Analytical Methods

Accepted Manuscript



This is an *Accepted Manuscript*, which has been through the Royal Society of Chemistry peer review process and has been accepted for publication.

Accepted Manuscripts are published online shortly after acceptance, before technical editing, formatting and proof reading. Using this free service, authors can make their results available to the community, in citable form, before we publish the edited article. We will replace this Accepted Manuscript with the edited and formatted Advance Article as soon as it is available.

You can find more information about *Accepted Manuscripts* in the **Information for Authors**.

Please note that technical editing may introduce minor changes to the text and/or graphics, which may alter content. The journal's standard <u>Terms & Conditions</u> and the <u>Ethical guidelines</u> still apply. In no event shall the Royal Society of Chemistry be held responsible for any errors or omissions in this *Accepted Manuscript* or any consequences arising from the use of any information it contains.



www.rsc.org/methods

Electrodeposited antimony and antimony-gold nano composite modified carbon paste electrodes for the determination of heavy metal ions



Sb film modified carbon paste electrode for the determination of Cd and Pb and Sb/Au composite material for the determination of Hg. Stripping plot Cd and Pb using Sb film modified carbon paste electrode and the stripping plot of Hg using Sb/Au composite modified carbon paste electrode are shown along with the SEM image of the Sb/Au composite material.

Electrodeposited antimony and antimony-gold nano composite modified carbon paste electrodes for the determination of heavy metal ions

> M.K.Dey, A.K.Satpati^{*} and A.V.R.Reddy Analytical Chemistry Division Bhabha Atomic Research Centre Trombay, Mumbai-40085 India

Abstract

Antimony film (Sb film) was electrodeposited the carbon paste electrode (CPE) surface for the determination of heavy metal ions like, Cd, Pb and Cu. An ex-situ analytical method based on this the Sb fim modified CPE proposed was proposed for the determination of heavy metal ions. Where the deposition of Sb film was performed in 0.02 M HCl solution and the determination of heavy metal ions was performed in sodium acetate media. For the determination Cu the pH of the solution was most crucial and it was optimised at a value of 6. For the determination of Hg, antimony and gold nano composite (Sb/Au nano composite) was deposited together over the carbon paste electrode surface. Modified electrodes were characterised using SEM and EDS measurements. On SEM measurements, Sb/Au nano composite have shown dendrimer type of morphology. Three sigma detection limits of Pb, Cd, Cu and Hg were obtained as 2.65, 2.32, 9.73, 0.052 µgL⁻¹ respectively. Finally the method was applied for the determination of Cd, Pb, Cu and Hg in real water samples.

Key wards: Antimony film (Sb film), Carbon paste electrode (CPE), Stripping voltammetry, heavy metal ions.

*corresponding author (A.K.Satpati), Fax: 91-22-25505151, Phone: 91-22-25590326 email: <u>asatpati@barc.gov.in</u>

