CARBON PASTE ELECTRODE AS A SUPPORT FOR MERCURY FILM IN POTENTIOMETRIC STRIPPING DETERMINATION OF HEAVY METALS

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Carbon paste electrodes containing silicone or paraffin oil as the pasting liquids, preplated with a mercury film, were tested for possible use in potentiometric stripping determination of heavy metals like lead, cadmium and copper. The detailed study has shown that the results are comparable with those obtained with widely used mercury-coated glassy carbon electrode with regard to the linear response at low ppb levels, detection limits, reproducibility, *etc.* The potentiometric stripping analysis with both electrode materials was used for the determination of lead and copper in a soot sample. No significant differences were found when these results were compared with a reference determination performed by graphite-furnace atomic absorption spectrometry.

Key words: Carbon paste electrodes; Glassy carbon electrode; Mercury-coated paste electrode; Potentiometric stripping analysis; Lead; Cadmium; Copper.

A hanging mercury drop electrode (HMDE) was the first working electrode used for determination of heavy metals by potentiometric stripping analysis (PSA) invented and first described by Jagner and Graneli[1]. Since then, different materials coated with a mercury film have been tested as supports for an appropriate replacement of the HMDE; glassy carbon seemed the best support for metallic films[2] and became the most frequently used for PSA (either with rotating or stationary electrode). Other carbon substrates such as carbon fibres were also found attractive and were often used in flow analysis or microanalysis[3]. To obtain reproducible and accurate results, the film stability ranks among the most appreciated features of materials mentioned above.

Only a few articles dealing with comparative studies on mercury film electrodes (and HMDE) were found in the literature. Wang and Tian[4] demonstrated the use of mercury-coated screen-printed electrodes for determination of lead in drinking water and urine, reporting good reproducibility and low detection limit. Panicheva and Filanovskii[5] have achieved a comparable performance of mercury-coated crystalline and glassy carbon electrodes in determination of lead in the presence of cadmium. Recently, Zhang and Huang[6] have published a paper on a mercury-coated silver electrode utilised for the determination of lead and cadmium in sulfanilic acid.

In the present contribution, determination of heavy metals was tested at mercury-coated carbon paste electrodes (MCCPE). For this purpose, carbon pastes with silicone or paraffin oil were prepared and tested in two ways, first using a mixture of copper, lead and cadmium solutions and, second, the behaviour of elements was followed separately. The experimental work was alternately carried out with the mercury-coated glassy carbon electrode (MCGCE). In contrast to stripping voltammetry[7,8], no report about MCCPE in PSA was found in the literature.

As the final step, copper and lead were determined in a soot sample using PSA with both electrode materials; graphite-furnace atomic absorption spectrometry was used as a reference method.

EXPERIMENTAL

Solutions

Standard solutions of Pb(II), Cd(II), Cu(II) with a concentration of 0.01 mol/l were prepared by dissolving appropriate weighed amounts of $Pb(NO_3)_2$, $CdCl_2 \cdot 2H_2O$ and $CuSO_4 \cdot 5H_2O$ in distilled deionised water, which was used throughout. A stock solution of Hg(II) was obtained by dissolving $Hg(NO_3)_2 \cdot H_2O$ in 1.3 M HCl to the total concentration of 800 ppm. Dilute solutions were freshly prepared daily.

Apparatus

A TraceLab potentiometric stripping unit PSU22 with a sample station SAM 20 was used and controlled by PC *via* the TAP2 program (all from Radiometer Analytical S. A., France). The three-electrode measuring cell has comprised a working electrode, either a CPE (see the next paragraph) or a GCE (F3600, Radiometer Analytical S. A., France), saturated calomel reference and auxiliary platinum electrodes.

Carbon Paste Electrodes

Carbon pastes were prepared by mixing a carbon powder (0.5 g) and a pasting liquid (0.2 ml). Two types of both components, *i.e.*, CR 5 (Tesla Lanškroun, Czech Republic) or RWB (Ringsdorff-Werke, Germany) as carbon powders, and silicone oil (Lučební závody

Kolín, Czech Republic) or paraffin oil (Uvasol, Merck) as pasting liquids, were used. For other details, see ref.[9]. The CR5 powder was mixed with both the liquids, while the RWB one only with silicone oil. The carbon paste materials were stored in home-made holders[9] with an active surface diameter of 3 mm. The electrode surface was renewed by removing a thin layer of the used paste by a wet filter paper.

