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CARBON PASTE ELECTRODES AND SCREEN-PRINTED SENSORS PLATED WITH MERCURY AND BISMUTH FILMS IN STRIPPING VOLTAMMETRY OF HEAVY METALS

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Dedicated to the Memory of Professor Stanislav Kotrlý

In this article, carbon paste electrodes and screen-printed sensors plated with mercury and bismuth films are presented in association with their applicability to the determination of Pb, Cd, and Zn in aqueous solutions using anodic stripping voltammetry. Both mercury and bismuth films were generated "in situ" either via modifying the carbon paste with the respective solid oxide (10 % m/m) or by plating the surface of screen-printed sensor in the sample solution spiked with Hg^{2+} or Bi^{3+} ions. Analytical performance of the individual types of film electrodes

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is examined and discussed based on the results and observations obtained by analysing tap and natural water samples.

Introduction

In voltammetric stripping analysis, the hanging mercury drop electrode (HMDE) has for long time been a standard building element of detection systems used for the determination of heavy metals [1]. At present, despite its excellent electrochemical characteristics, there is a growing tendency to choose the sensors made of less toxic electrode materials such as solid amalgams [2].

Valuable properties of metallic mercury can also be utilised in the configuration of the so-called mercury film electrode (MFE), representing a successful alternative to the HMDE already for several decades [3,4]. The MFE formed by inert electrode support plated with a microscopically thin mercury film practically eliminates problems associated with handling elemental mercury because the film is being prepared during measurements by electrolytic reduction of the Hg(II) species, usually using a solution of either $Hg(NO_3)_2$ or $HgCl_2$ [5]. Another possible alternative to both HMDE and MFE is a bismuth film electrode (BiFE) introduced recently [6]. In this case, also toxic bivalent mercury salts are completely replaced by environmentally friendly bismuth(III) compounds [7].

Some recent reports have demonstrated that both mercury and bismuth films can be generated *in situ* from some insoluble Hg(II) and Bi(III) compounds present directly in the electrode material. For instance, carbon inks containing precipitated HgO [8] or carbon pastes modified with Bi_2O_3 [9,10] were shown to act in this way. At present both these carbon substrates belong among prevailing electrode materials in the elaboration of new types of electrochemical sensors [11,12]. In this context it is interesting to notice their possible relation: the concepts of modification procedures developed and tested with carbon paste electrodes (CPEs) can often be utilised in the preparation of carbon inks used for mass production of screen-printed electrodes (SPEs [13]).

This article covers the continuing research work on carbon paste electrodes modified with mercury(II) and bismuth(III) oxides as well as the newly started studies with mercury and bismuth film-plated screen-printed electrodes, MF(SPEs) or BiF(SPEs), respectively. Whereas the previous investigations [14–17] were focused mainly on basic characterisation of newly proposed sensors and their analytical performance in stripping analysis, the present report archives the results and observations obtained by testing the individual electrodes for the determination of selected heavy metals in various water samples.

Experimental

Chemicals and Reagents

All the chemicals used for the preparation of stock and standard solutions were of analytical reagent grade and purchased from Lachema Brno (Czech Republic) if not stated otherwise. Stock solutions serving to prepare the supporting electrolytes, testing or sample solutions were made 1 mol l^{-1} in concentration; the standards being prepared as 0.01 mol l^{-1}. Where needed, these solutions were diluted as required. For interference studies, the standard of Ga(III) was prepared by dissolving the appropriate amount of metallic gallium in aqua regia on a heated plate. Oxides HgO ("yellow form") and Bi_2O_3 selected as carbon paste modifiers were used as solid substances (Merck). In some experiments, 5 % (m/m) aqueous solution of Nafion® (perfluorinated copolymer, Aldrich) was also used.

Water used throughout the experimental work was obtained by passing deionised water through a self-constructed distillation unit. All the solutions to be analysed were deoxygenated by purging with argon gas (purity 99.99 %, Linde Technoplyn).

