SCIENTIFIC PAPERS
OF THE UNIVERSITY OF PARDUBICE
Series A
Faculty of Chemical Technology
9 (2003)

INVESTIGATION OF CARBON PASTE ELECTRODES AS SUPPORTS FOR GOLD FILMS IN POTENTIOMETRIC STRIPPING DETERMINATION OF COPPER(II) AND MERCURY(II) TRACES

Elmorsy KHALED[a,b], Jiří KONVALINA[b], Karel VYTŘAS[b1] and Hassan N.A. HASSAN[a]
[a]Microanalytical Laboratory, National Research Center, Dokki, Cairo, Egypt,
[b]Department of Analytical Chemistry, The University of Pardubice, CZ–532 10 Pardubice

Received September 19, 2003

Carbon paste electrodes containing either silicone or paraffin oil as pasting liquids have been investigated as possible supports for gold film formed either in situ or by electrodeposition. These electrodes, preplated with a thin gold film, were tested for stripping potentiometric determinations of traces of copper(II) and mercury(II). A detailed study has shown that the results obtained using these inexpensive and easily prepared electrodes are comparable with those obtained using conventional glassy carbon electrodes. Under optimized experimental conditions, low detection limits (5.3 μg l^{-1} for copper and 2.0 μg l^{-1} for mercury and accumulation time of 10 min) and good precision (relative standard deviation

[1] To whom correspondence should be addressed.

of 1.1 % for 10 repetitive measurements of 200 $\mu g\, l^{-1}$ copper and 5.1 % for 6 repetitive measurements of 50 $\mu g\, l^{-1}$ mercury) were obtained. The calibration curves of both elements were linear in the range of 5 – 100 $\mu g\, l^{-1}$ with average recovery of 97.8 ± 1.8 % for mercury and 98.6 ± 0.2 % for copper. Compared with mercury film electrodes, the copper determination was more favorable on gold film electrodes due to lower RSD and higher slope of calibration curves.

Introduction

The usual choice of the working electrode in stripping potentiometry is the mercury film deposited on glassy carbon support, which can be used for determination of many elements. However, mercury has the main drawback of limited anodic range; this prevents its use for the determination of those elements that are oxidized at more positive potentials. That fact has promoted an increasing interest in other electrode materials [1]. Among others, gold was found a good alternative since it is a noble metal that can be deposited from an Au(III) solution to form a stable and reproducible film onto a suitable conducting material [1–3]. Platinum discs, carbon and gold fibres or glassy carbon belong to the most frequently used supports for a gold film [4–9].

Although carbon paste electrodes (CPEs) have been widely applied in various fields of electroanalysis [10–12], they were not frequently used as supports for metallic films and there are only a few articles reporting on such attempts [13–18]. CPEs plated with a gold film were recently used for the stripping voltammetric determination of mercury [17] and arsenic [18]. The objective of this article is to compare different carbon electrode materials for potentiometric stripping analysis of copper and mercury on gold film-plated electrode.

Experimental

Reagents and Solutions

Standard 0.01 M solutions of copper(II) and mercury(II) were prepared by dissolving appropriate weighed amounts of the corresponding salt in water, while the dilute solutions were freshly prepared daily. For determination of copper(II), acetate buffer solution was prepared giving the final composition of 0.1 M acetate + 0.2 M acetic acid + 0.004 M KCl (supporting electrolyte A). The other supporting electrolyte (B) was prepared for mercury(II) determination and consisted of 0.05 M H_2SO_4 and 0.002 M KCl. Stock 0.01 M $AuCl_4^-$ solution in 0.04 M HCl was used for the preparation of the plating bath. All chemicals used were of analytical grade, doubly distilled water was used throughout.

Apparatus

A PSU22 Trace Lab potentiometric stripping unit with a sample station SAM20 was used and controlled by PC *via* the TAP2 program (all from Radiometer Analytical S. A., France). The three-electrode measuring cell comprised a working electrode, a CPE (see the next paragraph) or a glassy carbon electrode (F3600, Radiometer), a saturated calomel reference an and auxiliary platinum electrodes.

