APPLICABILITY OF ANTIMONY FILM ELECTRODES IN ANODIC STRIPPING VOLTAMMETRY COMBINED WITH SEQUENTIAL INJECTION ANALYSIS

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The possibilities to employ antimony-film plated glassy carbon electrode (SbF-GCE) in anodic stripping voltammetry combined with sequential injection analysis (ASV-SIA) were examined and tested for the determination of Pb(II) and Cd(II) selected as the model ions. It has been found that SbF-GCE can be operated at the low $\mu g\ l^{-1}$ concentration level via the in-situ preparation — deposition from a plating solution of 0.5 M HCl, mixed with 0.75 mg l^{-1} Sb(III), and at a potential of –1.5 V vs. Ag/AgCl. The same solution could then be used for pre-concentration and stripping, when the reproducibility of the respective signals was characterised

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by means of the RSD < 2.8 %, and the detection limit (3σ) of about 1.2 µg l⁻¹
Pb(II) and 1.4 µg l⁻¹ Cd(II). Furthermore, as found, the presence of weakly
complexing halide salts, KCl or KBr, could further improve the overall signal-to-
noise ratio, whereas the addition of KSCN into the solution(s) offered the
possibility to detect some additional ions; namely, of highly electronegative metal
elements such as Zn(II), Mn(II), and Cr(III).

Introduction

In modern instrumental measurements, electrochemical stripping analysis (ESA) with pre-concentration step is still widely used for the determination of heavy metal ions at the trace or even ultratrace level [1]. Besides a number of well known advantages, the individual techniques of ESA can also be eventually coupled with flow injection analysis (FIA) or sequential injection analysis (SIA), thus offering further improvement of selectivity and, mainly, the automation of the whole analytical procedure [2-4]. Although the latter is also possible in the common stationary mode [5], both ESA-FIA and ESA-SIA combinations are preferable due to better availability of the respective instrumentation, as well as more effective electroanalytical performance [1,2].

According to the newest trends such as the "green chemistry concept" [6], the choice of the respective detection units for measurements in flowing streams usually comprises various types of non-mercury electrodes from which especially bismuth-based electrodes (BiEs [7-9]) have undergone a remarkable progress during the last decade [10], including successful applications in both FIA (see, e.g., Refs [11,12]) and SIA [13,14].

Another attractive group of non-mercury electrodes propagated recently is represented by antimony electrodes (SbEs), comprising (i) antimony film-plated carbonaceous substrate electrodes (SbFEs [15,16]), (ii) antimony(III) oxide, (iii) antimony(III) precipitate, or (iv) antimony powder bulk-modified carbon paste electrodes (i.e., Sb_2O_3-CPEs [17], SbOL-CPEs [18], and Sb-CPEs [19]), together with related configurations prepared via screen-printing technologies (e.g., Sb_2O_3-SPEs [20]). To date, the characterisation and selected applications of antimony-based electrodes were the subject of interest in a dozen of contributions [15-17,19-29]; none of which has dealt so far with their employment in flowing streams.

The first attempts for such a combination have been made by our group recently [30-32]; firstly, by employing a bismuth film-plated electrode [30], followed by experiments with the antimony analogue [31] in a motivation to unify important experimental parameters for using both BiEs and SbEs under the same conditions [32]. Since the previous reports have emphasised some principal differences in the behaviour of these electrodes (see, e.g., Refs [15] and [19]), such universal procedure would be a new finding, which is the key topic of the latter

article. Herein, the attention is paid again to the antimony film electrode configuration and its continuing examination for the determination of typical heavy metal ions by anodic stripping voltammetry in combination with sequential injection analysis (ASV-SIA). Furthermore, this article also presents the results of a special study focused on the supporting electrolyte composition and the effect of selected salts (namely: KNO_3, K_2SO_4, KCl, KBr, and KSCN) on the pre-concentration and stripping processes and the resultant signal-to-noise ratio.

Experimental

Chemicals and Reagents

All chemicals used were of analytical reagent grade and purchased from Sigma-Aldrich or Merck if not stated otherwise. Stock solutions of HCl and acetate buffer (CH_3COOH + CH_3COONa, 1:1; AcB) were made 1.0 mol l^{-1} in concentration. Stock solutions of Sb(III) used for film deposition were spectroscopic standards with a guaranteed content of 1.0000 ± 0.0001 g l^{-1} Sb(III), acidified to prevent hydrolysis in aqueous solutions. Stock standard solutions of 1.0 mg l^{-1} Zn(II), Pb(II), and Cd(II) were also acidified with HCl (to pH 2.0). The salts KCl, KBr, K_2SO_4, KNO_3 and KSCN purchased from Merck or Wako were made as 0.1 M stock solutions. Throughout the experimental work, all the solutions were prepared in doubly deionised water, obtained from a Milli-Q Millipore water purification system.