Apparatus

A polarographic analyzer (Model PAR 174, EG & G Princeton Applied Research, U.S.A.) was used either connected to an XY-recorder (model "HP 704P", Hewlett-Packard) or coupled with a personal computer via an interface card (PC AD/DA-14, Model FPC-011; Flytech Technology, U.S.A.), and controlled by an "ADDA-174 A" software [18]. Both assemblies were combined with an electrode stand adapted for measurements with CPEs and SPEs. For some measurements, a BAS 100B electrochemical analyser (Bioanalytical Systems, U.S.A.) equipped with the BAS 100W software and a PPA 02 polarographic analyser (LABIO a.s., Prague, Czech republic) were also employed.

Stirring was performed with a Teflon®-coated magnetic bar at approx. 300 rpm. The pH was measured using a digital pH meter (Model 420A, Orion, U.S.A.) equipped with a combined glass pH sensor (Model OP-0808P, Radelkis, Hungary). The ohmic resistance of SPEs was measured with a Voltcraft® multimeter (model VC 404, Conrad Electronics, Germany).

Electrodes

• *Carbon Paste Electrode Modified with Mercury(II) Oxide* ["HgO-CPE"]. The carbon paste was prepared by intimately homogenising a mixture of 0.50 g

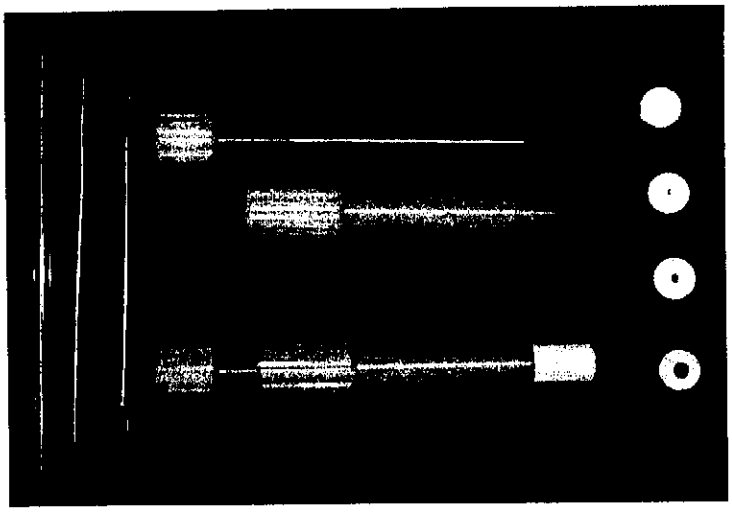

Fig. 1 Carbon paste electrode holder designed in mechanical workshops at the University of Pardubice. Imaged as the assembled and disassembled construction together with a set of exchangeable tips and the accessories for carbon paste filling

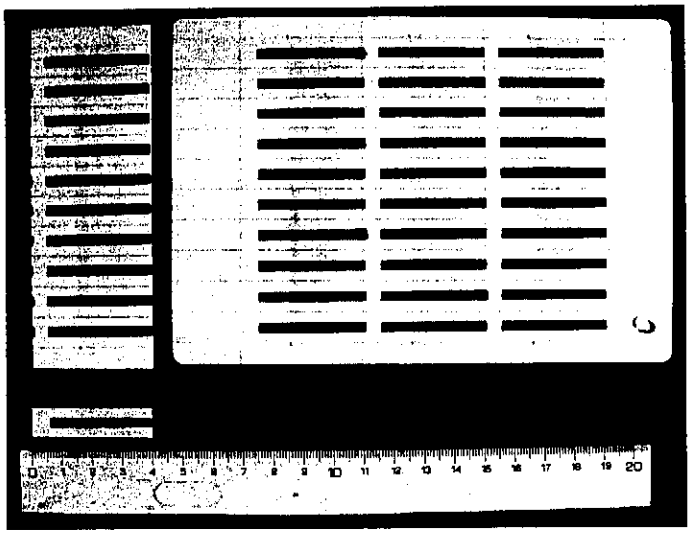

Fig. 2 Screen-printed sensors: Right – A plate with 30 electrodes obtained by the printing process; left – a part with 6 electrodes (the edges already removed); below – one SPE ("stripe") given along with a ruler in order to show the electrode size and dimensions