Analytical Methods

1. Introduction

Stripping voltammetry is one of the best methods for the determination of heavy metal ions. Metallic mercury has been used as electrode for decades due to the enormous good properties of mercury as electrode material. In the recent time it has become a phobia in using mercury as the working electrode in voltammetry due to its toxic effects. Researchers have been looking for electrode materials alternate to mercury for the stripping voltammetric analysis. Wang et al. have developed Bi-film as the electrode material for the determination of heavy metal ions [1]. It has been a quite successful material in stripping voltammetry when plated over glassy carbon (GC) electrode [2-8] or on carbon paste electrode (CPE) [9-12]. Later Sb film electrode was introduced which has been very successful in stripping analysis [13]. In majority of the papers published initially, Sb film was used by plating over glassy carbon electrode surface [13-20]. Later, Sb film was also deposited over carbon paste electrode surface for analytical applications [21-30]. Carbon paste electrode has the additional advantage of easy renewability over the glassy carbon electrode for regular applications. For the improvement of sensitivity and its application in specific purposes, Sb films were deposited over many substrates like, boron doped diamond electrode [31], silicon wafers [32] and carbon nano tubes [31, 33]. Sb micro electrode was formed by plating Sb film on single carbon fibre micro electrode [34]. Considering the easy fabrication and the cost effectiveness, carbon paste electrode is the ultimate choice [35]. For the determination of Cd and Pb, Sb film was applied successfully [13-16, 22]. However there are only a few reports on the determination of Cu and Hg [20, 28, 30]. Interestingly most of the previous reports, Sb film modified electrode was used in highly acidic media. Since its inception, Sb film electrodes were applauded for its excellent characteristics in highly acidic solution of pH ≤ 2 . Applications of Sb film electrodes were not well investigated in neutral solutions accept in one report [34] where near neutral pH was used. Applicability of such modified electrodes at neutral or mild acidic solution has advantage as it reduced the acidification step and the modified electrodes could be used directly onsite as a sensor. In this work we have investigated the electro-deposition of Sb film and Sb/Au nano composite film over CPE surface. Effect of pH on the stripping characteristics of Sb film was investigated. Analytical parameters were optimised for the determination Cd, Pb and Cu. Sb film alone was not suitable for the determination of Hg at $\mu g L^{-1}$ concentration levels. Sb/Au nano composites were deposited over the CPE surface to improve the sensitivity towards Hg. Modified electrodes were applied for the determination of heavy metal ions in real water samples.

2. Instrumentation and procedure

Electrochemical studies were carried out using the cell assembly with a threeelectrode configuration consisting of the modified CPE as the working electrode and saturated calomel electrode (SCE) as the reference electrode. The potentials applied, measured and reported in this study were with respect to the SCE reference electrode at room temperature (298 K). A platinum rod served as the counter electrode. Electrochemical measurements were performed using an Eco Chemie Potentiostat/Galvanostat, Autolab-302N; the data acquisition and analysis were carried out by GPES 4.9 software. Prior to electrochemical scan, voltammetric solution was purged with high purity nitrogen gas for 10 min. Water samples were not required to digest for the determination of metal ions using the modified electrode. Measurements were carried out in differential pulse voltammetry (DPV) mode with the experimental parameters as, step potential 0.00255 V, modulation amplitude 0.025 V, Modulation time 0.05 s. Voltammetric experiments were carried out in 0.1 M sodium acetate of pH 6.

2.1 Reagents and Solutions

All the chemicals used were either of E. Merck G. R. grade or BDH Anal R grade. Acids were of high purity BDH Aristar quality. Reagent solutions were prepared weighing appropriate quantity and then dissolving and diluting with ultrapure water. High purity nitrogen gas (from Indian Oxygen Ltd) was used for removing dissolved oxygen from the voltammetric solution.

2.2 **Preparation of carbon paste electrode**

Spectroscopic grade carbon powder was mixed with required quantity of paraffin oil (~20 %) and then the mixture was mixed well on a mortar pestle. It was kept under vacuum of a rotary pump for 2 hrs to remove any adsorbed gases. The paste was mixed further for a well mixed homogenized paste. The carbon paste was then filled inside a glass tube with 2 mm diameter from the bottom end; a platinum wire was used for the connection with the paste and the instrument.