Apparatus

The device for SIA consisted of a syringe pump (Carvo, Sci Inst., USA), an 8-port selection valve (Carvo), PTFE tubing (0.5 mm, i.d.) for flow lines and a holding coil (1.5 mm i.d.). The sequential injection system was controlled via PC and the respective software. An electrochemical analyzer (model 12000; CH Instruments, USA) was employed for all the measurements, when voltammetric experiments were carried out in the square-wave mode (SWV; for details, see below) when using a thin-layer flow cell (Bioanalytical System, USA) incorporating the glassy carbon electrode (GCE; the electrode substrate of choice for plating with antimony film), an Ag/AgCl/3M KCl as the reference, and a stainless-steel tube as the counter electrode, as well as the solution outlet. The proper running of the ASV-FIA assembly is schematised in Fig. 1 and further specified below — under Procedures

In comparative stationary (batch) measurements, and external electrode stand with a three-electrode cell (GCE, Ag/AgCl, and a Pt-wire as the auxiliary

electrode) was used, when the stirring was accomplished with a magnetic bar rotated at approx. 300 rpm. The pH was measured using a portable pH-meter in conjunction with a combined glass electrode (both Horiba, Japan), when its calibration was performed with a set of commercial buffers.
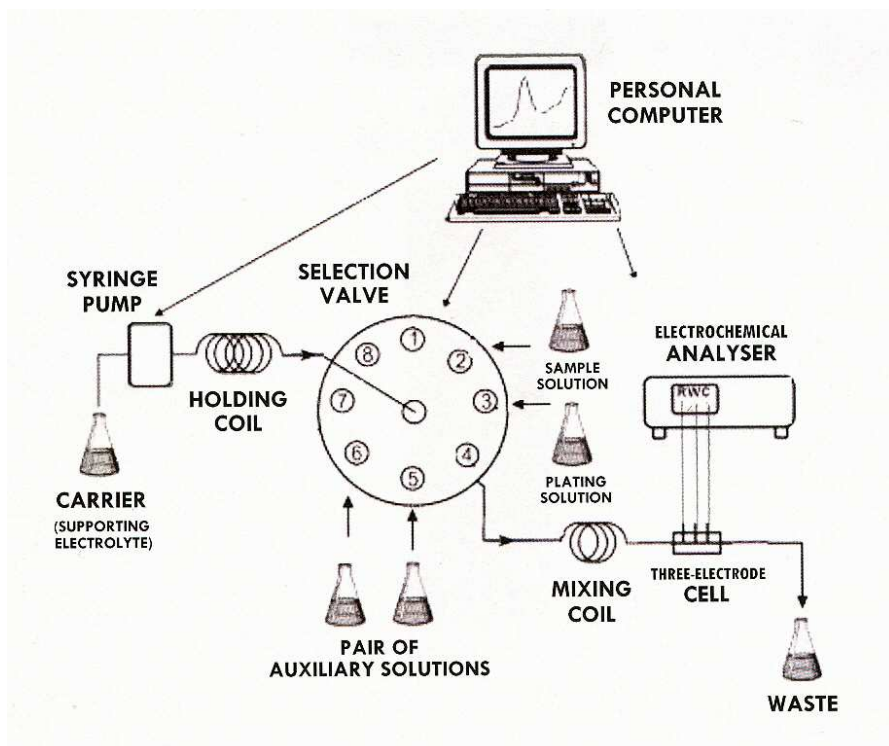

Fig. 1 The assembly for (SW)ASV-SIA measurements. A schematic view

Procedures

Preparation of the SbFE. For batch measurements and experiments in the ASV-SIA regime, the antimony film was deposited *in situ*; i.e., by potentiostatic electrolysis performed directly in sample solutions containing Sb(III) species. For the batch system, the plating was performed in a solution of 0.01 M HCl + 2.0 mg l^{-1} Sb(III) (pH 2.0) and at a potential of -1.40 V vs. ref. for 120 s [15], whereas, in the ASV-SIA procedure, the GCE was being plated in a solution of 0.5 M HCl + 0.75 μg l^{-1} Sb(III) at -1.50 V, at a flow rate of 0.5 ml s^{-1} [31,32]. In both cases, the film was removed electrochemically, at a potential of $+0.20$ V.

Cyclic Voltammetry (CV). The respective measurements were performed at a scan rate of 100 mV s^{-1}, when starting from the initial potential of $+0.50$ V vs. ref., going via the selected vertex potential(s) and, returning in the reversed direction to the starting point.

Square-Wave Anodic Stripping Voltammetry in the Stationary Arrangement (SWASV). The batch experiments comprised a potentiostatic pre-concentration ("accumulation step") at – 1.40 V vs. ref., followed by a 15s equilibration period and the proper anodic scanning ("stripping step") from – 1.40 V up to +0.20 V vs. ref.

