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**SCREEN-PRINTED CARBON ELECTRODES BULK-MODIFIED WITH  $\text{Bi}_2\text{O}_3$  OR  $\text{Sb}_2\text{O}_3$  FOR TRACE DETERMINATION OF SOME HEAVY METALS**

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*Screen-printed carbon electrodes (SPCE) bulk-modified with  $\text{Bi}_2\text{O}_3$  or  $\text{Sb}_2\text{O}_3$  have been investigated for their suitability to determine some selected heavy metals using anodic stripping voltammetry. At a SPCE modified with 1.25 % (w/w)  $\text{Bi}_2\text{O}_3$ , the corresponding re-oxidation peak potentials appeared at  $-0.785\text{ V}$  for Cd, or at  $-0.565\text{ V}$  for Pb. At a SPCE modified with 1.00 % (w/w)  $\text{Sb}_2\text{O}_3$ , the re-oxidation peak of Cd appeared at  $-0.805\text{ V}$ . Bulk-modified  $\text{Bi}_2\text{O}_3$ -SPCEs, after an electrochemical preconditioning, can be used for monitoring Cd and Pb at concentrations  $\geq 10\ \mu\text{g l}^{-1}$  with a preconcentration time of 600 s at  $-1.2\text{ V}$  vs.*

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*SCE. An analogous  $Sb_2O_3$ -SCPE displays a higher quantification limit for Cd ( $20 \mu g l^{-1}$ ) at the same conditions, whereas the determination of Pb seemed impossible by simple procedures. The SPCE modified with  $Bi_2O_3$  was applied for determination of Pb(II) in drinking water and urine.*

## **Introduction**

Recently, Wang's research group has introduced a new type of working electrode for voltammetric stripping analysis [1], a bismuth film-plated electrode (BiFE) that represents an attractive alternative to traditionally used mercury film electrodes. In the following studies [2-4] the authors demonstrated that the BiFE — as a mercury free and hence “environmentally friendly electrode” — offers a surprisingly good analytical performance, attributed to the property of bismuth to form “fused alloys” with heavy metals analogous to the amalgams formed with mercury [5]. Since their introduction, BiFEs have attracted attention of the electroanalytical community and several groups are conducting research in this area (see the first review dealing with the matter [6] and following papers [7–24].

As reported, the bismuth film can be plated on the same substrates as mercury. Among carbon substrates for BiFEs, we have shown [8,10] that carbon pastes may represent a nearly comparable alternative to commonly used glassy carbon. A role of the plating regime (external deposition or *in-situ* plating of the bismuth film) has also been investigated [25]. A simple modification of the carbon paste matrix with solid, water-insoluble  $Bi_2O_3$  as a source of the bismuth film seemed to be a logical consequence similar to sensors modified with HgO [26]. Already the first assays were successful [9,10,20] and especially this type of BiFEs seemed to offer attractive performance in anodic stripping voltammetry and/or stripping potentiometry of heavy metals.

From the viewpoint of miniaturisation, of course, the increasing application of microfabrication technologies like screen-printing has been made much more accessible. To produce such disposable carbon substrate-based sensors, particularly screen-printed carbon electrodes (SPCEs), carbon ink is usually used [27–32]. A report on the characteristics of SPCEs modified with  $Bi_2O_3$  or  $Sb_2O_3$  for use in stripping analysis of some trace metals is given in the present paper. As mentioned above, bismuth compounds as modifiers for different type of the carbon substrate-based electrodes are gaining increasing interest, while antimony oxide is used for the first time here.

## Experimental

### Apparatus

Stripping voltammetry was performed with a polarographic analyzer (model 264A EG&G Princeton Applied Research) combined with an X-Y recorder (Siemens Kompensograph X-Y C-1924). A screen-printed carbon electrode (1.0 cm<sup>2</sup> surface area) served as the working electrode, an aqueous saturated calomel electrode (SCE) and platinum wire were used as the reference and counter electrodes, respectively. All the experiments were carried out at room temperature.