spectroscopic graphite powder ("RW-B", Ringsdorff Werke, Germany) + 0.10 g HgO + 0.40 g silicone oil ("Lukoil MV 15500"; Lučební závody Kolín, Czech Republic) using a pestle and mortar. In the same way, the bare carbon paste was also prepared and used in some comparative experiments. The ready-to-use pastes were then packed into carbon paste holders equipped with a piston [19]. Their construction together with the individual components, exchangeable Teflon® tips and accessories are shown in Fig. 1, imaging also the assembling and disassembling of the whole set-up. In this work, a tip with the same end-hole (Ø = 2 mm) was always used.

• *Carbon Paste Electrode Modified with Bismuth(III) Oxide* ["Bi_2O_3-CPE"]. A mixture consisting of 0.50 g "RW-B" graphite + 0.05 g Bi_2O_3 + 0.40 g "Lukoil" silicone oil was prepared and packed into the electrode body identically as described above.

• *Mercury and Bismuth Film Plated Screen-Printed Electrodes* ["MF(SPEs); BiF(SPEs)"].

A portion of 4.5 g carbon ink (C50905DI, Gwent Pontypool, U.K.) was pretreated in an ultrasonic bath for ca 20 min and then immediately taken for fabrication of SPEs. For their screen-printing, inert laser pre-etched ceramic supports (Coors Ceramic, Chattanooga, U.S.A.) were used. The preparation consisted of applying thick layers (0.05 mm) of the ink onto the ceramic material through an etched stencil with the aid of a screen printing device (Model SP-200; MPM, USA). The resultant plate bearing 30 pieces of SPEs in a regular structure of separated black stripes (see Fig. 2) was dried at 60 °C for approx. one hour. Afterwards, the all SPEs were successively protected by an insulating layer of a dielectric substance brushed onto their surface so that each sensor had an active (i.e., uncovered) area of ca 10 mm^2. Prior to use, the individual electrodes were obtained by careful breaking the plate at the pre-cut lines. Each SPE chosen for measurement was provided with electrical contact *via* an ordinary crocodile clamp.

Onto the SPE supports, both mercury and bismuth films were deposited *in situ* when using a spike of either 0.01 M $Hg(NO_3)_2$ or $Bi(NO_3)_3$ to the supporting electrolyte. Their total concentration in the solution was chosen to be at least one order higher than that of the ions to be analysed [3]; e.g., 250 ppb for determinations of heavy metals in an interval from 1 – 50 ppb or 2.5 ppm for a concentration level of 100 – 500 ppb.

• *Reference and Auxiliary Electrodes*. A self-made Ag/AgCl electrode (containing 1 M KCl as the inner electrolyte) as the reference and a Pt-plate (ca 0.5 cm^2) as the counter electrode completed the cell.

Solutions for Analysis

Model Solutions. They were made as the appropriate spikes of the corresponding heavy metal(s) in a defined volume of distilled water acidified with 65 % HNO_3 to pH 2. Where necessary, specification of the individual model solutions is given later in the text.

Tap Water Samples. Samples were collected from a common water-supply pipeline in laboratories at University of Ljubljana, University of Pardubice, and in a flat at suburb "Polabiny" in Pardubice. Water was sampled either immediately after opening the pipe or by allowing water to flow out in a full stream through the open pipe for 5 min before sampling. The individual samples were acidified again with 65 % HNO_3, transferred to polyethylene bottles, and stored in a refrigerator at 4 °C.

Natural Water Samples. The first sample was obtained from a sand pond in Hrádek (ca 5 km north of Pardubice), the second one from a small lake Bajkal in Pardubice. Also these specimens were promptly stabilised by acidification and placed to a fridge prior to analysis.