The SWV modulation ramp comprised the following parameters: frequency, f_{SW} = 50 kHz; scan rate, v_{SW} = 30 mV s^{-1}, potential increment, i_{SW} = 6 mV; amplitude, ΔE_{SW} = 50 mV. Prior to each measurement, the electrode surface of the bare ("stripped") electrode substrate was conditioned / regenerated by applying a potential of +0.20 V vs. ref. for a period of 30 s.

Square-Wave Anodic Stripping Voltammetry Combined with Sequential Injection Analysis (SWASV-SIA). The individual sequences can be described by means of a schematic manual that has comprised a string of the consecutive steps (i = 1-7) with the corresponding experimental/instrumental parameters. Specifically: Step (1) ... Aspirate (i.e., start to suck) the sample solution into the holding coil (HC) and set the following parameters: the valve position (V), 2; pump status (P): "aspirate"; flow rate (v_i); 1200 ml s^{-1}; electrode potential (E_i) vs. ref., –1.5 V vs. ref.; time period/duration (t_i), 30 s. (2) Aspirate the solution of Sb(III) into HC, when setting: V = 3, P: "aspirate", v_i = 1200 ml s^{-1}, E_i = +0.20 V, t_i = 10 s. (3) Dispense the solution of Sb(III) + sample solution into flow cell and perform the deposition step (accumulation), when having set: V = 4, P: "deliver", v_i = 500 ml s^{-1}, E_i = –1.5 V, t_i = 100 s. (4) Perform the equilibration step, when setting: V = 4, P: "deliver", v_i = 0, E_i = –1.5 V, t_i = 15 s. (5) Perform the stripping step and record voltammogram, when having set: V = 4, P: "deliver", v_i = 0, E_i = from –1.5 to +0.10 V (anodic scanning), t_i = 15 s. (6) Aspirate the solution of 0.5 M HCl into HC, when setting: V = 5, P: "aspirate", v_i = 1200 ml s^{-1}, E_i = +0.20 V, t_i = 30 s. (7) Dispense the solution of 0.5 M HCl into flow cell and clean the electrode cell, when having set: V = 4, P: "deliver", v_i = 1200 ml s^{-1}, E_i = +0.20 V, t_i = 30 s.

Regarding the square-wave modulation, the parameters of choice were the same as those applied in the stationary SWASV measurements being specified in the previous section. Finally, when running SVASV-SIA, the electrode cleaning had already been included at the end of the measuring cycle and without any regeneration.

Results and Discussion

The composition of the sample solutions, as one of the key parameters for the resultant quality of antimony films formed, was investigated first. It is known (see, e.g., Refs [7-9]) that the preferably used solution for the preparation of related similar BiFEs is being based on acetate buffer with pH ca. 4.5, but strongly acidic

solutions of 1 M HCl are occasionally applicable as well [14]. In order to understand the electrochemical behaviour of the SbFE, it is wise to check the deposition/dissolution scheme of the antimony film at the supporting electrode surface in both media [33,34]. Figure 2 shows the cyclic voltammograms recorded for the plating solutions of Sb(III) (3 mg l^{-1}) in HCl (pH ≈ 0) (set "A") and AcB (pH 4.5) ("B"). As indicated by the dissolution peak of antimony, the respective film starts to grow at the potentials more negative than −0.40 V, reaching the maximum at −0.60 V (A) and −0.80 V (B).
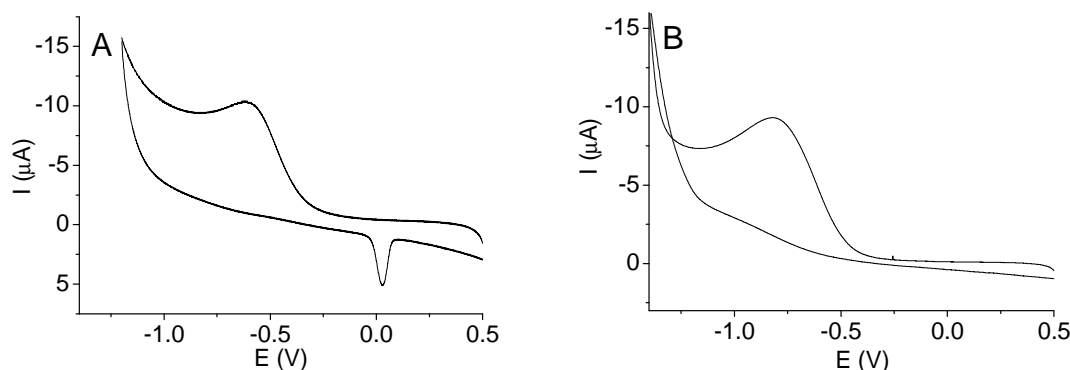

Fig. 2   Cyclic voltamograms of 3000 μg l^{-1} Sb(III) in 0.1 M HCl (pH 2.0, set "A") and acetate buffer (pH 4.5; set "B"). Experimental conditions: scan rate, 100 mV s^{-1}; initial potential, +0.50 V; vertex potentials, −1.2 V and −1.4 V; final potential, +0.50 V vs. ref.

