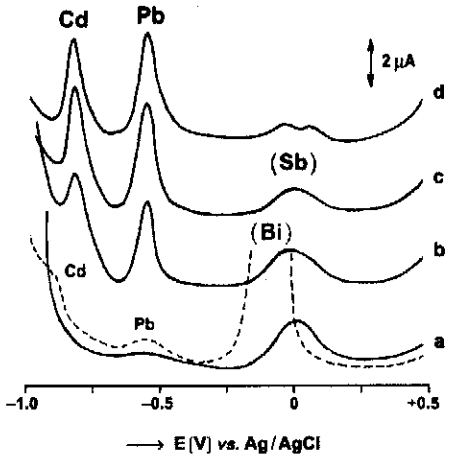


Fig. 2 Performance of the SbF-CPE in the supporting electrolyte based on solutions of HCl and its optimisation with respect to the overall acidity. Legend: —— ... SbF-CPE, a) 0.5 M HCl (pH ~ 0), b) 0.1 M HCl (pH 0.85), c) 0.05 M HCl (pH 1.30), d) 0.01 M HCl (pH 1.95); – – – ... BiF-CPE, 0.5 M HCl. Experimental conditions: square-wave anodic stripping voltammetry, SWASV, C/SO; $c$(Sb,Bi) = 1 mg $l^{-1}$; $c$(Pb,Cd) = 100 μg $l^{-1}$; $t_{ACC}$ = 60 s; $t_R$ = 15s; $E_{ACC}$ = –1.0 V; $E_R$ = –1.0 V → +0.5 V; square-wave frequency, $f_{SW}$ = 25 Hz, amplitude, $\Delta E_{SW}$ = 50 mV, potential increment (step), $i_{SW}$ = 4 mV

rence with respect to behaviour of bismuth electrodes used under identical conditions can be explained by lower stability of the $Sb^{III}$ compared to $Bi^{III}$ species in aqueous solutions, causing hydrolytic transformations of the former at pH > 3-4.

The behaviour of the $Sb^{3+}$ ions at a given pH and typical function of the SbF-CPE in ASV were also of interest in a special assay illustrated in Fig. 3. First, the ASV experiment was performed in a model solution of acetate buffer (pH 4.5) with a spike of 100 ppb $Pb^{2+}$ + $Cd^{2+}$ (for each ion). The ensuing voltammogram only exhibited the large signal for dissolution of antimony (with $E_P$ = –0.15 V; see curve a). Then, the same solution was acidified with a few droplets of 1 M HCl up to pH 2 and the entire test was repeated, giving rise to a markedly different record with two well-developed stripping peaks for Pb and Cd (b). Finally, the solution was re-buffered back to pH 4.5 and analysed in the third sequel of this test, yielding a voltammogram (c) where both stripping peaks of model ions had disappeared, thus resembling the results of the starting experiment (a).

Such changes in the performance of the SbF-CPE have confirmed its principal dependence upon the pH chosen, which is a phenomenon unnoticed with BiF-CPE [19] or other bismuth-based electrodes [2-5,19]. Also, this behaviour probably explains a worse experience with antimony-based electrodes during their very first testing in ASV (performed by Kalcher *et al.* [11,12]), when experiments had been based on unsuitable acetate buffers,

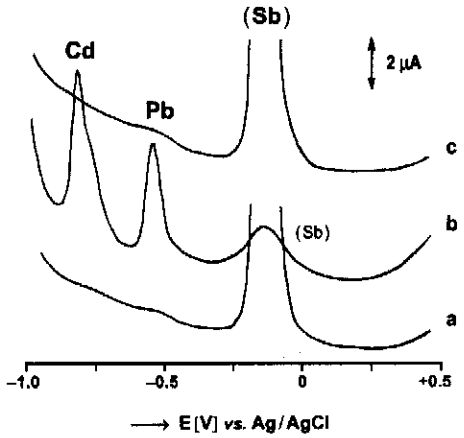


Fig. 3 Operability of the SbF-CPE in anodic stripping voltammetry depending on pH. Legend: a) 0.1 M $CH_3COOH$ + $CH_3COONa$ (1:1) (pH 4.5), b) acidified with HCl (to pH 2.0), c) buffered with 1 M $CH_3COONa$ (to pH 4.5). Experimental conditions: SWASV, C/SO, $c$(Sb) = 1 mg $l^{-1}$; $c$(Pb,Cd) = 100 μg $l^{-1}$. For other parameters, see legend in Fig. 2

adopted from the previous procedures recommended for measurements with BiF-CPEs.