Working Electrodes

When glassy carbon electrode was used, it was first polished with an alumina powder to achieve a mirror-like surface, then cleaned with 95 % ethanol to remove alumina, and finally rinsed with distilled water before use. Carbon paste electrodes were prepared by intimate mixing a carbon powder (0.5 g) and a pasting liquid (0.2 ml). CR-5 (Tesla Lanškroun, Czech Republic) or RW-B (Ringsdorff-Werke, Germany) carbon powders and silicone oil (Lučební závody Kolín, Czech Republic) or paraffin oil (Uvasol, Merck) as pasting liquids were used. The resulting pastes were used to fill the home-made electrode holders [19] with an active surface diameter of 3 mm. The electrode surface was renewed by removing a thin layer of the used paste with a wet filter paper. For determination of copper, the working electrode (either glassy carbon or carbon paste electrode) was plated by immersing the working electrode into a plating bath described above and applying stepwise descending potentials of +0.4 V, +0.1 V, –0.1 V, –0.3 V, –0.5 V (each for 30 s) and, finally, –0.6 V for 120 s, with a moderate stirring. For determination of mercury(II), the gold film was prepared *in situ* as described below.

PSA Procedures

Determination of copper(II). The preplated working electrode was immersed into the non-deaerated acetate-based supporting electrolyte (A) with varying additions of copper(II) solution at the ppb level. After a preconditioning step (10 s at +0.5 V), deposition was carried out at –0.1 V and at a stirring speed of 1500 rpm. The deposition time varied in the range 2 – 10 min, depending on the copper concentration. After an appropriate rest time (10 s) at the same electrode potential, the stripping curve was recorded by applying a constant current (15 μA) until the electrode potential reached +0.8 mV (before oxidation of the gold film started). For calibration, the analytical signal was evaluated as the peak area (given in ms) and related to the copper concentration. The detection limit estimated as the 3:1 signal-to-noise ratio was investigated by running blank solutions with a long

deposition time of 10 min.

Determination of mercury(II). The working electrode was immersed into the non-deaerated H_2SO_4 - KCl supporting electrolyte (B) (20 ml) and a solution of 0.01 M $AuCl_4^-$ in 0.04 M HCl (30 µl) was added for the *in situ* gold film plating. After a mercury-containing solution was added to the measuring cell, the deposition step was carried out at –0.05 V and at a stirring speed of 1500 rpm. The deposition time varied in the range of 2 – 10 min, depending on the mercury concentration. After appropriate rest time (10 s) at the same potential, the stripping curve was recorded by applying a constant current (7 µA) until the electrode potential reached +0.8 V. In order to construct the calibration curve, the analytical signal evaluated as the peak area (in ms) was related to the mercury concentration.

Results and Discussion

Determination of Copper(II)

Effect of supporting electrolyte. In stripping analysis of copper employing a gold film electrode, considerable attention must be paid to optimum composition of the supporting electrolyte as its nature influences the mechanism of the stripping process [20]. Gil and Ostapczuk [1] recommended a mixed medium consisting of H_2SO_4 and KCl. This electrolyte was also tested in the present study together with others where sulfuric acid medium was replaced by various acids, such as perchloric, hydrochloric or nitric acid, as well as by acetate buffer (see Table I).

Table I Effect of supporting electrolyte on the constant-current potentiometric stripping determination of copper at the glassy carbon-based gold film electrode at an accumulation time of 1 min

Supporting electrolyte	Peak potential, mV	Hydrogen evolution	Gold film stability
H_2SO_4	235	+	unstable
H_2SO_4-HCl	272	+	unstable
HCl	300	–	relatively stable
HNO_3	270	–	less stable
$HClO_4$	278	++	unstable
AcOH-AcONa	260	–	very stable
AcOH-AcONa-KCl	260	–	very stable

Different sulfuric acid concentrations ranging between 0.05 and 0.25 mol l^{-1} were used. Lower concentrations of the acid gave a lower copper response while higher concentrations caused splitting of the copper peak and evaluation of hydrogen gas at the electrode surface which produced errors in measuring both the background signal and the copper peak.