Sample Pretreatment

Two samples of tap and natural water were divided to two fractions ("sub-samples"). The first fraction was taken for analysis without any treatment (except previous acidification), the second underwent an irradiation by UV-light for approx. 30 min. No chemical agent was used during this decomposition process.

Procedures

Renewal of the Carbon Paste Electrode Surface. In the case of both HgO- and Bi_2O_3 - CPEs as well as the bare CPE, approx. 0.5 mm carbon paste was extruded from the electrode holder, cut off, and the surface was smoothed with a wet filter paper. Typically, such mechanical renewal was made only when starting a new series of experiments (e.g., prior to analysis of sample solutions and the following measurements after the corresponding standard additions).
Activation of Screen-Printed Electrodes. Selected series of SPEs was exposed to a potential cycling between −1.0 V and +1.0 V in a solution of 0.01 M $HClO_4$ [11]. In this way, ten successive cycles with each electrode were carried out.
Pretreatment of Screen-Printed Electrodes with Nafion®. The part with the active surface was shortly immersed in a solution of Nafion® and dried under an IR-lamp.

Then, the SPEs so pretreated were immediately used for measurements.
Stripping Voltammetry. After preparation of the solution to be analysed and its deaeration with argon, the accumulation ("preconcentration step") was performed while stirring at selected accumulation potential, E_{ACC}, for a given period, t_{ACC}. After the equilibrium period, t_{EQ}, in quiet solution (usually for 15 s), the voltammetric measurement was performed by anodic scanning from the E_{ACC} to a final potential, E_{FIN}. Again, these stripping parameters are specified later under discussion of the individual experiments. Regarding other conditions, typical scan rate was 20 mV s^{-1}, the pulse height, ΔE, -50 mV and the sampling rate 5 data s^{-1}.

Data Processing and Evaluation

To quantify the concentration, the standard addition method with at least two aliquots was used. The analytical signals were computed as peak areas. Some experiments were evaluated by means of a statistical method for small sets of data [20].

Results and Discussion

HgO Bulk-Modified Carbon Paste Electrode

With the HgO-CPE, a mercury film is generated *in situ* during the preconcentration step similarly as with the bare electrode support plated with mercury in the solution to be analysed spiked with the Hg(II) species [3]. However, compared to such Florence's MFE, the film generated from HgO-bulk modified CPE exhibited a rather noisy base-line. This can be seen in Fig. 3 when comparing the respective sets of stripping voltammograms that were obtained by analysing the same sample of natural water. Undesirable disturbances accompanied practically each measurement with the HgO-CPE and efforts to suppress the noise by optimising the content of HgO in the paste were almost unsuccessful.

Thus, although the HgO-CPE offer detection limits down to 1 ppb for Pb and somewhat higher for Cd when the corresponding signals could be reproduced within ±5 – 10 % [21], the use of the HgO-CPE in practical analysis has been found rather problematic. The signals of interest were often distorted by the noise or even totally overlapped, which was in contrast with fine measurements using the MF(CPE) prepared in Florence's way (again, compare the voltammograms in Fig. 3). Parallel tests with two sub-samples of non-treated water and water irradiated by UV-lamp revealed that the distorted signal at the HgO-CPE was not caused by eventual interactions between the electrode and matrix constituents in