### Chemicals and Solutions

All solutions were prepared with highly pure Mili-Q water, resistance ~ 18 Ω. The cadmium and lead standard stock solutions (1000 mg l<sup>-1</sup>) were obtained from Merck and dissolved as required. An acetate buffer solution (0.1 mol l<sup>-1</sup>, pH 4.5) was used as supporting electrolyte as it was optimised in Refs [1,3].

### Working Electrodes

A semi-automatic screen printer (Model SP-200, MPM, Franklin, MA) was used for printing the working electrodes. Carbon ink (Gwent Electronic Materials Ltd., UK) was mixed with Bi<sub>2</sub>O<sub>3</sub> or Sb<sub>2</sub>O<sub>3</sub>. After intensive mechanical mixing for 30 min, the mixture was put into a sonicator for 15 min, then printed through a screen (100 μm thick) onto 11.4 × 16.4 cm alumina ceramic plates containing 30 strips (of 1 × 4 cm). The geometric working area of one of such electrodes was 1 cm<sup>2</sup>. The resulting printed patterns were cured at 50 °C for 60 min. Silver ink was applied to one end of the SPCE to guarantee a good contact for the electrode connection.

### Procedure

Prior to analysis, SPCEs were electrochemically activated in the potential range from -1.5 to +1.5 V (for Bi<sub>2</sub>O<sub>3</sub>-modified) or from -2.0 to +2.0 V (for Sb<sub>2</sub>O<sub>3</sub>-modified) for 80 – 100 cycles with a scan rate 100 mV s<sup>-1</sup> in an acetate buffer solution. The potential of pre-concentration of Cd and Pb was usually -1.2 V under stirring (usually 600 s). The equilibration time was 15 s, followed by recording the voltammograms by applying a positive-going differential pulse voltammetric potential scan (pulse height 50 mV, scan rate 10 mV s<sup>-1</sup>). The scan

was terminated at  $-0.3$  V for  $\text{Bi}_2\text{O}_3$ -modified SPCEs, or at  $-0.5$  V for  $\text{Sb}_2\text{O}_3$ -modified ones.

### Analytical Samples

Drinking water and urine were used as samples. Drinking water was collected from the tap, evaporated with concentrated  $\text{HNO}_3$  (due to the interference of some possible organic traces present in the water), and re-dissolved to one-tenth of the original volume. Human urine was mineralised similarly with concentrated  $\text{HNO}_3$  as described above but re-dissolved to the original volume.

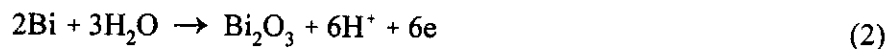
## Results and Discussion

### SPCEs Modified with $\text{Bi}_2\text{O}_3$

SPCEs modified with  $\text{Bi}_2\text{O}_3$  should be activated electrochemically by cyclic voltammetry (CV) within a particular potential range in order to increase the sensitivity to accumulate small amounts of  $\text{Pb(II)}$  and  $\text{Cd(II)}$ . An example of such activation of the electrode is shown in Fig. 1. The first cycle differs significantly when compared to cyclic voltammograms obtained in the following cycles. Obviously, the electrode surface must be conditioned by cycling the potential; potential range within  $-1.5$  and  $1.5$  V was found as an optimum. It should be mentioned that a weakly acidic solution must be used as a supporting electrolyte for SPCEs bulk-modified with bismuth oxide because in alkaline solutions,  $\text{Bi}_2\text{O}_3$  reacts with  $\text{OH}^-$  at negative potentials (approx. at  $-0.8$  V) [21,33,34]. A reduction peak was observed at  $-0.68$  V of the cathodic scans, and this peak shifted to more negative potentials with increasing number of cycles. It corresponded to the reduction of  $\text{Bi}_2\text{O}_3$  to the metal [35]



Re-oxidation of Bi was observed at  $0.32$  V, and it shifted to less positive potentials with subsequent cycles



Thus,  $\text{Bi}_2\text{O}_3$  is re-deposited and concentrated onto the surface, increasing its