Concerning application of hydrochloric acid, either copper(I) or copper(II) species are formed in dependence on the chloride concentration in the stripping medium when amalgamated copper is oxidized [21]. If Cl^- concentration is lower than ca. 1 mmol l^{-1}, copper(II) predominates; at higher Cl^- concentrations, copper(I) prevails. Thus, an increase in the Cl^- concentration results in lowering of the peak area since only one electron is involved in the oxidation step. In the present work, this effect was also studied for 0.002 – 1.0 M HCl. The medium of 0.004 M HCl was found to be the best as increasing the acid concentration resulted in a decrease in the peak area and increase in the background signal. Further, the stability of the gold film improved in the medium of less concentrated acid, as it was less prone to breakdown as a consequence of hydrogen evolution.

Application of nitric acid is not favourable as its higher concentrations caused a splitting of the copper peak and appearance of a new peak at +0.6 V; the measured signal is not reproducible [1]. It was confirmed in this study that using HNO_3, the gold film was less stable as well and the electrode had to be plated with a new film after each measurement. Applying perchloric acid was not favourable either as hydrogen gas evolved at the electrode surface, which produced a very high background signal.

The application of acetate buffer as a supporting electrolyte for copper determination was also investigated by using equimolar acetic acid - acetate buffers of concentrations ranging between 0.05 and 1.0 mol l^{-1}. With increasing buffer concentration, the peak area decreased and also the peak shape became worse (the optimum concentration seemed to be 0.1 mol l^{-1}). Changing the acetic acid concentration added to 0.1 M acetate, we found a buffer composed of 0.1 M acetate and 0.2 M acetic acid to be the best. Further acidification of the solution caused a decrease in the peak area. It was also found that addition of chloride improved the sensitivity; final composition of the supporting electrolyte was 0.1 M acetate - 0.2 M acetic acid - 0.004 M KCl.

Effect of plating procedures. As well known, the performance of the metallic film significantly depends on both the plating regime and the nature of the electrode surface. In this study, the gold film electrode was prepared using plating solutions containing $AuCl_4^-$ concentrations ranging from 0.50 to 3.0 mg l^{-1} by applying the potential of +0.4 V, +0.1 V (each for 90 s), –0.1 V for 120 s and –0.3 V for 180 s. The film preplated from 3.00 mg l^{-1} gold(III) solution gave the best performance as indicated by the higher slope of the calibration graph and a better linearity at higher copper(II) concentrations. It was also observed that, together with the gold film thickness, the peak potential was shifted towards more positive

potentials. With respect to that — as confirmed by microscopic studies [18] — it should be mentioned that gold deposited either *in situ* or externally in a plating solution forms a compact layer of unconsolidated structure which approximately copies the surface topography of the carbon paste itself.