3. Results and discussion.

3.1 Deposition of the Sb film and Sb/Au nano composite.

Analytical Methods

Sb film was deposited over CPE surface by constant potential deposition technique. Similar to the previously reported literature an acidic solution was desirable for the Sb deposition [13]. In the present case antimony trichloride of 10 mM concentration in 0.02 M of HCl was used for the electrodeposition of Sb films. At higher pH values, Sb(III) would hydrolyse. For the deposition of Sb films, deposition potential was varied from -0.2 V to -1.0 V. A deposition potential of -0.6 V was optimised for faster deposition of Sb films. At more negative deposition potential than -0.6 V, there was hydrogen evolution from the electrode surface which made the films unstable. Morphological information about the film was obtained from scanning electron microscopy (SEM) imaging and the results are shown in Figure 1 A and B. SEM of Sb films on carbon paste electrode surface are shown in Figure 1 A. It was observed that the Sb nano deposits of 50 to 100 µm diameter were well dispersed over the carbon paste electrode surface. This substrate was used for the analysis of Cd, Pb and Cu. For the analysis of Hg, gold was deposited along with Sb to make the Sb/Au nano composite modified CPE. SEM images of those deposits are shown in Figure 1 B. Sb deposits were globular in shape, dispersed well all over the carbon paste substrate. Whereas, the SEM images of Sb/Au nano composite films have shown dendrimeric structured deposits. Sb films alone were non structural, with the incorporation of Au, the Sb/Au nano composite material has shown structural deposits. In a recently published report co-deposited antimony and bismuth film was characterised by SEM. In that report the Sb film was reported as separate agglomerate and bismuth film with more crystalline deposits [37], supports our observation on the Sb films. SEM with energy dispersive spectra (EDS) for area scan and point scan of the Sb-Au nano composite film with pre-concentrated Hg is shown in Figure S1 and S2 respectively in the supporting information. Presence of Sb on the Sb deposited carbon paste electrode was clearly observed in both the area and point scans. Signature due to the Au, Hg was also observed on EDS measurements on the Sb/Au nano composite modified were also observed.



(B)

(A)

Figure 1. (A) SEM micrograph of Sb-film modified CPE (B) SEM micrograph of Sb/Au nano composite modified CPE used for Hg determination.

3.0kV

SEI

x 50,000

100nm SAIFIITB

WD 6

SEM

7/26

6:50:1

Analytical Methods

Analytical Methods Accepted Manuscript

3.2 Effect of pH on the stripping peak of Sb films deposited over carbon paste electrode surface.

In stripping voltammetric measurements the stripping peak of Cu appears after the stripping peak of Sb. Thus it was required to separate these two stripping peaks to observe the stripping response of Cu on Sb film modified CPE. Deposition of Sb film was always carried out in 0.02 M HCl media and the dissolution behaviour of antimony after deposition was investigated in two supporting electrolyte media; HCl and sodium acetate at different pH values. This was to ensure about the dissolution characteristics of Sb film and also to optimise the supporting electrolyte media to get clear separation from the between Sb and Cu stripping peaks. The stripping response of the deposited Sb films in HCl solution of different pH values are depicted in Figure.2. Two stripping peaks, during the anodic dissolution of the Sb film were observed [37]. This potential region, where the peaks were observed, was the active dissolution range of antimony. At highly acidic pH values in the range of 1 to 2, two stripping peaks of Sb were observed one at -0.07 V and the other at 0.06 V respectively. With increase in the pH of the stripping solution the stripping peak was shifted towards more negative directions and the stripping peak height was reduced. At pH 4 the stripping peak of Sb was observed at around -0.16 V. At pH value higher than 4 the stripping peak was reduced further and almost vanished at pH 5 and above. It was observed that the Sb film was not so stable on repeated use of the modified electrode during standard addition method in hydrochloric acid solution. Sodium acetate of 0.1 M concentration was chosen as an alternate stripping solution as it was a good supporting electrolyte media in stripping analysis. Effect of pH on the stripping peak of Sb film was investigated in sodium acetate solution and the results are shown in Figure.3. Similar to that of HCl solution, two stripping peaks were observed. With increase in the pH of the solution the stripping peaks were negatively shifted in acetate media. At pH 6 the stripping peak of Sb was reduced but unlike in HCl solution it was not vanished completely. The second stripping peak was reduced significantly, this has made a well observable stripping peak of Cu, separated from the Sb stripping peak. Thus, by adjusting the pH of the solution it was possible to shift the stripping peak of Sb towards negative direction so that the Cu stripping peak could be separated from the Sb peak. At higher pH values, the Sb film was oxidised to form Sb oxide passive film at the electrode surface which has reduced the stripping current of Sb. Furthermore at lower pH value, of around 1, the corrosion potential of Sb remained in active region. At that high acidic pH range Sb dissolved with following two steps [37].