After reversing the potential scan direction, the total oxidation of antimony (i.e., its dissolution or "stripping", resp.) can be observed at +0.03 V in the case of HCl solution. In contrast to this, the reduction peak in AcB has no oxidation counterpart; i.e., there is no expected dissolution/stripping scheme. This phenomenon can be explained by assuming that in the acetate media (due to a relatively high pH), antimony(III) oxide, Sb_2O_3, can be formed, which is probably the main reason for the unfavourable behaviour of the electrode in this medium, observed previously for the ASV determinations [20].

In the SWASV-SIA measurements, the shape and intensity of the oxidation peaks of Cd, Pb and Sb have been found to be significantly influenced by the concentration of HCl: in the concentration range of 0.01-0.1 M HCl (see Fig. 3 A) the oxidation peaks of Pb and Cd are small or missing completely, which can be attributed to the insufficient amount of metallic antimony at the GCE surface. The increase in the HCl concentration from 0.3 to 0.6 mol l^{-1} (Fig. 3 B) resulted in an increase in the intensity of the oxidation/stripping signals for Pb(II) and Cd(II). This can then be explained in terms of increased solution conductivity and decreased degree of hydrolysis, yielding an Sb(III) compound that is more easily discharged, having a favourable effect on the accumulation and stripping processes of both Pb(II) and Cd(II). It should be noted that more negative reduction

potentials could also cause a decrease in the oxidation peak because of more pronounced effect of the hydrogen evolution.
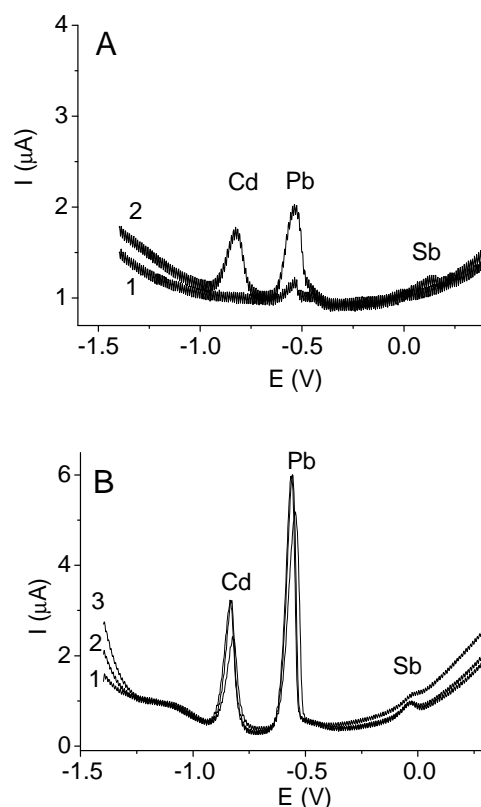

Fig. 3 Effect of the solution acidity upon the SWASV-SIA signals for 50 $\mu g\,l^{-1}$ Pb(II)and Cd(II) at upon (mol l^{-1}). A: 1) 0.01 and 2) 0.1 M HCl and B: 1) 0.4, 2) 0.5, and 3) 0.6 M HCl. Experimental conditions: 750 $\mu g\,l^{-1}$ Sb(III); deposition potential, −1.50 V vs. ref.; deposition time, 100 s; equlibrium time, 15 s; scan rate, 30 mV. For other parameters, see Experimental