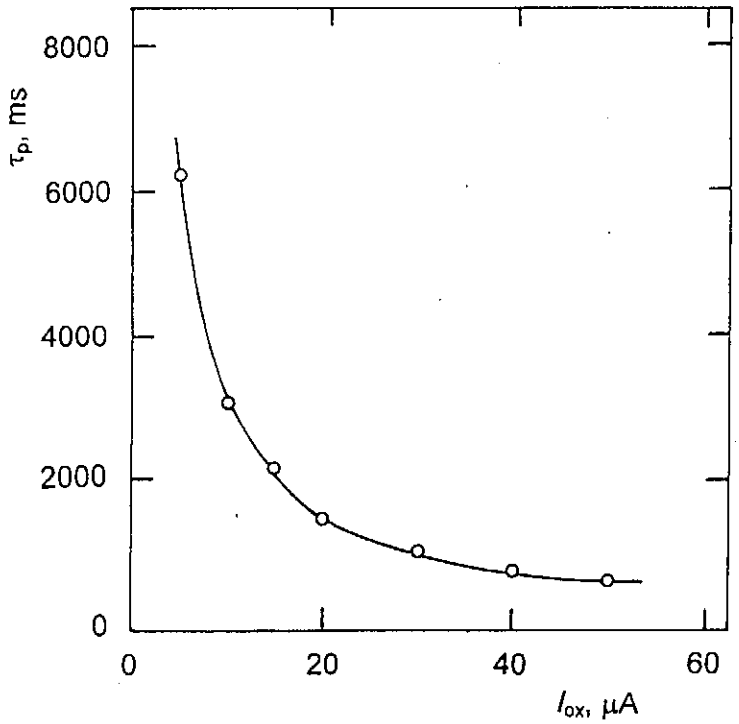

Fig. 1 Effect of the oxidation current on the copper peak. Axes: peak area (τ_p, ms), oxidation current (I_{ox})

The effect of the plating potential was also investigated by changing the plating regime. All the potentiograms obtained were reproducible but the procedure described in Experimental was found the best, producing the highest slope of the calibration graph. A well-plated, homogeneous and mechanically stable gold film was obtained with a lifetime allowing more than 200 analyses without obvious changes in the stripping signal. Formation of the gold film *in situ* was also examined but the resulting responses and reproducibility were worse than those obtained with preplated film electrodes.

Effect of oxidation current. The theory of potentiometric stripping predicts a linear relationship between the inverse current (I^{-1}) and peak area [22]. This fact makes the use of low currents desirable when the concentration to be determined is very

low. Unfortunately, the response increase is accompanied by a corresponding increase in the background noise. The stripping current has a profound effect on the copper response. A nearly exponential decrease in the peak area is observed upon increasing the stripping current from 5 to 50 μA. Such profile reflects a faster oxidation, i.e., shorter stripping times at higher currents (Fig. 1). A stripping current of 15 μA was chosen as a suitable value as it gave a satisfactory calibration graph and a considerable signal-to-noise ratio. Lower currents introduced a higher and unacceptable background which caused errors in measuring the peak area. In addition, the oxidation peak of copper(I) appeared. At higher currents, the oxidation of gold film started at lower potentials than expected, and corresponding potentiograms were not acceptable.

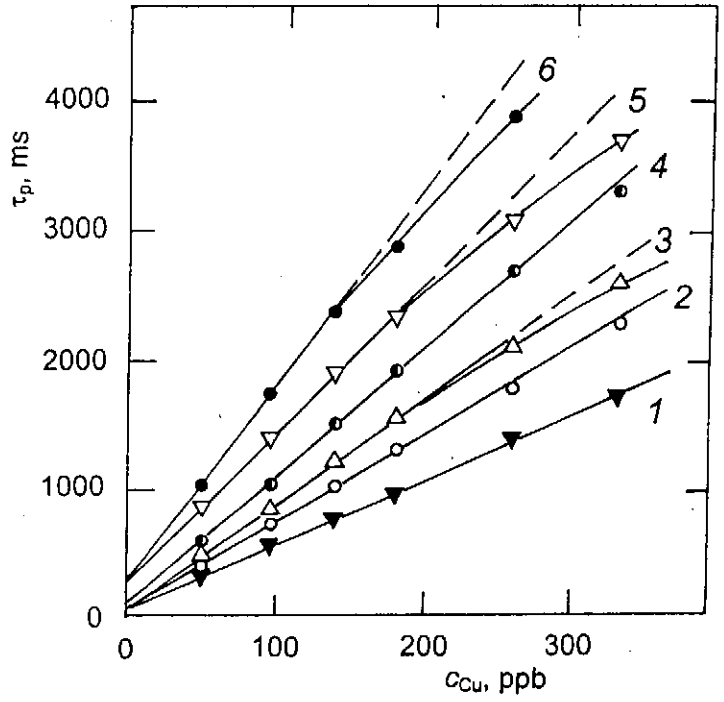

Fig. 2 Calibration dependences for copper(II) at the glassy carbon-based gold film electrode. Accumulation time (t_{acc}, s): 1 60, 2 90, 3 120, 4 150, 5 180, 6 300. Axes: peak area (τ_p, ms), copper concentration (c_{Cu})

Effect of deposition potential. Only a slight change in the copper response was observed by lowering the deposition potential between +0.1 and –0.6 V. No change in the peak area was observed down to potentials around –0.1 V. At more negative potentials (lower than –0.3 V), the interference of hydrogen evolution at

the electrode surface during deposition started, which influenced quality of the electrode surface and gave an irregular and irreproducible background. Thus, the potential of –0.1 V was chosen as an optimum.