A series of experiments in Fig. 3 as well as the previous set of voltammograms in Fig. 2 illustrate another specific response of the antimony film; i.e., a very small signal for the reoxidation $Sb^0 \rightarrow Sb^{III}$ at low pH values in HCl-based media. Moreover, this response slightly decreases in more diluted solutions (see Fig. 2 a-c), having tendencies to split into two partially overlapped peaks (Fig. 2 d).

Although the origin of this unique feature — again, unknown for bismuth-based electrodes [4,5,19] — is not yet fully explained, from an electroanalytical point of view, such a small peak is beneficial for the base-line in the proximity of the anodic potential limit, which can be advantageous in measurements of signals with very small intensities reaching down to the level of the residual currents [29].

Regarding a direct comparison of antimony- and bismuth plated carbon paste substrates with respect to their performance in a solution of 0.01 M HCl, — i.e., under acidity conditions optimised for the former, the corresponding experiments are depicted in Fig. 4.

As seen, the SbF-CPE responds more sensitively to both lead and cadmium and another distinct difference between both voltammograms is their base-line when the already discussed specific dissolution of antimony and its much less developed signal affects only negligibly the overall signal-to-noise characteristics of the respective film electrode.

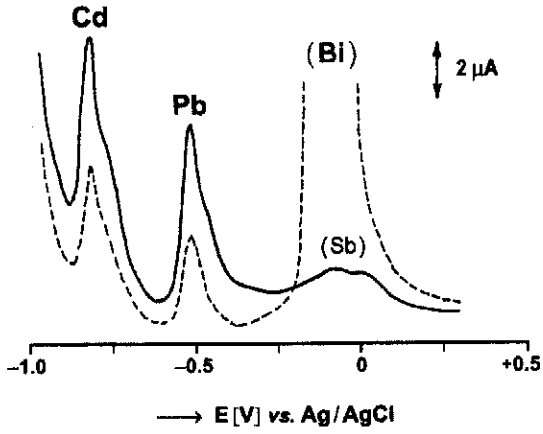


Fig. 4 The ASV performance of SbF-CPE and BiF-CPE in 0.01 M HCl. Legend: ——... SbF-CPE, – – – ... BiF-CPE. Experimental conditions: SWASV, C/SO, $c$(Sb,Bi) = 1 mg $l^{-1}$; $c$(Pb,Cd) = 100 μg $l^{-1}$; $E_R$ = –1.0 V → +0.3 V. For other parameters, see legend in Fig. 2

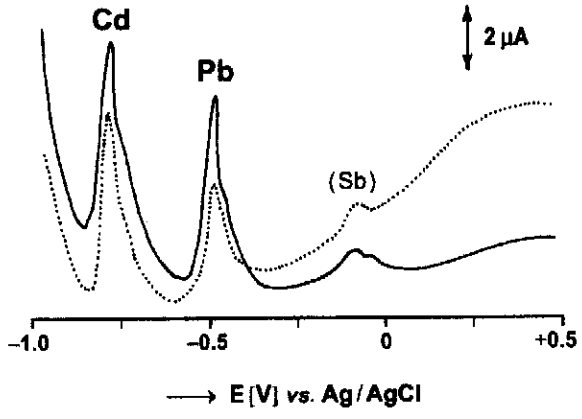


Fig. 5 The performance of SbF-CPE and SbF-GCE in 0.01 M HCl. Legend: ——... SbF-CPE, ..... ... SbF-GCE. Experimental conditions: SWASV, $c$(Sb,Bi) = 1 mg $l^{-1}$; $c$(Pb,Cd) = 100 μg $l^{-1}$. For other parameters, see legend in Fig. 2

*Antimony Films and Effect of Substrate.* Already within initial studies on antimony film electrodes performed with the GCE substrate, some tests were made with carbon paste. Although the respective experiments had not been included in the final version of our introductory report [15], the results with SbF-CPE were promising and the proper functioning of this configuration has been confirmed in all newly performed measurements. In some assays with more diluted solutions of HCl, the SWASV performance of the SbF-CPE (full line) was even better than that of SbF-GCE (dotted line). One of such comparisons is shown in Fig. 5.