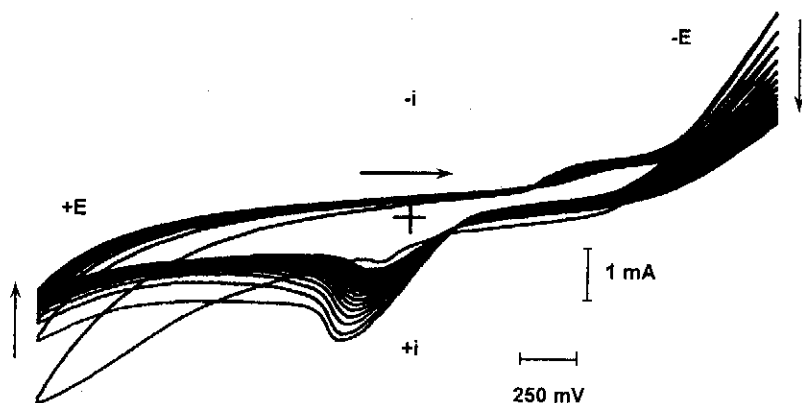


Fig. 1 Cyclic voltammograms of activation of SPCE bulk-modified with  $\text{Bi}_2\text{O}_3$  in an  $0.1 \text{ mol l}^{-1}$  acetate buffer (pH 4.5), potential range from  $-1.5$  to  $+1.5 \text{ V}$ , scan rate  $100 \text{ mV s}^{-1}$

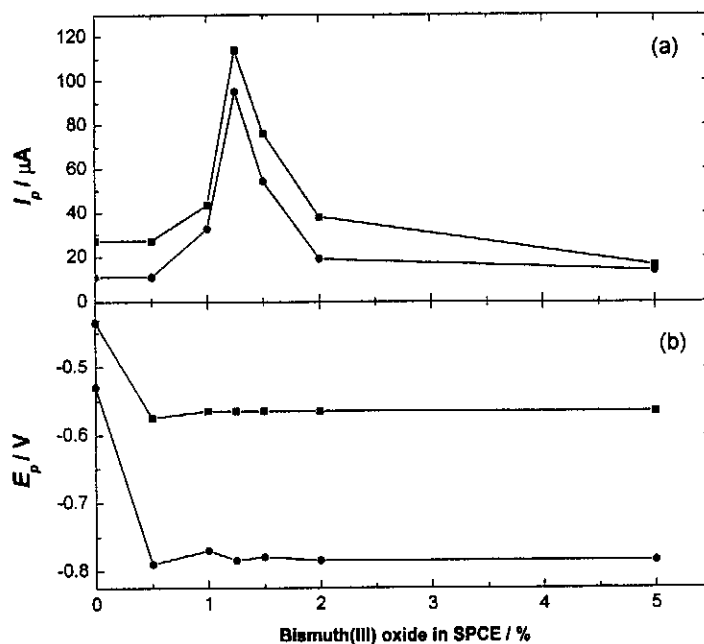


Fig. 2 Dependence of re-oxidation peak current (a) and potential (b) of Cd and Pb ( $50 \mu\text{g l}^{-1}$  both of metals) on composition of SPCE modified with  $\text{Bi}_2\text{O}_3$ . Supporting electrolyte  $0.1 \text{ mol l}^{-1}$  acetate buffer (pH 4.5); pre-concentration time  $600 \text{ s}$  at  $-1.20 \text{ V}$ , scan rate  $10 \text{ mV s}^{-1}$ , pulse height  $50 \text{ mV}$

electrochemical activity during cycling (Fig. 1), since partial dissolution of bismuth oxide occurred easily due to cycling [33,34,36,37]. Both peaks corresponding to either reduction or oxidation decreased with each potential cycle until stable voltammogram was obtained after ~70 cycles. Probably, it led to the uniform conductive thin  $\text{Bi}_2\text{O}_3$  film formation at the electrode surface, which caused a higher sensitivity to some heavy metals [9].

After activation, the electrode could be used for the determination of  $\text{Pb}^{2+}$  and  $\text{Cd}^{2+}$  ions. The height of the re-oxidation peak depended on the concentration of  $\text{Bi}_2\text{O}_3$  in SPCE (Fig. 2). The best composition of SPCE was 1.25 % (w/w) of  $\text{Bi}_2\text{O}_3$  in the carbon ink, while lower or higher mass fraction of the modifier caused lower peak current. Thus, this composition was chosen for further investigations.