Effect of accumulation time. The influence of the accumulation time on the slope of the calibration was investigated. These values increased linearly with increasing accumulation time, thus reflecting the enhancement of copper concentration in the gold film until saturation of the electrode was reached (Fig. 2).

Comparison of different supports. The performance of the gold film on the traditional glassy carbon electrode was compared with those plated on carbon paste electrodes. Under the same conditions of plating and copper accumulation, carbon paste electrodes showed better behaviour from the point of view of lower background and higher sensitivity as manifested by higher slopes of corresponding calibration graphs. The detection limit for copper determination was much lower in the case of the carbon paste electrode than that of glassy carbon. Recovery for 200 ppb Cu reached nearly 100 % when working with carbon paste electrodes, which was not achieved with glassy carbon electrodes. The dissolution of the gold film occurred approximately at the same potential (0.95 V) on all supports but with different backgrounds, the lowest being obtained when a CPE containing paraffin oil was used. The results obtained were comparable with those presented recently by Gil and Ostapczuk [1] having used gold film-plated glassy carbon electrodes.

Determination of Mercury(II)

Effect of plating procedures. The effect of co-deposition of Au with mercury during the accumulation was investigated. A preplated gold film was prepared as in the case of copper and compared with that plated *in situ.* The results showed that the film plated *in situ* yielded a linear calibration dependence within the concentration range measured (Fig. 3). Also the signals measured with *in situ* plated electrodes were more reproducible (RSD 5.1 %) than those obtained with preplated electrodes (RSD 6.5 %), both evaluated for 6 measurements at the 50 ppb Hg concentration level. It should be mentioned that similar observations were reported for voltammetric determination of mercury with gold film electrodes on carbon paste supports [17].

Effect of supporting electrolyte. For the electrochemical stripping determination of mercury on a gold film electrode, the supporting electrolyte must contain a species capable of complexing Hg(II), since the interaction of this element with gold is very strong [1]. Chloride is mostly used, but care should be taken not to force the potential to too positive values, which could give rise to oxidation of gold surface. The influence of the nature of the mineral acid employed for the determination (HCl, HNO_3, H_2SO_4 and their mixtures) was also investigated; the supporting electrolyte composed of 0.05 M H_2SO_4 and 0.002 M KCl .

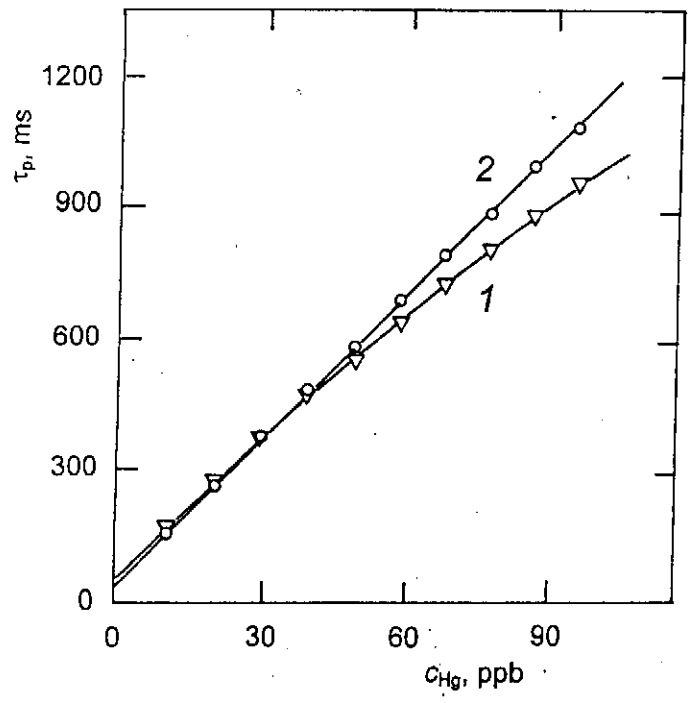

Fig.3 Calibration dependences for mercury(II) at the carbon paste-based gold film electrode. Gold film prepared by 1 precoating the support, 2 *in situ* plating. Axes: peak area (τ_p, ms), mercury concentration (c_{Hg})