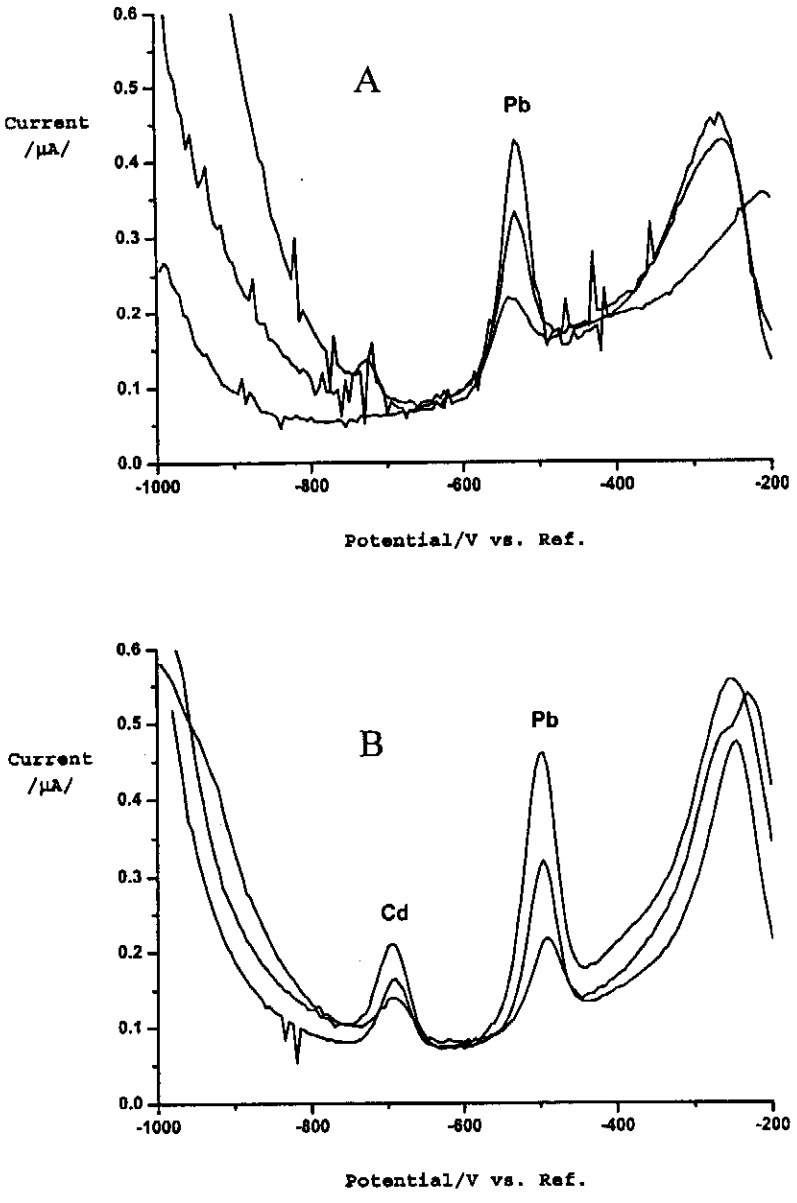

Fig. 3 Anodic stripping voltammograms of Pb obtained by analysing the sample with two different mercury film-plated carbon paste electrodes: A – HgO-CPE; B – MF(CPE) prepared by plating *in situ* [3]. 1) sample solution (see below), 2–3) standard additions (two aliquots) of A – 10 ppb Pb^{2+}, and B – 10 ppb Pb^{2+} + 5 ppb Cd^{2+}. Experimental conditions: BAS 100B analyser; DPASV; silicone oil-based CPE; supporting electrolyte (s.e.), A – 18 ml sample of sand pond water + 2 ml 1 M HCl, B – s.e. + 20 μl 0.001 M Hg^{II}; E_{ACC} = -1.0 V vs Ag/AgCl; E_{FIN} = -0.2 V; t_{ACC} = 5 min; t_{EQ} = 15 s

the sample.

It seems that problems with unstable response of the HgO-CPE noticed already during the initial studies [14] may originate from the chemical stability of mercury oxide and its unwillingness to be reduced electrolytically. The occurring noise could also be due to a certain dissolution of HgO in acidic media because such "bleeding" is from time to time observed at CPEs modified with insufficiently immobilised or in water slightly soluble substances [22].

Apparently, it will be necessary to seek an alternative compound to be used instead of HgO for the film generation in the carbon paste bulk. Perhaps, some of mercury(I) derivatives that are generally easily reducible and minimally soluble in aqueous solutions would be the substances of choice [23].