As expected, the peak current of the re-oxidation depended also on the concentration of these ions, and the relationship was practically linear up to  $100 \mu\text{g l}^{-1}$  (Fig. 3). The limit of detection ( $3\sigma$ ) was  $10 \mu\text{g l}^{-1}$  for both  $\text{Cd}^{2+}$  and  $\text{Pb}^{2+}$ . The peak potential of the re-oxidation was  $-0.785 \text{ V}$  for Cd, and  $-0.565 \text{ V}$  for Pb. Probably,  $\text{Bi}_2\text{O}_3$  forms some intermediate compounds with both the metals [36], which could be a reason why the peaks occur at less negative potential values than those at mercury films [1]. Calibration plots were recorded in the solution of both cations in acetate buffer (pH 4.5) using different SPCEs in the same batch. The relative standard deviation was 3.4 – 4.9 % for cadmium and 3.0 – 4.1 % for lead (10 measurements, 20 and  $50 \mu\text{g l}^{-1}$ ). The correlation coefficients ( $r^2$ ) of these curves were 0.9964 and 0.9987 for Cd and Pb, respectively, corresponding equations calculated by the linear regression were  $y = 1.549x$  (for Cd) and  $y = 1.841x$  (for Pb), where  $x$  is the metal ion concentration (given in  $\mu\text{g l}^{-1}$ ) and  $y$  is the re-oxidation current (given in  $\mu\text{A}$ ). The correlation of the measurements was similar to that obtained earlier [9] at similarly modified carbon paste electrodes where the correlation coefficients were found 0.9966 for Cd and 0.9971 for Pb, while the slopes of the calibration curves were higher than those in the case of carbon paste electrodes ( $1.315$  and  $1.115 \mu\text{A l} \mu\text{g}^{-1}$  for Cd and Pb, respectively). When compared to mercury film electrodes [1], the re-oxidation current density was lower at SPCEs modified with  $\text{Bi}_2\text{O}_3$ .

As mentioned above, the SPCE modified with  $\text{Bi}_2\text{O}_3$  was used for the determination of lead and cadmium in drinking water and urine. The recommended upper limits for drinking water according to Environmental Protection Agency are  $15 \mu\text{g l}^{-1}$  and  $5 \mu\text{g l}^{-1}$  for Pb and Cd, respectively. The recommended values for urine are  $80 - 120 \mu\text{g l}^{-1}$  and up to  $2.6 \mu\text{g l}^{-1}$  for lead and cadmium, respectively [38]. Lead could be detected in drinking water following the practical procedure given in the experimental part, but the concentration of cadmium was below the limit of detection. Results of analyses compared to those obtained with a bismuth film-coated carbon paste electrode (Bi film generated also from  $\text{Bi}_2\text{O}_3$ , see [9]) are listed in Table I. In urine samples, however, only Pb could be determined. The rea-