Mercury Film Preparation

Before applying a plating procedure, the glassy carbon electrode (GCE) was polished with an aluminium oxide powder supplied by Radiometer whilst for CPE piece of wet filter paper was used. The working electrodes were then preplated with a mercury film from a nondeaerated 160 ppm Hg(II) solution in 0.25 M HCl at a stepwise changing potential (–300, –600 and –900 mV) and preplating time (1, 2 and 3 min). The solution was stirred during the plating procedure at 900 rpm. After that, the working electrode was kept at a constant potential of –50 mV because of the film cleaning prior to measurements. Such preplated electrodes could be used for many hours without changes in signal response.

PSA Procedure

The preplated working electrode was immersed into the supporting electrolyte of 0.1 M HCl and 10 ppm of Hg(II) which contained the required concentration of either one or more metals. During the accumulation step, the constant potential of -900 mV was applied for different time (from 1 to 5 min depending on metals concentrations) and the solution was stirred at 1 500 rpm. The potentiometric stripping step which followed was carried out using an open electrical circuit in unstirred solution in the presence of Hg(II) ions. The recording of potentiograms started at –900 mV and stopped at –50 mV before the mercury film reoxidation could take place preventing thus the mercury film from any possible damage. At the same time, the surface was cleaned before subsequent measurements were started.

RESULTS AND DISCUSSION

The carbon paste as a very cheap and easy-to-get electrode material was tested for the performance in the determination of heavy metals in a simple way. No special pretreatment of electrodes, such as preanodisation of at a high positive potential or other auxilliary procedure either before or during measurement, was used except for a routine polishing of the GCE and CPE.

Figure 1 presents a comparison of potentiograms recorded under the same conditions in the solution containing 0.16 ppm cadmium, 0.32 ppm copper and 0.16 ppm lead at the MCGCE (Fig. 1a) and MCCPE (Fig. 1b; in this case CR5/SO). As expected, responses look similar and peaks are well defined with both materials. The most remarkable change can be seen in the peak shape of copper. A lower and wider peak should result from a bit different relations among a carbon paste surface, mercury and copper in contrast to a system involving a glassy carbon, while cadmium and lead peaks are analogous. This fact, however, excludes some possible changes in

the mercury film structure on the carbon paste supports in contrast to the glassy carbon material. Peak potentials remained unchanged provided that we can neglect very slight shifts of 10 mV for cadmium and lead and 30 mV for copper.

Figure 2 brings a comparison of calibration curves for lead measured at the MCGCE and three different MCCPE in the presence of cadmium and copper. There is no significant difference among these curves and all curves are more or less linear. This indicates a very similar quality of the mercury film obtained on each electrode and its similar behaviour to the metal mix-

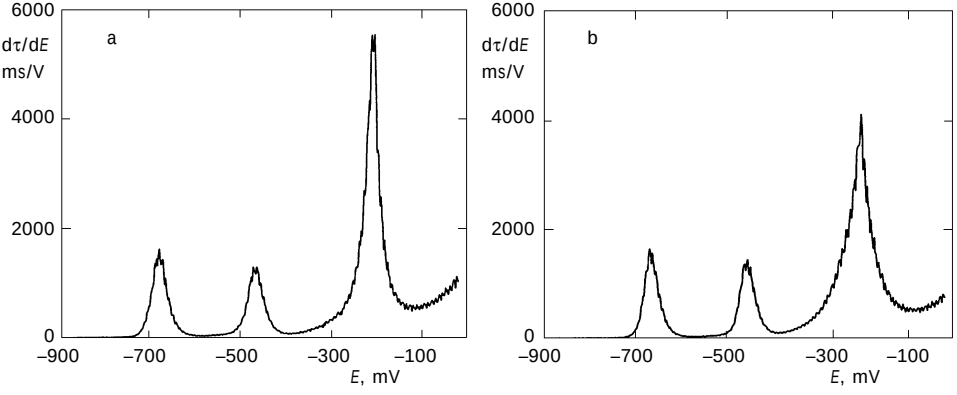

FIG. 1

Typical potentiograms at the mercury-coated GCE (a) and the mercury-coated CPE (CR5/SO; b). Conditions: 0.16 ppm Cd(II), 0.16 ppm Pb(II), 0.32 ppm Cu(II) and 10 ppm Hg(II) in 0.1 M HCl; accumulation potential –900 mV; accumulation time 60 s; peak potentials in mV: Cd –676 (–670), Pb –466 (–458), Cu –210 (–182)