$$Sb + H_2O \longrightarrow SbO(ads) + 2H^+ + 2e^-$$

SbO(ads) \longrightarrow Sb(O)⁺ + e⁻

With the increase in pH a passive film was formed with inner layer of porous antimony oxide (Sb_2O_3) and the outer layer of antimony pentoxide (Sb_2O_5) [37]. At higher pH the passive oxide film was formed predominantly, which shifted the peak potential towards negative potentials. The stripping peak current was reduced due to the passivation of the electrode surface. This interesting property of Sb –film has attracted its use in stripping voltammetry predominantly for the determination of metal ions with peak potentials close to the Sb stripping peak [13, 20, 30]. In the present study 0.1 M sodium acetate of pH 6 was optimised as the supporting electrolyte media for all the metal ions investigated.



Analytical Methods

Figure 2. Effect of pH on the Sb stripping characteristics in HCl solution: Sb deposition was carried out from 10mM Antimony trichloride solution (in 0.02M HCl): deposition potential - 0.6V for 100sec.



Figure 3. Effect of pH on the Sb stripping characteristics in sodium acetate solution: Sb deposition was carried out from 10mM Antimony trichloride solution (in 0.02M HCl): deposition potential -0.6V for 100sec.

3.3 Voltammetric behaviour of the Sb-film modified electrode.

The Sb film deposited over the carbon paste electrode surface was applied for the determination of heavy metal ions. Thickness of the Sb film was optimised by measuring the stripping response of Cd with variation of the deposition time during Sb film deposition; corresponding results are shown in Figure.4. A thin film with the deposition time of 50 s and 100 s have shown better stripping response of Cd. At higher deposition time of 150 s and 200

Analytical Methods

s the stripping response of Cd was reduced. Present results reflected that the thin Sb film was important for the stripping voltammetry. In that case the pre-concentrated Cd would remain predominantly at the surface of the film as the surface to volume ratio of a thin film is higher than that of a thick film. Formation of intermetallic compounds also played important role in the stripping response. From the present observation a deposition time of 100 s for Sb film deposition was optimised. Content of Sb for the ultimate stripping signal was also investigated before for the determination of Pb and Cd [34] and for Cu [19]. Similar observation was also reported in previous investigation where beyond a certain amount of Sb, relative to the presence of the analytes, the stripping response of the heavy metal ions was reduced. In the present investigation the film thickness was optimised using the Cd stripping signal. This was due to the fact that the presence of Cd in natural water is much lower concentrations than Pb and Cu, thus it was advisable to optimise the sensor response with respect to Cd. It is however observed that sensitivity of the measurements for Pb and Cu was very good at the Sb film thickness optimised by measuring Cd stripping response.



Analytical Methods

Figure 4. Optimization of deposition time of antimony on CPE from 10mM antimony trichloride solution (in 0.02M HCl): Deposition potential: -0.6V with different deposition time. Cd concentration was 75 μ g L⁻¹ in sodium acetate of pH 6 and deposition potential was for Cd deposition was-1V for 300s in sodium acetate solution at pH 6.0.

3.4 Analytical Performance of the modified electrode

Analytical performance of the Sb film modified CPE was investigated after optimization of the deposition time of the Sb film and pH of the supporting electrolyte media. The Sb film modified CPE was applied at pH 6 in 0.1 M sodium acetate supporting electrolyte media. Cd and Pb were determined simultaneously and corresponding voltammetric plots at different concentrations are shown in Figure.5. Peaks for Pb and Cd were appeared at -0.56 V and at -0.80 V respectively. These peaks were negatively shifted compared to their positions with mercury electrode. Present results were compared with the reported results on Sb film modified electrode surface. It was observed that this is the usual position of the Pb and Cd stripping peaks on Sb film modified electrodes and present results were agreed well with the published reports on Sb film electrodes [13]. Corresponding linear calibration plots are shown in the inset of Figure .5. Calibration of Pb followed the linear equation with the slop of the calibration plot as $4.42 \text{ A/\mu gL}^{-1}$ of Pb and the correlation coefficient of 0.998. The calibration plot of Cd followed the linear relation with the slop as 3.42 A/ μ gL⁻¹ of Cd with the correlation coefficient of 0.997. Three sigma detection limits of Pb and Cd were obtained as 2.65 μ gL⁻¹ and 2.32 μ gL⁻¹ respectively. Deposition and stripping of Cd and Pb was carried out in the solution pH of 6 to keep an uniform solution pH for all the determination as a higher pH was required for the determination of Cu. The modified electrode worked well for Pb and Cd at pH 6 and also acidic solution, though the results in highly acidic solution are not shown in the present study.