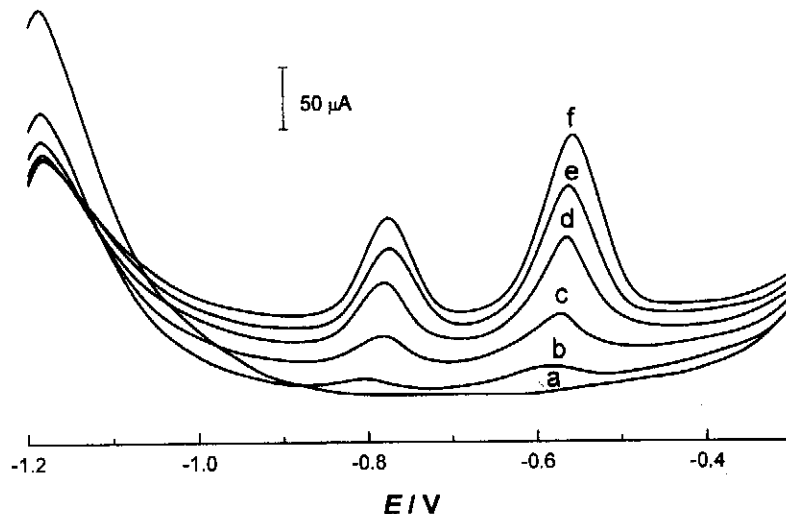


Fig. 3 Differential pulse stripping voltammograms of different concentrations (in  $\mu\text{g l}^{-1}$ ) of Cd(II) and Pb(II) in the same solution on SPCE bulk-modified with  $\text{Bi}_2\text{O}_3$  in an  $0.1 \text{ mol l}^{-1}$  acetate buffer (pH 4.5): 0 (a), 10 (b); 25 (c); 50 (d); 75 (e) and 100 (f). Pre-concentration time 600 s at  $-1.20 \text{ V}$ , scan rate  $10 \text{ mV s}^{-1}$ , pulse height  $50 \text{ mV}$

Table I Determination of lead in drinking water and urine. Comparison of data obtained using both SPCE and carbon paste electrode (CPE) modified with  $\text{Bi}_2\text{O}_3$

Sample	SPCE Pb found, $\mu\text{g l}^{-1}$	CPE [9] Pb found, $\mu\text{g l}^{-1}$
Drinking water	$23.6 \pm 1.2^*$	$19.3 \pm 0.6^*$
Urine	$123.5 \pm 6.2$	$117.7 \pm 3.5$

Intervals indicating arithmetic means  $\pm$  standard deviation always calculated from 6 measurements are given. \* Concentrated ten times after mineralization (see the text)

son was that after the mineralization procedure applied, a large peak of some unknown species (probably nitrate) occurred at of  $-0.95 \text{ V}$  and overlapped the re-oxidation peak of Cd.

All the results were compared with reference determinations carried out using ICP-MS. The results of the water samples differed by about  $+3.8 \%$  (higher with the SPCEs), whereas the result of urine had a deviation of  $+10 \%$ .

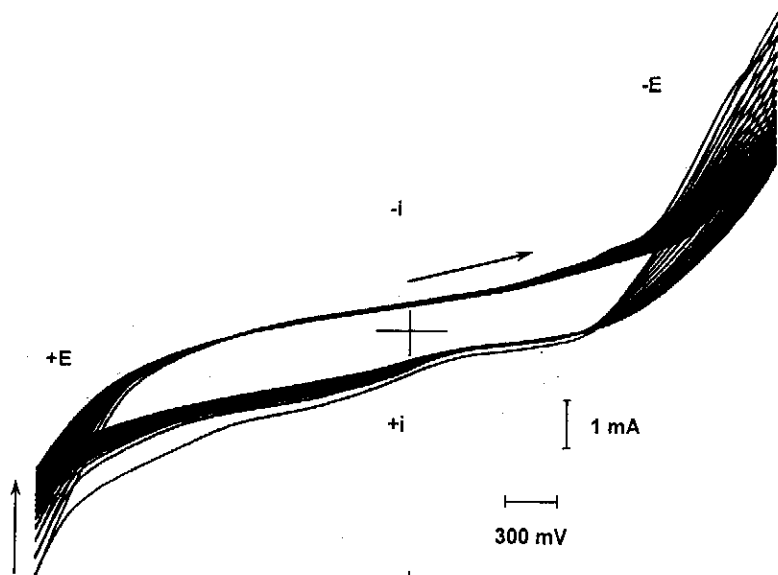
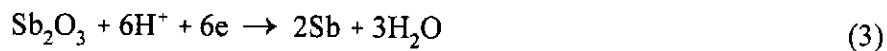


Fig. 4 Cyclic voltammograms of activation of SPCE bulk-modified with  $\text{Sb}_2\text{O}_3$  in  $0.1 \text{ mol l}^{-1}$  acetate buffer (pH 4.5), potential range from  $-2.0$  to  $+2.0 \text{ V}$ , scan rate  $100 \text{ mV s}^{-1}$

#### SPCE Modified with $\text{Sb}_2\text{O}_3$

Antimony(III) exhibits similar chemical properties as bismuth(III) but has a slightly more negative reduction potential. Therefore, antimony oxide was also investigated as a possible modifier for screen-printed carbon electrodes to evaluate its characteristics with respect to forming metal film electrodes.