Bi_2O_3 Bulk-Modified Carbon Paste Electrode

In contrast to the previous bulk modification with HgO, the use of Bi_2O_3 in the carbon paste substrate was found to be a very convenient concept for obtaining the electrode material capable of generating the film *in situ*. Bismuth film generated at the Bi_2O_3 - CPE exhibited a sufficient stability in acidic media and its sensitivity towards heavy metals tested was fully comparable to that observed with a CPE plated in the solution spiked with Bi^{III} ions.

Basic characterisation of the Bi_2O_3 - CPE in anodic stripping voltammetry of Pb, Cd, and Zn [24] has brought results that can be summarised as follows: (i) optimal supporting electrolyte, acetic buffer (pH 4.5), (ii) 10 % Bi_2O_3 in the paste; no mechanical renewal of the electrode surface between the successive scans within a series of measurements; (iii) linearity in the concentration ranges: 1 – 5 and 10 – 100 ppb Pb, 10 – 50 Cd, and 100 – 1000 ppb Zn; detection limits for a 10 min accumulation (estimated as 3 σ): 1 ppb Pb, 2 ppb Cd, and approx. 50 ppb Zn. A lesser content of Zn in the sample was not detectable due to the limited cathodic range of the electrode caused by the interfering background from hydrogen evolution. Moreover, there was a serious interference from copper(II) in the determination of Zn due to the formation of intermetalic compounds of the Cu_aZn_b type [25]. Reportedly, at a BiFE prepared by pre-plating, it can be suppressed by adding Ga^{3+} to the solution where a concurrent intermetallite Cu-Ga is formed [26]. As depicted in Fig. 4, the same principle could successfully be applied with Bi_2O_3 - CPE.

In Table I, some results of studies on the signal stability at the Bi_2O_3 - bulk modified carbon paste electrode are summarised. The data document satisfactory reproducibility of the signal for Pb over a relatively wide concentration range. However, at the upper limit, one can already notice a certain trend in the response increase (see the set "n_1, n_2,...n_6" for sample No. 2). This is in accordance with some previous observations [16,17] that BiF(CPEs) utilising plating *in situ* are less

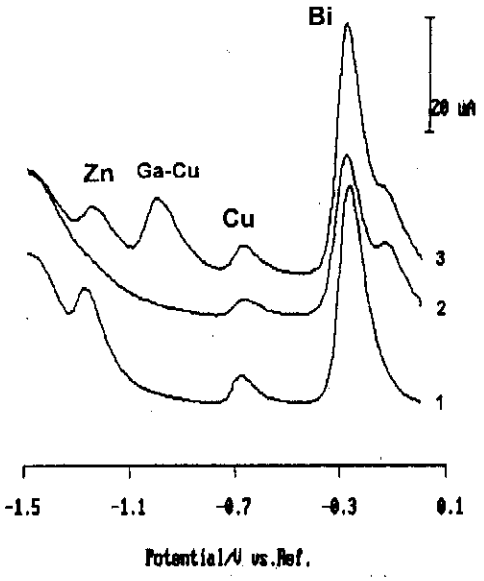

Fig. 4 Interference from copper in the determination of zinc and its suppression by the gallium(III) ions. 1) 50 ppb Pb^{2+} + 100 ppb Zn^{2+}, 2) after addition of 50 ppb Cu^{2+}, 3) and of 500 ppb Ga^{3+}. Experimental conditions: PAR 174A polarographic analyser coupled with PC; Bi_2O_3-CPE; s.e., 0.3 M acetate buffer; E_{ACC} = -1.5 V; E_{FIN} = -0.2 V; t_{ACC} = 30 s; t_{EQ} = 15 s. Other conditions as in Fig. 3

Table I Analysis of model solutions at the Bi_2O_3-bulk modified carbon paste electrode. Studies on the signal stability

Solution spiked with Pb[a]	Number of replicates[b]	Individual peak heights for Pb-signal (for n_1, n_2, ... n_6), μA						Resultant peak height[c], μA
No. 1	6	2.20	2.25	2.35	2.50	2.35	2.50	2.36 ± 0.12
No. 2	6	33.9	34.2	34.5	35.0	35.6	35.9	34.8 ± 0.8

Notes: [a]1:2 ppb, 2:100 ppb Pb^{2+}; [b]successive measurements at the same film; [c]given as intervals $x \pm k_M.R$, where x is the arithmetic mean, R denotes the range of measurements, and k_M is a statistical criterion (for details, see Ref. [20])

reliable for detection of higher concentrations (above the trace level).