Figure 5. Voltammetric plot of Cd and Pb with varying concentrations on Sb film modified carbon paste electrode: Sb deposited from 10 mM antimony trichloride solution (in 0.02M HCl at -0.6V for100sec). Cd and Pb deposition was carried out at -1.0V for 300s in 0.1 M sodium acetate solution at pH 6.0. Inset: corresponding linear calibration plot.

One of the important advantage of the Sb film is the weak stripping signal while the scanning the potential anodically [13, 20, 30]. As reported in the previous section of effect of pH, the stripping response of Sb film could be reduced further at pH 6 in 0.1 M sodium acetate supporting electrolyte solution. This has improved its application to the determination of Cu, whose stripping response appeared at a more positive potential to that of Sb film substrate. Stripping voltammetric plots with different concentrations of Cu are shown in Figure.6. In this case the Sb film was freshly deposited every time it was used for the deposition and stripping of Cu. Stripping peak was well separated from the Sb peak and also the stripping response of Sb was much low and the Cu stripping peak was well observable. Voltammetric response was increased with the increase in the Cu concentration;

Analytical Methods

corresponding calibration plot is shown in the inset of Figure 6. Calibration plot was linear with the slop of 4.42 A/ μ gL⁻¹ of Cu and the correlation coefficient of 0.998. Three sigma detection limit of Cu was obtained as 9.73 µgL⁻¹. In a recent report determination Cu using Sb film electrode was reported [28] with in-situ electrodeposition of Sb film and determination of Cu. In the present method Sb film was deposited ex situ where presence of Sb concentration relative to the concentration Cu to be determined is not so crucial. In a recent report determination of Hg was reported using Sb film electrode [30]. In our observation the stripping response of Hg could not be detected at 1 ugL^{-1} and low concentration range on bare Sb film electrode. To improve the sensitivity Sb/Au nano composite material was prepared using electrodeposition route. Composite of Sb/Au was electrodeposited simultaneously from 10 mM antimony trichloride solution and 1 mM of auric chloride solution in 0.02M HCl at -0.6V for 100 sec. SEM characteristics of those composite materials were reported in the earlier section. Deposition conditions and solution conditions were optimised by observing the deposits under microscope and SEM measurements. At the optimised deposition conditions dendrimeric deposits of Sb/Au nano composite material have shown good sensitivity towards Hg. This composite modified electrode applied for the determination of Hg and the voltammetric plots of Hg stripping peaks using the Sb/Au nano composite material were shown in Figure 7. Deposition condition for Hg was optimised at -0.6 V for 300 s (results on the variation of deposition potential and time were not shown). For the deposition of Hg the response did not increase at deposition potential beyond -0.6 V. There was possibility of hydrogen evolution from Sb/Au composite material due to the presence of gold. Good stripping response due to 0.5 μ gL⁻¹ of Hg on Sb/Au nano composite modified CPE was observed. The linear calibration plot was shown in the inset of Figure 7. Stripping peak was increased linearly with the Hg concentration with slope of 4.12 $A/\mu g L^{-1}$ and correlation coefficient of 0.998. Three sigma detection limit of $0.052 \ \mu g L^{-1}$ was obtained.

Gold nano particle modified carbon paste electrode is also sensitive for the determination of Hg(II). In our recent study determination of mercury using gold nano particle modified carbon paste electrode was reported [38]. In the present case of Sb/Au composite electrode material the gold nano particles were embedded well inside the Sb matrix, which has improved the overall and inter-particle conductivity of the composite materials. Detection limit was improved from 0.24 μ gL⁻¹ in gold nano particle modified carbon paste

electrode.