SPCEs modified with  $\text{Sb}_2\text{O}_3$  were activated by cyclic voltammetry as well, but in the potential range from  $-2.0$  to  $+2.0 \text{ V}$ . The number of the cycles was the same as in the case of SPCE modified with  $\text{Bi}_2\text{O}_3$  (80 – 100 cycles), i.e., until stable voltammograms were obtained. The oxidation current in the first cycle was much higher as compared with subsequent cycles. In case of  $\text{Sb}_2\text{O}_3$ , the peaks were less pronounced than with bismuth oxide (Fig. 4). There was a large reduction peak at  $-1.8 \text{ V}$  in the cathodic scan, which corresponded to reduction of antimony oxide [39],



and at  $-1.95 \text{ V}$  the evolution of hydrogen began. The re-oxidation of Sb occurred



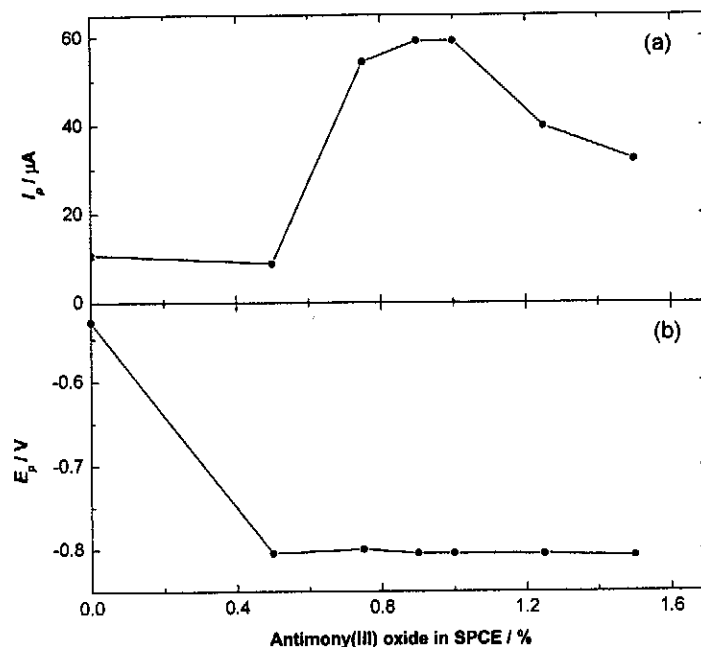
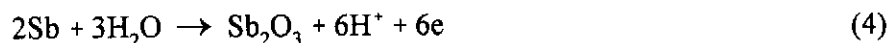


Fig. 5 Dependence of re-oxidation peak current (a) and potential (b) of Cd ( $50 \mu\text{g l}^{-1}$ ) on composition of SPCE modified with  $\text{Sb}_2\text{O}_3$ . Supporting electrolyte  $0.1 \text{ mol l}^{-1}$  acetate buffer (pH 4.5); pre-concentration time 600 s at  $-1.20 \text{ V}$ , scan rate  $10 \text{ mV s}^{-1}$ , pulse height 50 mV

at around  $+0.02 \text{ V}$



and an anodic current plateau shows the growth of the antimony oxide film on the surface of the electrode. Evolution of oxygen begins at  $+2 \text{ V}$  in the anodic scan. It seems from the cyclic voltammograms that  $\text{Sb} \rightleftharpoons \text{Sb}_2\text{O}_3$  redox process is irreversible. It should be mentioned that such an irreversible reduction of adsorbed oxygenous Sb-species deposited on gold was reported in the literature [40,41].