## Antimony Powder-Modified Carbon Paste Electrode (Sb-CPE) and Its Specifics

According to a surprisingly good experience with electroanalytical performance of bismuth powder-dispersed carbon paste electrode (Bi-CPE) [21,22], its antimony analogue has also been tested and one of the first experiments — taken from our newest investigations [30] — is shown in Fig. 6, illustrating a very good function of both metallised carbon paste substrates.

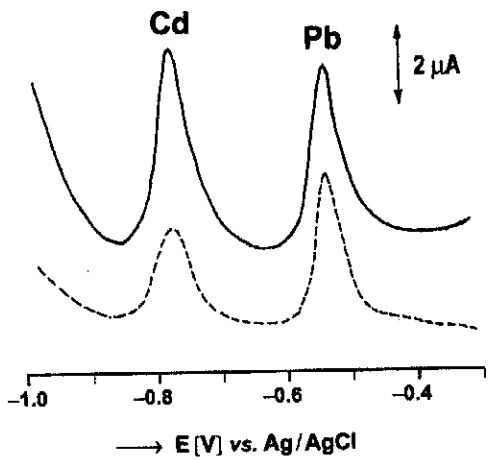


Fig. 6 The performance of Sb-CPE ( —— ) in SWASV of $Pb^{2+}$ and $Cd^{2+}$ ions and its comparison with related Bi-CPE ( – – – ). Experimental conditions: carbon pastes modified with 17% (w/w) antimony- and bismuth powder, both C/SO types; 0.01 M HCl, $c$(Pb,Cd) = 50 μg $l^{-1}$; $t_{ACC}$ = 120 s; $E_R$ = −1.0 V → −0.3 V. For other parameters, see legend in Fig. 2

As can be seen, the SWASV performance of the Sb-CPE is yet superior to its bismuth equivalent, especially for the detection of cadmium. This finding is particularly valuable, considering the fact that the stripping characteristics for this metal have already been found to be extraordinary with bismuth-based electrodes [4,5,21]. Thus, in order to determine electrochemically similar $Pb^{2+}$ and $Cd^{2+}$ ions in a mixture or, eventually, the $Cd^{2+}$ alone, the choice of the Sb-CPE would lead to a further enhancement in sensitivity towards the latter, which may be crucial for analysis of real water samples where cadmium is usually present at a substantially lower concentration compared to the natural content of lead [28].

As already stated above, the studies devoted to the basic electrochemical behaviour of antimony and bismuth at CPEs have revealed a very interesting possibility to determine antimony at a bismuth electrode. As found, such a determination can be accomplished *via* a specific signal which appears during reoxidation of antimony at a potential of about –0.4 V vs. AgCl and which is particularly developed when using a bismuth film electrode. Despite the fact that origin for this signal is hitherto uncertain, the peak is well reproducible and proportional to the concentration of $Sb^{III}$ down to the nanomolar level.

In preliminary investigations, the experimental conditions used have included (i) *in-situ* prepared and operated BiF-CPE, (ii) 0.5 M HCl as supporting electrolyte, and (iii) deposition at –0.8 V vs. Ag/AgCl for 60 s with the scanning from –0.8 V to –0.2 V as the main experimental parameters of the corresponding ASV procedure. All the tests were carried out in the SWASV mode and the peak of interest could be calibrated in the concentration range of 10-100 ppb $Sb^{III}$ with a reproducibility of ca. ± 5 %. Typical set of such calibration voltammograms is shown in Fig. 7.