Analytical features of the present method were compared with the some recent literature reports and shown in Table 1. Limit of detection of Hg in the present paper was superior compared to the literature report. In the case of Cu, Pb and Cd the limit of detection in the present report was higher than the reported values or comparable in some cases. The method could be applied in the determination of heavy metal ions in natural water samples. Applicability of presently modified electrode in neutral solution has the additional advantage.



Figure 6. Voltammetric plot of Cu with varying concentrations on Sb film modified carbon paste electrode: Sb deposited from 10mM antimony trichloride solution (in 0.02M HCl at - 0.6V for 100sec). Cu deposition: at -1.0 V for 300s in 0.1 M Sodium acetate solution at pH 6. Inset: corresponding linear calibration plot.



Figure 7. Hg Voltametric plot of Hg using Sb/Au nano composite modified carbon paste electrode. Hg deposition and stripping was carried out in 0.1 M sodium acetate solution. Inset: corresponding linear calibration plot.

Reference	Element	Modified electrode	Solution condition	Detection limit
28	Cu	Sb film modified CPE	pH 2	1.45 and 1.10 μg L ⁻¹
30	Hg	Sb film modified CPE	1 M HCl	1.3 μgL ⁻¹

Table 1. Comparison of the analytical parameters of the present method with the results published in literature.

Present	Hg, Cu, Pb	Sb/AuNPs modified	pH 6	0.052, 9.7, 2.65 and 2.32
work	and Cd	CPE for Hg and Sb		μgL ⁻¹ respectively μgL ⁻¹
		film modified CPE		
		for Cu, Pb and Cd		
20	Hg	Sb film modified	1 M HCl	$0.39 \ \mu g L^{-1}$
	C	CPE		10
37	Ph Cd	Sh and Bi co-	nH 2	1 4 and 1 1 µg I ⁻¹
51	10, Cu	denosited film	p11 2	respectively
		modified CPF		respectively

3.5 Recovery test and analysis real water sample using the modified electrode

Recovery test was carried out in tap water samples by spiking known concentration of Hg, Cu, Pb and Cd and determination was carried out using the Sb film modified carbon paste electrode. The test results are shown in Table.2. It was observed that all the elements were recovered within 10% deviation from the added concentration. The modified electrode was applied in the determination of heavy metal ions in real water samples. Two water samples collected; one from Powai lake, situated at a Mumbai suburban area and another sample was a ground water sample from OSCOM (Odissa sands company) mining area. The analysis results are shown in Table 3. Analytical results were cross verified using the results from inductively coupled plasma atomic emission spectrometry (ICPAES) technique for Cu, Cd and Pb. Total mercury analyser based on thermal decomposition atomic absorption technique for Hg was used for the verification of the results of Hg. It was observed that the analytical results in most of the measurements agreed well between two methods. Hg content in Powai lake water sample determined using the modified electrode was not agreed with the measured value from total mercury analyser. In Powai lake water sample Pb was preconcentrated by evaporation preconcentration method. The water sample from OSCOM was collected from a mining area where the heavy metal ion content was higher due to the mining activities. Hg content in that sample was significantly higher than the prescribed limit by World Health Organization (WHO) in potable water.

Element	Spiked Concentration (µgL ⁻¹)	Recovery concentration (μgL ⁻¹)	% of Recovery
Hg	5	5.03	100.6%
Cu	20	21.5	107.5%
Pb	10	9.6	96%
Cd	5	5.3	106%

Table 2 Recovery test result of Hg, Cu, Pb and Cd using the modified electrode.

Table 3 Analysis results of Cu, Pb, Cd and Hg in two samples collected from two regions of India, using the modified electrode.