In view of the observation that the oxidation signals of both metals were particularly well defined in 0.5 M HCl (Fig. 3 B, curve 2), as well as due to the fact that this positive effect of HCl in flowing streams was also noticed recently by other authors [15,21], the half-molar concentration of HCl was finally chosen as the optimum for the determinations in the ASV-SIA regime. It enabled to detect both Cd(II) and Pb(II), selected as model ions of the two typical heavy metals, at the low $\mu g\,l^{-1}$ level as proved in a detailed study on the electroanalytical performance of the SbFE. It is illustrated in Fig. 4, showing the linear stripping responses of the two metals of interest in a concentration range of 5-120 Cd(II) and of 4-100 $\mu g\,l^{-1}$ Pb(II), with the resultant $r^2 = 0.997$ and 0.999. The respective LOD values (estimated via the 3σ criterion) were 1.4 $\mu g\,l^{-1}$ Cd(II) and 1.2 $\mu g\,l^{-1}$ Pb(II), with the corresponding relative standard deviations (RSDs) of ±2.8 % and ±2.6 % for six repetitive measurements ($n = 6$) and the concentrations chosen of 50 $\mu g\,l^{-1}$ Cd(II) and Pb(II). Yet lower LODs may perhaps be expected when using appropriately prolonged deposition times as there were no evident saturation ten-
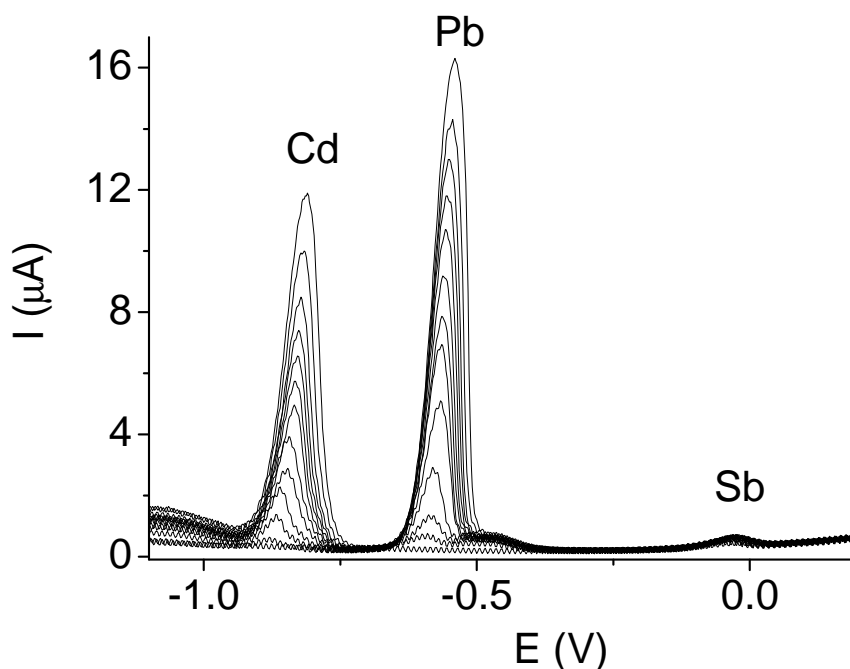
Fig. 4 SWASV-SIA measurements with SbF-GCE for different concentrations of Pb(II) and Cd(II). Experimental conditions and instrumental parameters: see Fig. 3 and Experimental

dencies (not shown).

A special attention was paid to the effect of some salts in the sample solution. Specifically, of interest were nearly chemically inert salts of K_2SO_4 and KNO_3, as well as complex-forming halides and pseudohalides: namely, KCl, KBr, and KSCN. All these salts were added at a relatively high concentration (typically as $10\,mg\,l^{-1}\,X^-$) in order to ensure their complexing capabilities or even some other effect. As seen, the individual anions had affected the stripping processes of lead and cadmium — and, eventually, of other metal ions tested — in different ways (Figs 5 and 6). As expected, the presence of K_2SO_4 had almost no effect and the two SWASV signals observed remained unchanged. Furthermore, the presence of both KCl and KBr had caused only minimal increases of the oxidation peaks (Fig. 5 A). Rather unexpected was the effect of nitrate, when its addition caused noticeable shifts in the peak potentials, giving rise to a coincidence of the Cd-peak with the first signal of antimony, accompanied by a 10-fold decrease of the Pb-peak and its overlap with the second Sb-peak.

Moreover, the remaining third oxidation peak of antimony significantly increased compared to the situation in the absence of KNO_3 (see Fig. 5 C). Finally, the presence of KSCN (Fig. 5D) had only little effect upon the signals for Cd and Pb; however, having enabled to register also the oxidation peak for zinc, which could not be seen in any of the previous cases. (As found in a brand new and parallel study [35], much more pronounced effect of the thiocyanate anion can be achieved in less acidic solutions and at lower concentration of SCN^- (of ca. 0.001
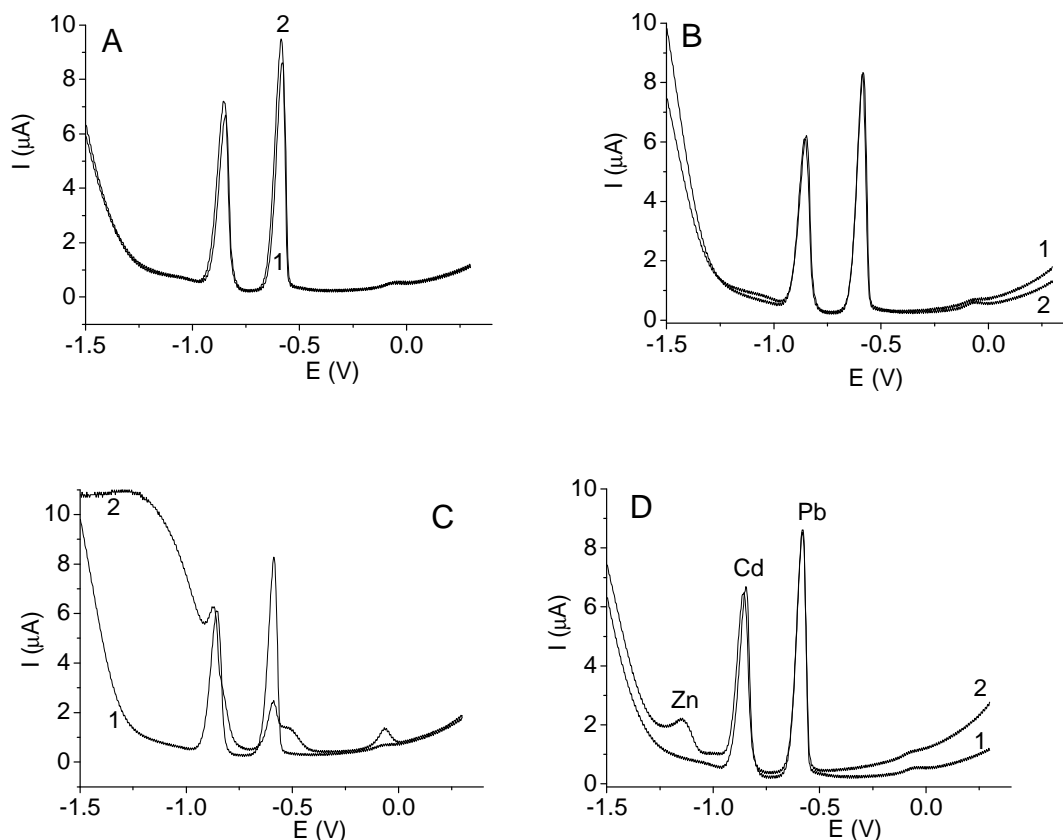
Fig. 5 Effect of the presence of salts in the supporting electrolyte of 0.5 M HCl upon the SWASV-SIA curves obtained in the mixture of 50 µg l^{-1} Cd(II) + Pb(II) + Zn(II) in the absence (1) and presence (2) of the same concentration of the respective salt (c = 10 mg ml^{-1}): A) KCl, B) K$_2$SO$_4$, C) KNO$_3$, and D) KSCN. For experimental conditions, see Table I and Fig. 3