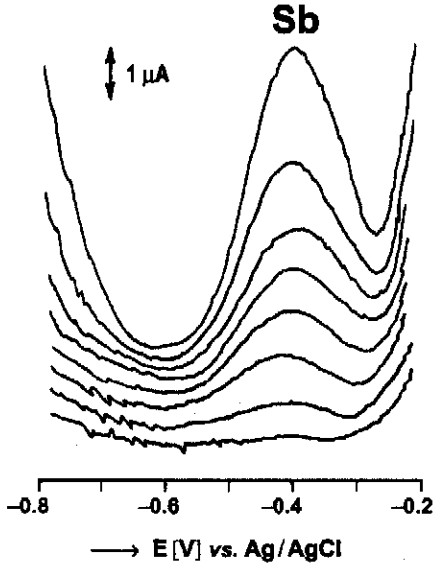


Fig. 7 Calibration voltammograms for the determination of Sb(III) at BiF-CPE (*in situ*). Legend: a) base-line (0.5 M HCl + 1 ppm $Bi^{3+}$), b-h) 10, 20, 30, 40, 50, 75, and 100 µg $l^{-1}$ $Sb^{3+}$. Experimental conditions: SWASV, C/SO; $t_{ACC}$ = 60 s; $E_{ACC}$ = –0.8 V; $E_R$ = –0.8 V → –0.2 V. For other parameters, see legend in Fig. 2

At present, the activities of our team are focused on this topic again [30] in an effort to carry out some optimisation measurements and complete the method development with interference and validation studies. It is believed that, within the palette of methods that have already been proposed for bismuth-based electrodes [3-5], a new procedure for the determination of $Sb^{III}$ would belong to other attractive contributions published in the last years.

## Conclusion

In this article, two types of antimony-modified carbon paste electrodes are presented as new alternatives to momentarily very popular bismuth-based electrodes. Similarly to the recently introduced antimony film-plated glassy carbon electrode (SbF-GCE [15]), its carbon paste analogue, SbF-CPE, offers some specific features and a promising performance in ASV. Nearly the same can be stated about the metallised carbon paste, Sb-CPE, with emphasising that this variant can be operated without antimony film and hence with desired simplification of the respective measuring procedure(s). Regarding both SbF-CPE and Sb-CPE with respect to their mutual comparison with the SbF-GCE, the former is more flexible thanks to the use of carbon paste-based substrates which can easily be regenerated and their properties controlled *via* the actual carbon paste composition [20,23].

In confrontation with all the existing types of bismuth electrodes and their applicability to the determination of common heavy metals, antimony-based counterparts were shown to be superior in more acidic solutions, which can be exploited in analysis of various water samples. These are usually stabilised during / after collection [28] by adding a mineral acid ($HNO_3$ or HCl) to adjust the total acidity to pH 2; it means at a value, which has been found optimal for measurements with antimony-modified electrodes. Their electroanalytical performance, including a possible applicability to water samples, is now being examined in more detail [30]. New studies with SbF-GCE, SbF-CPE, and Sb-CPE, involving specification of typical analytical parameters such as calibration data, limits of detection, reproducibility, interference effects or recovery rates, are in progress and after having evaluated all the relevant results, the respective report(s) will be given.

**Acknowledgements**

*Financial grants from the Ministry of Education, Youth, and Sports of the Czech Republic (projects Nº MSM0021627502 and LC06035) and from the Czech Science Foundation (Nº 203/05/2106) are gratefully acknowledged. Furthermore, all the authors have also co-operated thanks to a bilateral scientific project (BI-CZ/07-08-008) and a support from the Slovenian Research Agency (projects P1-0034 and Z1-6370).*