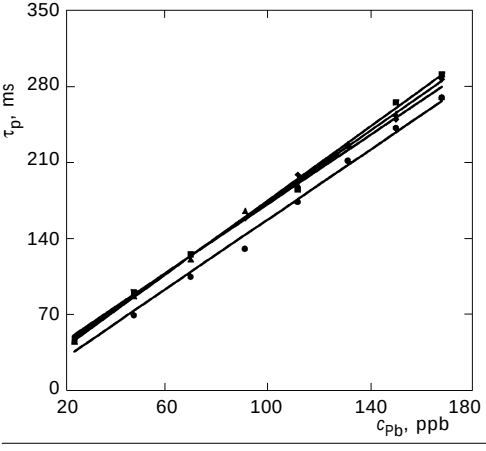

FIG. 2

Calibration curves for lead in the presence of cadmium and copper obtained with different electrodes: ◆ GCE, ■ CR5/SO, ▲ CR5/Uv, ● RWB/SO. Conditions: eight consecutive additions of 0.5 ml of mixed solution containing 1 ppm Cd(II), 1 ppm Pb(II) and 2 ppm Cu(II) to 20 ml of the supporting electrolyte (10 ppm Hg(II) in 0.1 M HCl); accumulation potential –900 mV; accumulation time 60 s. Axes: peak time (τ_p), lead concentration (c_{Pb})

ture. The same results follow from Fig. 3, where a 1 ppm lead solution has been stepwise added instead of solution containing all metals. A bit higher sensitivity, however, was reached with the MCCPE (CR5/SO). Moreover, the experimental points fit better to calibration curves as indicated also by the reproducibility data summarised in Table I. The obtained relative standard deviations (RSD) are in most cases lower in solutions containing only one element than in mixtures. A possible explanation can be found in intermetallic interactions[10], which becomes significant at appropriate concentration ratios. Intermetallic compounds are generally the most serious source of interferences discovered so far in PSA (ref.[3]). Analogous conclusions were also found for the behaviour of cadmium and copper, but their calibration curves which are similar to Figs 2 and 3, are not shown.

TABLE I

Reproducibility of ten consecutive measurements of the peak area for cadmium, copper and lead with different electrodes. The values *M* and *F* denote RSD (in %) for the given metal in the presence and in the absence of the other metals, respectively

Metal	GCE		CR5/SO		RWB/SO		CR5/Uv	
	M	*F*	*M*	*F*	*M*	*F*	*M*	*F*
Cu	3.4	3.1	3.8	2.7	4.2	4.7	2.9	2.1
Pb	3.0	2.2	4.6	5.1	3.7	3.3	3.5	–
Cd	2.6	2.1	5.0	3.9	4.2	3.7	3.7	4.2

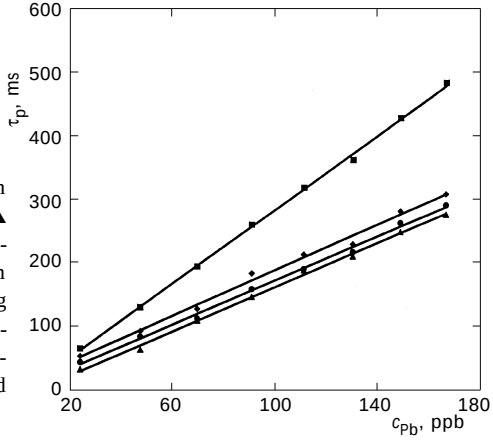

FIG. 3

Calibration curves for lead obtained with different electrodes: ◆ GCE, ■ CR5/SO, ▲ CR5/Uv, ● RWB/SO. Conditions: eight consecutive additions of 0.5 ml of a 1 ppm Pb(II) solution to 20 ml of the supporting electrolyte (10 ppm Hg(II) in 0.1 M HCl); accumulation potential –900 mV; accumulation time 60 s. Axes: peak time (τ_p), lead concentration (c_{Pb})

While the concentrations of heavy metals should be in most cases lower than in the previous work, we have examined analytical response reaching the limit of determination (under conditions of this work). Thus, Fig. 4 shows a comparison of calibration curves for lead recorded with MCGCE and with MCCPE (CR5/SO appeared to be the best of the tested carbon pastes). We have achieved good linearity at the concentration range 5–35 ppb for the 3-min accumulation period. Similar curves were also obtained for cadmium and copper (not shown) in concentration levels 1–25 and 20–70 ppb, respectively.