mol l^{-1}) then, it is possible to enhance also both Cd-peaks and Pb-peaks up to 3-fold increase compared to their original intensity.)

Since the visualisation of the Zn-response had implied some positive effect of KSCN upon the stripping of other electronegative elements, this pseudohalide was also examined for eventual detection of two hardly reducible species – chromium(III) and manganese(II). As seen in Fig. 6 C and D, some evidence for Cr- and Mn-peaks could be noticed due to the effect of KSCN, but both responses were poorly developed and scarcely applicable in practical analysis at this stage of experimentation. Nevertheless, this study together with the above-mentioned investigations of similar focus [35] have shown clearly that there is still unexploited field in using the complex-forming reagents for the overall improvement of electroanalytical performance of both SbFEs and BiFEs.

Last but not least, the multi-elemental analysis of a model mixture of toxic metal ions, including the addition of 50 µg l^{-1} Hg(II), is illustrated in Fig. 7. The resultant voltammogram demonstrates that the presence of bivalent mercury has influenced the potential window available, when changing also the respective
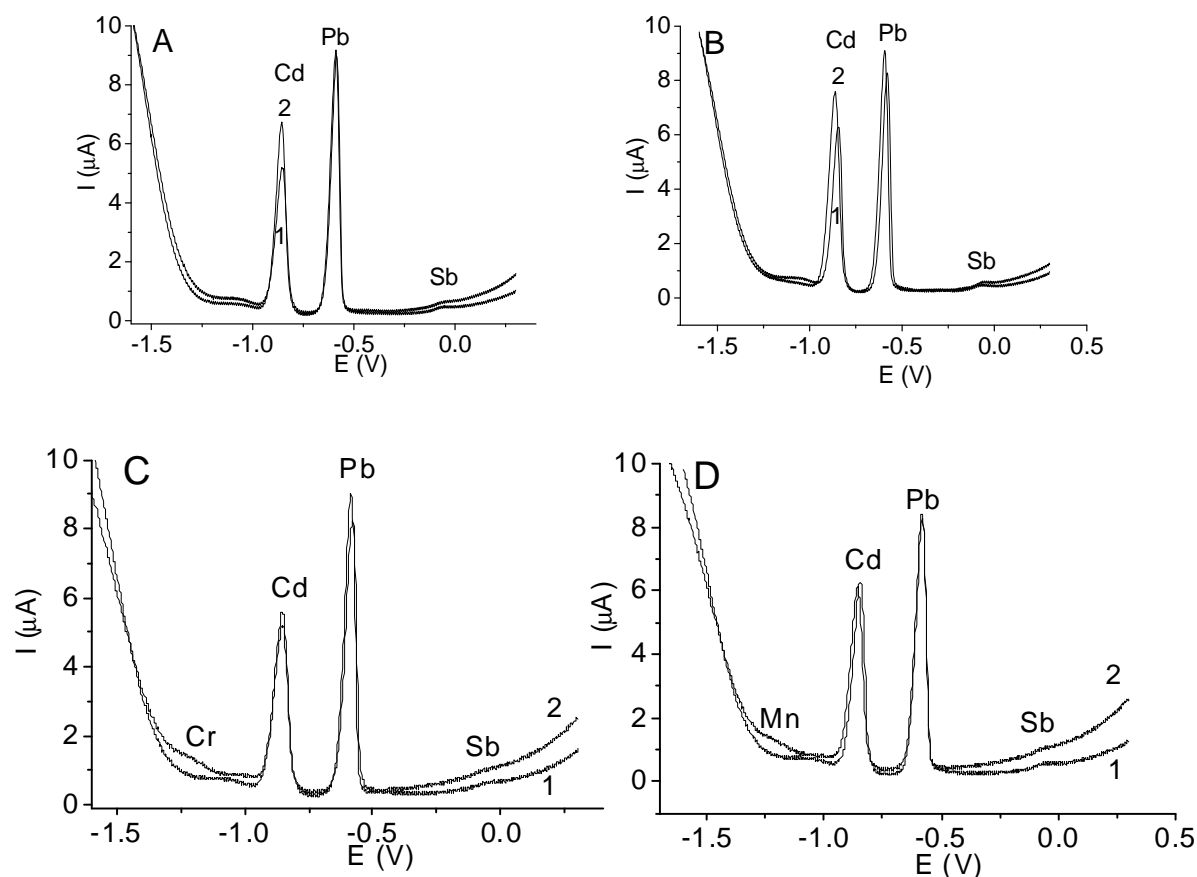
Fig. 6 Effect of KBr (A and B) and of KSCN (C and D) upon the SWASV-SIA responses in 0.5 M HCl containing the mixtures of 50 µg l⁻¹ Cd(II) + Pb(II) + Mn(II) (A and C) or Cd(II) + Pb(II) + Cr(III) (B and D) in the absence (1) and in the presence of 10 mg ml⁻¹ salt (2). For other conditions and parameters: see Fig. 3 and Experimental