Sample	Cu (µgL ⁻¹)	Pb (µgL ⁻¹)	Cd (µgL ⁻¹)	Hg (μgL ⁻¹)
Powai lake	26 (30)*	12(10)*	Not detected	0.25 (0.55)*
OSCOM	49 (63)*	50(56)*	10(11)*	145 (134)*

*Values under the bracket are determined using inductively coupled plasma atomic emission spectrometry (ICPAES) technique for Cu and using total mercury analyzer based on atomic absorption technique for Hg. Percent standard deviation for Cu, Pb, Cd and Hg were 5.3 %, 6.2 %, 4.6 % and 4.8% respectively for 6 repetitive measurements.

4. Conclusion

In this paper Sb film was electrodeposited over the carbon paste electrode surface. Morphology of the deposits was obtained from the SEM measurements. Stripping response of Cd and Pb was obtained and these metal ions were determined simultaneously in water samples using Sb film modified CPE. Cu was determined separately and a solution pH of 6 was optimised for the determination to obtain the better separation from the stripping peak from the substrate. Antimony gold nano composite materials were deposited electrochemically over carbon paste electrode surface and the composite materials were characterised using SEM and EDS measurements. SB/Au nano composite modified PE has shown good sensitivity for the determination of Hg with limit of detection of $0.052 \ \mu g L^{-1}$.

Analytical Methods

Analytical Methods Accepted Manuscript

Most importantly the modified electrodes were demonstrated for application at near neutral solution of pH 6. Water samples were not required to be digested before analysis. This has opened up the possibility of fabrication of sensors based on such modified electrodes in field application. The modified electrode was applied to the determination of heavy metal ions in water samples. Analytical results were cross verified using the ICPAES and total mercury analyser. Hg content in the ground water collected from OSCOM mining site sample was significantly higher than the WHO limits for potable water.

References

- [1] J. Wang, J. Lu, S.B. Hocevar, P.A.M. Farias, Anal. Chem. 2000, 72, 3218.
- [2] J. Wang, J. M. Lu, U. A. Kirgoz, S. B. Hocevar, B. Ogorevc, Anal. Chim. Acta, 2001, 434
- (1), 29.
- [3] J. Wang, U. A. Kirgoz, J. M. Lu, Electrochem. Commun. 2001, **3**, 703.
- [4] S. B. Hocevar, J. Wang, R. P. Deo, B. Ogorevec, Electroanalysis, 2002, 14, 112.
- [5] S. B. Hocevar, B. Ogorevc, J. Wang, B. Pihlar, Electroanalysis, 2002, 14, 1707.
- [6] J. Wang, J. Lu Electrochem. Commun. 2000, 2, 390.
- [7] G. Kefala, A. Economou, A. Voulgaropoulos, M. Sofoniou, Talanta, 2003, 61, 603.
- [8] A. Alberich, N. Serrano, C. Arino, J. M. Diaz-Cruz, M. Esteban, Talanta, 2009, 78, 1017.
- [9] A. Krolicka, R. Pauliukaite, I. Svancara, R. Metelka, A. Bobrowski, E. Norkus, K. Kalcher, K. Vytras, Electrochem. Commun. 2002, 4, 193.
- [10] G. U. Flechsig, M. Kienbaum, P. Grundler, Electrochem. Commun. 2005, 7, 1091.
- [11] K. Vytras, I. Svancara, R. Metelka, Electroanalysis, 2002, 14, 1359.
- [12] M. K. Dey, A. K. Satpati, S. Sahoo, R. Kameswaran, A. V. R. Reddy, T. Mukherjee, Anal. Methods, 2011, **3**, 2540.
- [13] S.B. Hocevar, I. Svancara, B. Ogorevc, K. Vytras, Anal. Chem., 2007, 79, 8639.
- [14] V. Guzsvany, H. Nakajima, N. Soh, K. Nakano, I. Svancara, K. Vytras, L. Bjelica, T. Imato, Electroanalysis, 2011, 23, 1593.
- [15] H. Xu, P. Yang, Q. Zheng, J. Liu, L. Jin, Chinese J. of Chem., 2010, 28, 2287.
- [16] V. Jovanovski, S.B. Hocevar, B. Ogorevc, Electroanalysis, 2009, 21, 2321.
- [17] H. Sopha, V. Jovanovski, S.B. Hocevar, B. Ogorevc, Electrochem. Commun., 2012, 20, 23.
- [18] B. Nigovica, S.B. Hocevar, Electrochim. Acta, 2011, 58, 523.