Detection limits were evaluated as well. The measurements with the 5-min accumulation period were carried out in the supporting electrolyte containing a total concentration of 1 ppb cadmium or lead and 5 or 10 ppb copper. Compared to the same supports as mentioned in the previous paragraph, we get detection limits of 0.1 and 0.2 ppb for cadmium, 1.0 and 0.4 ppb for lead and 3.0 and 1.5 ppb for copper. These values are comparable with those obtained for cadmium and lead on mercury-coated screen printed electrodes[4]; the method, however, comprised a twice longer accumulation period. The 3 : 1 signal-to-noise ratio was used to evaluate all detection limits.

To get an idea about precision and accuracy of results, we have determined a recovery at given concentrations achieved by the addition of the metal into the supporting electrolyte. All concentrations were evaluated by the standard addition method (mostly three additions). The recovery results for each metal and electrode are summarised in Table II. While satisfactory results were obtained for cadmium and lead, the copper determination suffered from serious difficulties. The GCE and CPE (CR5/Uv)

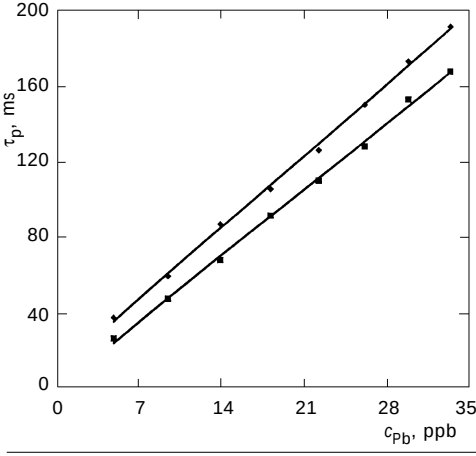

FIG. 4
Calibration curves for lead obtained with a mercury-coated GCE (◆) and with mercury-coated CPE (■) in low concentration range. Conditions: eight consecutive additions of 0.5 ml of an 0.2 ppm Pb(II) solution to 20 ml of the supporting electrolyte (10 ppm Hg(II) in 0.1 M HCl); accumulation potential –900 mV; accumulation time 180 s

yielded results with a precision better then 10%) while for others an error within 25% was achieved. This failure can be partly explained by the complicated electrochemical behaviour of copper itself[3,10]. In addition, Jagner *et al.* got very similar results by determining copper in drinking water[11], where the concentrations were evaluated by the internal standard method.

Finaly, both supports were compared in the determination of copper and lead in a soot sample. No complicated sample preparation was necessary. The soot sample was treated for 15 min by an ultrasonic leaching procedure in 1 M nitric acid, filtered and filled up to the required volume. As a reference method, determination by graphite-furnace atomic absorption spec-

TABLE II
Recovery determination for cadmium, copper and lead with different electrodes

Metal	Concentration, ppb				
	Given	Found			
		GCE	CR5/SO	RWB/SO	CR5/Uv
Cu	50	43.9	39.4	–	54.9
	100	93.3	78.5	75.0	89.5
Pb	25	25.7	25.5	24.1	22.8
	50	52.8	51.4	45.6	46.1
Cd	25	26.3	23.7	23.1	19.1
	50	51.2	43.9	45.9	44.3

TABLE III
Comparison of real sample analyses by graphite-furnace (GF) AAS and PSA with different electrodes

Method	c_{Cu}(mean), ppm (RSD, %)	c_{Pb}(mean), ppm (RSD, %)
GF-AAS	0.281 (0.320)	15.89 (1.38)
PSA/MCCPE(CR5/SO)	0.288 (7.060)	15.85 (1.84)
PSA/MCGCE	0.304 (4.270)	15.82 (2.40)

trometry was chosen. Table III summarises the data obtained by the analysis. The accuracy agreement between average concentrations of both metals achieved using PSA method and GF-AAS is apparent. In the case of copper, however, this agreement is surprisingly good because of the worse recovery measurement obtained in the electrochemical way.

CONCLUSION

Carbon paste electrodes were applied in potentiometric stripping analysis[12–15] several times, but their use in trace metal analysis as the support for mercury film is introduced for the first time. It was confirmed that carbon paste is able to offer very similar results as the well established glassy carbon electrode keeping all advantages and disadvantages connected with PSA method[3]. It is even possible to obtain higher sensitivity than with MCGCE, but the signal is a bit less reproducible (typical of these electrodes[8]). In addition, easy and very cheap preparation of CPE and no risk of mechanical damage of the electrode material is very advantageous. These facts predetermine MCCPE for the use even under unusual conditions.

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