The results of practical analyses surveyed in Table II show a good performance of the Bi_2O_3-CPE for the determination of both Pb and Zn in water sample with a simpler matrix. In case of the determination of the latter, no Ga(III) was added as the content of the Cu^{2+} ions was assumed to be sufficiently low with respect to Zn^{2+}, which was also confirmed by the analyses themselves. By comparing the

corresponding concentrations of Pb and Zn determined in untreated and UV-irradiated water together with those ascertained by AAS, it is evident that even mild acidic acetate buffer is able of deliberating single ions for their detection at the Bi_2O_3-CPE. Furthermore, it is necessary to emphasize that rather high concentration of lead found in tap water depended upon sampling (see Notes). If water had been left to flow out the pipe for a while, the content of this heavy metal decreased down to 2 ppb as found by the respective analyses with both DPASV at Bi_2O_3-CPE and AAS. Table II does not include the determination of Cd because, as expected, the analytical performance of the electrode towards cadmium was not sufficient to identify its traces in tap water (found 0.4 ppb only when employing reference AAS determination [24]).

Table II Analysis of tap water at the Bi_2O_3-bulk modified carbon paste electrode. Results of determination

Sample[a]	Content of Zn and Pb found, ppb			
	DPASV with Bi_2O_3-CPE		Reference AAS	
untreated water	Zn	525.2		
	Pb	25.1		
			Zn	576
			Pb	27.8
Water irradiated by UV-light	Zn	561.2		
	Pb	27.5		

Notes: [a]Collected at the University of Ljubljana; [b]sample taken immediately from the pipe

Mercury- and Bismuth Film Plated Screen-Printed Electrodes

As already mentioned, SPEs can be employed — similarly as CPEs — in the form of a substrate allowing one to generate metallic films either in a solution of the corresponding ions or from a substance embedded in the ink. Also because of this, SPEs have become one of the objects being newly investigated in our research group [27]. Until now, more conclusive results were obtained with mercury- and bismuth film plated SPEs prepared in the former manner, i.e., using solutions of mercury(II) and bismuth(III) salts [28].

Table III offers the results of analyses with both MF(SPEs) and BiF(SPEs) evaluated as recovery rates for the determination of Pb, Cd, and Zn in model solutions. The data summarised show that detection capabilities of both types of film-plated SPEs do not compete yet with analogous metallic films deposited onto

Table III Analysis of model solutions using screen-printed electrodes plated *in situ* with : A) mercury- and B) bismuth film. Determination of Pb, Cd, and Zn

Supporting electrolyte[a] spiked with	Added, ppb	Found, ppb	Recovery rate, %
Pb^{2+}	100	115.0[A]	115
	60	54.2[B]	90.3
Cd^{2+}	170	169.0[A]	100.7
	40	37.1[B]	92.8
Zn^{2+}	300	283.7[B]	97.6

Notes: a) A: 0.1 M HCl + 1×10^{-5} M Hg^{2+}, B: 0.1 M acetate buffer + 2×10^{-5} M Bi^{3+}

CPEs. The screen-printed sensors from the series tested exhibited a considerably high background, less favourable signal-to-noise characteristics, which resulted in worse analytical performance. Owing to this, mercury- and bismuth-plated SPEs could not reach the trace concentration level of any heavy metal and, hence, their practical applicability was very limited. Only a high content of zinc in tap water sampled from a laboratory pipe could be detected and quantified, the corresponding analysis revealing 810 ppb Zn whereas reference AAS found 926 ppb. The concentrations of Zn in the remaining two samples (tap water collected in a flat and lake water) were far below the detection capabilities of the BiF(SPE) chosen for these experiments. This was confirmed by a reference AAS ascertaining 23 ppb and 9 ppb Zn, respectively.