When compared to the above  $\text{Bi}_2\text{O}_3$ -SPCE, the activity of the  $\text{Sb}_2\text{O}_3$ -SPCE is less dependent on the modifier concentration, the optimum composition was observed for around 0.9 – 1.0 % (w/w) of  $\text{Sb}_2\text{O}_3$  in carbon ink (Fig. 5). The dependence of the Cd re-oxidation peak on the carbon ink composition had no clear maximum like in the case of  $\text{Bi}_2\text{O}_3$ , the content of 0.95 % (w/w) of  $\text{Sb}_2\text{O}_3$  was therefore used in further investigations. It was observed that the activated

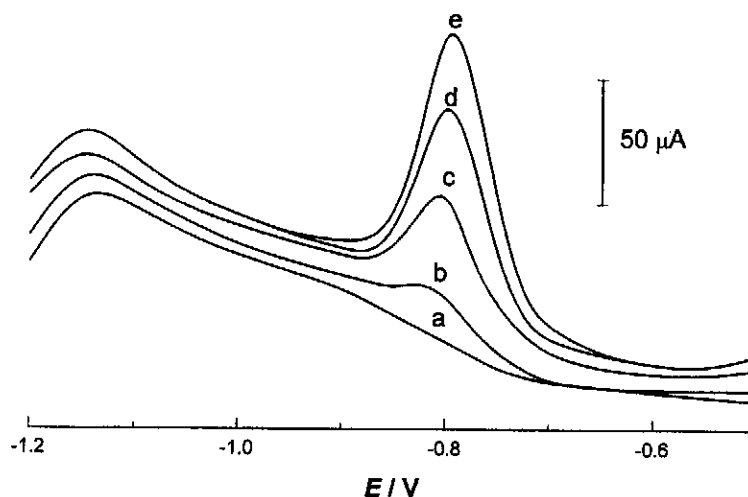


Fig. 6 Differential pulse stripping voltammograms of different concentrations (in  $\mu\text{g l}^{-1}$ ) of Cd(II) on SPCE bulk-modified with  $\text{Sb}_2\text{O}_3$  in an  $0.1 \text{ mol l}^{-1}$  acetate buffer (pH 4.5): 0 (a); 25 (b); 50 (c); 75 (d) and 100 (e). Pre-concentration time 600 s at  $-1.20 \text{ V}$ , scan rate  $10 \text{ mV s}^{-1}$ , pulse height  $50 \text{ mV}$

$\text{Sb}_2\text{O}_3$ -screen printed carbon electrode could be applied for the determination of cadmium (re-oxidation potential  $-0.805 \text{ V}$ ) but not for that of lead because at its trace levels, the resulting peak of the Pb re-oxidation did not linearly depend on its concentration. This was probably because Sb forms some stable intermetallic compound with Pb [42]; a linear dependence of the corresponding re-oxidation peak height observed on the  $\text{Sb}_2\text{O}_3$ -SPCE was obtained only for lead concentrations above  $100 \mu\text{g l}^{-1}$ .

The dependence of the re-oxidation current of Cd on the concentration is shown in Fig. 6. When compared to SPCEs modified with  $\text{Bi}_2\text{O}_3$ , the peak height is smaller. The calibration curve does not pass the intersection of axes and the limit of quantification is  $20 \mu\text{g l}^{-1}$ . This could be attributed to the worse solubility of cadmium in metal antimony or to the formation of some extent compounds with antimony like  $\text{Cd}_2\text{Sb}_2\text{O}_{6,8}$  [43], etc. Even so, the dependence of the re-oxidation current of Cd on its concentration was linear within the range from 20 to  $100 \mu\text{g l}^{-1}$ , with a relative standard deviation from 5.3 to 8.8 %. The corresponding linear regression equation is  $y = 1.750x - 24.954$  and the correlation coefficient was equal to 0.9979 (where  $y$  is the re-oxidation current in  $\mu\text{A}$  and  $x$  is cadmium concentration in  $\mu\text{g l}^{-1}$ ). Thus, based on data from Refs [1,9,44] and the above observations, it seems that the modification of such carbon substrate-based electrodes with  $\text{Sb}_2\text{O}_3$  or other Sb(III) compounds, or plating them with analogous Sb film, resp., has not so optimistic future as it was in the case of bismuth.

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