responses at the SbFE; especially, the re-oxidation signal for cadmium having increased markedly.

One of possible explanations can be associated with the beneficial effect of the amalgamation between Hg and Cd, which is a spontaneous process with markedly higher effectiveness compared to a concurrent alloy formation with Sb [8,15,19].

Conclusion

In this article, the electroanalytical performance the SbF-GCE operated *in situ* has been optimised in an effort to outline its practical application in the SWASV-SIA measuring regime and for the determination of lead(II) and cadmium(II) at the low µg l⁻¹ concentration level and, possibly for some other metal ions like Zn(II), Mn(II), or Cr(III).

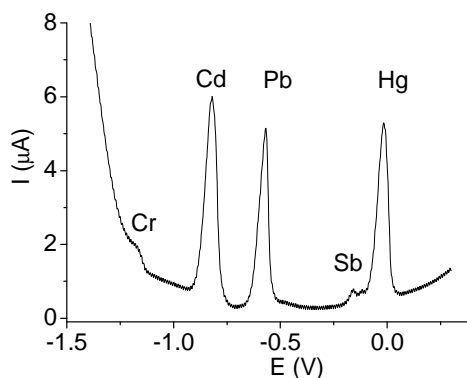In this respect, the basic characterisation for the determination of Cd(II) and

Fig. 7   SWASV-SIA detection of 50 μg l⁻¹ Hg(II) in the presence of 50 μg l⁻¹ Cd(II) + Pb(II) + Cr(III) in the supporting electrolyte of 0.5 M HCl. For other conditions and parameters: see Fig. 3 and Experimental

Pb(II) has been successfully completed and the optimal experimental conditions found (among others, the plating regime, the supporting electrolyte/sample solution composition, plus other experimental conditions associated). Furthermore, the effect of some selected anions has also been studied, finding that weakly complexing halide salts, namely KCl and KBr, had had a favourable effect upon the shape and intensity of the re-oxidation signals for both Cd and Pb. Moreover, the presence of KSCN in the plating solution has led to a visualisation of some highly electronegative elements, thus allowing us to examine a multi-target analysis — a simultaneous detection of of Cd(II) and Pb(II) together with Zn(II), Mn(II), and Cr(III).

It can be concluded that the SWASV-SIA/SbF-GCE combination used throughout the work seems to be beneficial with respect to the following features. The assembly proposed permits a simple *in-situ* preparation of the SbF-GCE, together with its effective regeneration and renewal, reduces the risk of sample contamination, spares the amounts of solutions and samples, and mainly opens up the possibilities for full automation of the measuring process. Due to the initial character of the entire study, all these benefits will have to be proved in practical analysis of real samples.

Acknowledgements

References

[1] Wang J.: *Analytical Electrochemistry*, 3rd Ed., Wiley-VCH, Hoboken, 2006.

[2] De Castro M.D.L., Izquierdo A.: Electroanalysis **3**, 457, (1991).

[3] Gharib Naseri N., Baldock S.J., Economou A., Goddard N.J., Fielden P. R.: Anal. Bioanal. Chem. **391**, 1283 (2008).