One of reasons why SPEs operated in this way was probably the fact that a series of screen-printed sensors used for the testing was manufactured more than one year ago and could, therefore, undergo some ageing, deteriorating their overall quality. Coincidentally, such a phenomenon has also been observed with some carbon pastes [11].

In order to improve the performance of SPEs as supports for both mercury and bismuth films, some special pretreatments were examined. Occasionally recommended surface activation by cycling between highly positive and highly negative potentials [23] was found ineffective. On the other hand, a test with Nafion® used for protecting the electrode surface [29] brought a certain improvement, namely a noticeable increase in the response of interest. This beneficial effect of the copolymer layer seems to have some promise, but it still requires further investigation.

Despite high detection limits, measurements with most of MF(SPEs) and BiF(SPEs) were quite well reproducible and repeatable, which is illustrated in Fig. 5 depicting an overlay of voltammograms recorded with a set of ten sensors taken

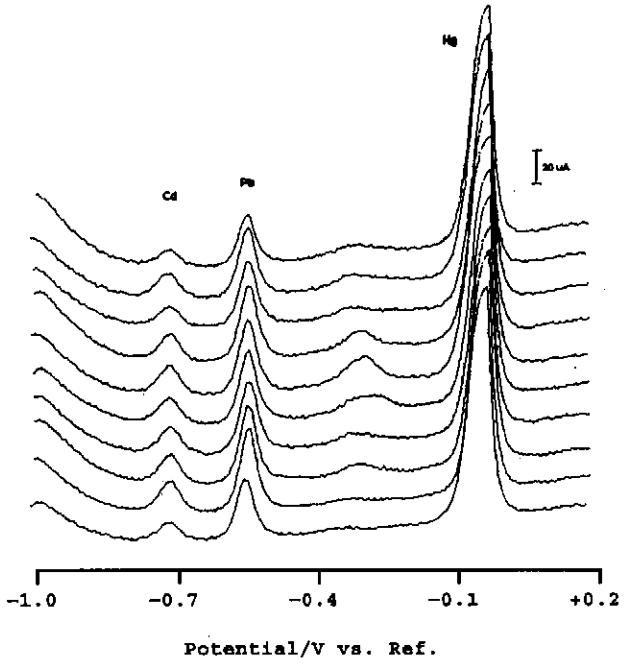

Fig. 5 DPASV signals for Pb and Cd obtained at mercury films plated onto ten different SPEs from one production series. Experimental conditions: PPA 02 polarographic analyser; s.e., 0.1 M HCl + 5×10^{-5} M Hg^{2+} (10 ppm); $c(Pb^{2+},Cd^{2+})$ = 3×10^{-6} mol l^{-1} (600 and 360 ppb, resp.); E_{ACC} = −1.0V; E_{FIN} = +0.5 V; t_{ACC} = 2 min s; t_{EQ} = 10 s. Other conditions as in Fig. 3

from one production series and used as supports for a mercury film. When evaluating these curves obtained by testing one piece after the other, the signal for Pb could be repeated within an error of ± 9.7 % and a smaller response for Cd with a deviation of ±16.1 %. It should be emphasised that the corresponding analytical signals at each support *extra* could be reproduced within ±3 % only.

The individual voltammetric experiments also helped to confirm a close relation between the printing process and the quality of the individual sensors [30]. It was ascertained that the SPE printed as stripes near the edge of ceramic plate exhibited somewhat worse electrochemical characteristics compared to those of sensors located in the centre. This can be associated with the previous experience that the different position of the stripes across the plate was reflected in their ohmic resistance: it varied from 100 to 200 Ω, the latter being typical for the edge-placed stripes [28].

It can be stated that the above-described studies have demonstrated the inevitability of electrochemical characterisation and testing of each newly made

series of SPEs as well as the principal importance of the screen-printing process as such.

Acknowledgements

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