**References**

[1] Wang, J.: *Analytical Electrochemistry*, 3rd Ed.; Wiley-VCH, (NJ, USA), 2006.
[2] Schwabe K.: Pharmazie **3**, 449 (1948).
[3] Wang J., Lu J.-M., Hočevar S. B., Farias P. A. M., Ogorevc B.: Anal. Chem.**72**, 3218 (2000).
[4] Economou A.: TrAC–Trends Anal. Chem. **24**, 334 (2005).
[5] Švancara I., Vytřas K.: Chem. Listy **100**, 90 (2006).
[6] Skogvold S. M., Mikkelsen Ø., Schrøder K. H.: Electroanalysis **17**, 1938 (2005).
[7] Legeai S., Bois S., Vittori O.: J. Electroanal. Chem. **591**, 93 (2006).
[8] Korolczuk M., Tyszczuk K., Grabarczyk M.: Electrochem. Commun. **7**, (2005) 1185.
[9] Korolczuk M., Tyszczuk K.: Anal. Chim. Acta. **580**, 231 (2005).
[10] Tyszczuk K., Korolczuk M., Grabarczyk M.: Talanta **71**, 2098 (2005).
[11] Pauliukaitė R., Kalcher K., in: *YISAC '01, Young Investigators' Seminar on Analytical Chemistry*, Book of Abstracts, pp. 10-11. University of Pardubice, Pardubice, 2001.
[12] Pauliukaitė R., Metelka R., Švancara I., Królicka A., Bobrowski A., Norkus E., Kalcher, K., Vytřas K.: Sci. Pap. Univ. Pardubice, Ser. A **10**, 47 (2004).
[13] Svehla Gy: *Vogel's Qualitative Inorganic Analysis*, 7th Ed; pp. 79-83 and 99-104. Longman, Singapore, 1996.
[14] Vydra F., K. Štulík K., Juláková E.: *Rozpouštěcí polarografie a voltametrie*, pp. 194-198, SNTL, Prague, 1977.
[15] Hočevar S. B., Švancara I., Ogorevc B., Vytřas K.: Anal. Chem. **79**, 8639 (2007).

[16] Uhl A., Kestranek W.: Monatsh. **44**, 22 (1923).
[17] Čihalík J.: *Potenciometrie*, pp. 178-181 and 218. NČSAV, Prague, 1961.
[18] Švancara I., in: *Možnosti inovací v elektroanalytické chemii* (Barek J. *et al.*, eds.), pp. 59-68. VŠCHT Praha, 2006.
[19] Królicka A., Pauliukaitė R., Švancara I., Metelka R., Norkus E., Bobrowski A., Kalcher K., Vytřas K.: Electrochem. Commun. **4**, 193 (2002).
[20] Kalcher K., Švancara I., Metelka R., Vytřas K., Walcarius A., in: *Encyclopedia of Sensors*, Vol. 4 (Grimes C.A., Dickey E.C., Pishko M.V., eds.), pp. 283-430. American Scientific Publishers, Stevenson Ranch (CA, USA), 2006.
[21] Hočevar S. B., Švancara I., Ogorevc B., Vytřas: Electrochim. Acta **51**, 706 (2005).
[22] Švancara I., Baldrianová L., Tesařová E., Hočevar S. B., Elsuccary S. A. A., Economou A., Sotiropoulos S., Ogorevc B., Vytřas K.: Electroanalysis **18**, 59 (2006).
[23] Švancara I., Schachl K.: Chem. Listy **93**, 490 (1999).
[24] Švancara I., Metelka R., Vytřas K., in: *Sensing in Electroanalysis* (Vytřas K., Kalcher K., eds.), pp. 7-18. University of Pardubice, Pardubice, 2005.
[25] Švancara I., Fairouz M., Ismail Kh., Metelka R., Vytřas K.: Sci. Pap. Univ. Pardubice, Ser. A **9**, 5 (2003).
[26] Metikoš Huković M., Babić R., Brinić S. J.: Power Sources **157**, 563 (2006).
[27] Balasz L., Breunig H. J.: Coordination Chem. Rev. **248**, 603 (2004).
[28] Florence T. M., in: *Trace Element Speciation: Analytical Methods and Problems*, (Batley G. E., ed.), pp. 77-116. CRC Press, Boca Raton (FL, USA), 1989.
[29] Švancara I., Kalcher K., Diewald W., Vytřas K.: Electroanalysis **8**, 336 (1996).
[30] Tesařová E., Baldrianová L., Hočevar S. B., Švancara I., Vytřas K., Ogorevc B.: Anal. Chim. Acta. – submitted.