Analytical Methods

- [20] S. Dal Borgo, V. Jovanovski, S.B. Hocevar, Electrochim. Acta, 2013, 88, 713.
- [21] E. Tesarova, L. Baldrianova, S.B. Hocevar, I. Svancara, K. Vytras, B. Ogorevc, Electrochim. Acta, 2009, **54**, 1506.
- [22] W.-J. Yi, Y. Li, G. Ran, H.-Q. Luo, N.-B. Li, Mikrochim. Acta, 2012, 179, 171.
- [23] E. Svobodova-Tesarova, L. Baldrianova, M. Stoces, I. Svancara, K. Vytras, S.B. Hocevar, B. Ogorevc, Electrochim. Acta, 2011, **56**, 6673.
- [24] H. Sopha, L. Baldrianova, E. Tesarova, S.B. Hocevar, I. Svancara, B. Ogorevc,K.Vytras, Electrochim. Acta, 2010, 55, 7929.
- [25] E. Tesarova, K. Vytras, Electroanalysis, 2009, 21, 1075.
- [26] I. Svancara, K. Bartos, M. Stoces, Scientific Papers of the University of Pardubice, Series A: Faculty of Chemical Technology, 2011, **17**, 5.
- [27] E. Svobodová, L. Baldrianová, S.B. Hocevar, I. Svancara, Int. J. Electrochem. Sci., 2012, 7, 197.
- [28] A.M. Ashrafi, K. Vytras, Electrochim. Acta, 2012, 73, 112.
- [29] A.M. Ashrafi, K. Vytras, Int. J. Electrochem. Sci., 2012, 7, 68.
- [30] A.M. Ashrafi, K. Vytras, Talanta, 2011, 85, 2700.
- [31] K. Toghill, L. Xiao, G. Wildgoose, R. Compton, Electroanalysis, 2009, 21, 1113.
- [32] C. Kokkinos, A. Economou, I. Raptis, T. Speliotis, Electrochem. Commun., 2009, **11**, 250.
- [33] X. Niu, H. Zhao, M. Lan, Electrochim. Acta, 2011, 56, 9921.
- [34] M. Slavec, S. B. Hocevar, L. Baldrianova, E. Tesarova, I. Svancara, B. Ogorevc, K. Vytras, Electroanalysis, 2010, **22(14)**, 1617.
- [35] I. Svancara, K. Kalcher, A. Walcarius, K. Vytřas, Electroanalysis with Carbon Paste Electrodes, within Analytical Chemistry Series; CRC Press, Boca Raton (Fl, USA), 2012
- [36] A. M. Ashrafi, K. Vytřas, Int. J. Electrochem. Sci. 2013, 8, 2095.
- [37] Omar E. Linarez Pérez, Manuel A. Pérez, Manuel López Teijelo, J. Electroanal. Chem.,2009, 632, 64.
- [38] S. Sahoo, A. K. Satpati and A. V. R. Reddy, Electrochemically Deposited Gold Nanoparticles on Carbon Paste Electrode Surface for the Determination of Mercury, J.AOAC International (manuscript id 13-0355, in press)

Supporting information



(B)

Figure S1. SEM (A) with EDS of area scans (B) spectra of Sb-Au composite film on which Hg was pre-concentrated.



Figure S2. SEM (A) with EDS of point scans (B) spectra of Sb-Au composite film on which Hg was pre-concentrated.

Electrodeposited antimony and antimony-gold nano composite modified carbon paste electrodes for the determination of heavy metal ions



Sb film modified carbon paste electrode for the determination of Cd and Pb and Sb/Au composite material for the determination of Hg. Stripping plot Cd and Pb using Sb film modified carbon paste electrode and the stripping plot of Hg using Sb/Au composite modified carbon paste electrode are shown along with the SEM image of the Sb/Au composite material.