[4] Rodriguez J., Ibarra I.S., Galan Vidal C.A., Vega M., Barrado E.: Electroanalysis **21**, 452 (2009).

[5] Graabæk A.M., Jeberg B.: Inter. Labor. **22**, 33, (1992).

[6] Wang J.: Ass. Chem. Res. **35**, 811, (2002).

[7] Wang J.: Electroanalysis **17**, 1341 (2005).

[8] Economou A.: TrAC – Trends Anal. Chem. **24**, 334 (2005).

[9] Kokkinos C., Economou A.: Curr. Anal. Chem. **4**, 183, (2008).

[10] Švancara I., Prior C., Hočevar S. B., Wang J.: Electroanalysis **22**, 1405 (2010).

[11] Hutton E. A., Ogorevc B., Smyth M. R.: Electroanalysis **16**, 1616 (2004).

[12] Sattayasamitsathit S., Thavarungkul P., Kanatharana P.: Electroanalysis **19**, 502 (2007).

[13] Economou A., Voulgaropoulos A.: Talanta **71**, 758 (2007).

[14] Chuanuwatanakul S., Dungchai W., Chailapakul O., Motomizu S.: Anal. Sci. (Japan) **24**, 589 (2008).

[15] Hočevar S. B., Švancara I., Ogorevc B., Vytřas K.: Anal. Chem. **79**, 8639 (2007).

[16] Tesařová E., Baldrianová L., Hočevar S. B., Švancara I., Vytřas K., Ogorevc B.: Electrochim. Acta **54**, 1506 (2009).

[17] Pauliukaitė R., Kalcher K., in: *8th Young Investigators' Seminar on Analytical Chemistry* (*YISAC'01*), Book of Abstracts, pp. 10-11, University of Pardubice, Pardubice, 2001.

[18] Švancara I., Florescu, M., Stočes M., Baldrianová L., Svobodová E., in: *Sensing in Electroanalysis – Vol. 5* (K. Vytřas, K. Kalcher, I. Švancara, Eds.), pp. 109-125, University of Pardubice, Pardubice, 2010.

[19] Švancara I., Hočevar S. B., Baldrianová L., Tesařová E., Vytřas K.: *Sci. Pap. Univ. Pardubice*, *Ser. A 13* (2007) 5-19.

[20] 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).

[21] Tesařová E., Vytřas K.: *Electroanalysis 21*, 1075 (2009).

[22] Toghill K., Xiao L.-H., Wildgoose G., Compton R.: Electroanalysis **21**, 1113 (2009).

[23] Jovanovski V., Hočevar S.B., Ogorevc B.: Electroanalysis **21**, 2321 (2009).

[24] Kokkinos C., Economou A., Efstathiou C. E.: Electrochem. Commun. **11**, 250 (2009).

[25] Jiang X.-C., Sun Q., Zhang J.-L., Wang B.-Z., Du X.-Y.: Sensor Lett. **7**, 91

(2009).

[26] Zhang J.-L., Shan Y.-J., Ma J., Li X., Du X.-Y.: *Sensor Lett.* **7**, 605 (2009).

[27] Slavec M., Hočevar S. B., Baldrianová L., Tesařová E., Švancara I., Ogorevc B., Vytřas: Electroanalysis **22**, 1617 (2010).

[28] Urbanová V., Vytřas K., Kuhn A.: Electrochem. Commun. **12**, 114 (2010).

[29] Sopha H., Baldrianová L., Tesařová E., Hočevar S. B., Švancara I., Ogorevc B., Vytřas K.: Electrochim. Acta **55**, 7929 (2010).

[30] Guzsvány V., Nakajima H., Soh N., Nakano K., Imato T., *Sensing in Electroanalysis*, *Vol. 4* (K. Vytřas, K. Kalcher, I. Švancara; Eds). pp. 121-134, University of Pardubice, Pardubice, 2009.

[31] Guzsvány V., Nakajima H., Soh N., Nakano K., Imato T.: Anal. Chim. Acta **658**, 12 (2010).

[32] Guzsvány V., Nakajima H., Soh N., Nakano K., Švancara I., Vytřas K., Bjelica L., Imato T.: Electroanalysis, submitted (2010).

[33] Švancara I., Baldrianová L., Vlček M., Metelka R., Vytřas K.: Electroanalysis **17**, 120 (2005).

[34] Švancara I., Baldrianová L., Tesařová E., Vlček M., Vytřas K., Sotiropoulos S., in: *Sensing in Electroanalysis – Vol. 2* (K. Vytřas, K. Kalcher, Eds), pp. 35-58. University of Pardubice, Pardubice, 2007.

[35] Bartoš K.: *Deposition of the Bismuth and Antimony Films from Atypical Solutions with Possible Applicability in Electroanalysis*. Diploma Thesis (MSc), University of Pardubice, Pardubice, 2010.