Comparison of different supports. Two different carbon paste electrodes were prepared using CR-5 or RW-B carbon powders and silicone oil as a pasting liquid. A small difference in the slopes of corresponding calibration graphs (9.17 ms ppb^{-1} for CR-5 and 7.99 ms ppb^{-1} for RW-B) was observed.

Conclusion

Detection limits for both the copper(II) and mercury(II) determinations were investigated for a long deposition time (10 min). The 3:1 signal-to noise ratios were used to evaluate both detection limits, which were 5.3 $\mu g\ l^{-1}$ for copper(II) and 2.0 $\mu g\ l^{-1}$ for mercury(II). The results showed that the CPE containing silicon oil as a pasting liquid is a convenient support for gold film and can be recommended as a working electrode for the determination of copper(II) or mercury(II) ions. In addition, an easy and very cheap preparation of CPEs and no risk of mechanical damage of the electrode material make the electrode attractive.

In contrast to relatively difficult regeneration of solid electrodes, a CPE surface can quickly be renewed. Finally, these new procedures eliminate possible hazard of mercury in analytical laboratories.

Acknowledgements

The authors are grateful for the financial support of the Ministry of Education, Youth and Sports of the Czech Republic (contract No. 253100002).

References

[1] Gil E.P., Ostapczuk P.: Anal. Chim.. Acta **293**, 55 (1994).
[2] Hátle M.: Talanta **34**, 1001 (1987).
[3] Wang J.: *Stripping Analysis*, p. 75, VCH, Deerfield Beach, 1985.
[4] Švancara I., Vytřas K., Kalcher K.: Sci. Pap. Univ. Pardubice, Ser. A **3**, 207 (1997).
[5] Jagner D., Renman L., Stefansdottir S.H.: Electroanalysis (N.Y.) **6**, 201 (1994).
[6] Huang H.L., Jagner D., Renman L.: Anal. Chim. Acta **201**,1 (1987).
[7] Wang J., Šucman E., Tian B.M.: Anal. Chim.. Acta **286**, 189 (1994).
[8] Lexa J., Štulík K.: Talanta **30**, 845 (1983).
[9] Bradshaw M.P., Scollary G.R.: Electroanalysis (N.Y.) **9**, 320 (1997).
[10] Kalcher K.: Electroanalysis (N.Y.) **2**, 419 (1990).
[11] Kalcher K., Kauffmann J.-M., Wang J., Švancara I., Vytřas K., Neuhold C., Yang Z.P.: Electroanalysis (N.Y.) **7**, 5 (1995).
[12] Švancara I., Vytřas K., Barek J., Zima J.: Crit. Rev. Anal. Chem.. **31**, 311 (2001).
[13] Kauffmann J.-M., Laudet A., Patriarche G. J.: Anal. Lett. **15**, 763 (1982).
[14] Říha V., Jr.: *Determination of Trace Concentrations of Heavy Metals Using Inverse Voltammetry* (in Czech), M.S. Thesis, University of Chemical Technology, Pardubice, 1987.
[15] Švancara I., Pravda M., Hvízdalová M., Vytřas K., Kalcher K.: Electroanalysis (N.Y.) **6**, 663 (1994).
[16] Konvalina J., Khaled E., Vytřas K.: Collect. Czech. Chem. Commun. **65**, 1047 (2000).
[17] Švancara I., Matoušek M., Sikora E., Schachl K., Kalcher K., Vytřas K.: Electroanalysis (N.Y.) **9**, 827 (1997).
[18] Chadim P., Švancara I., Pihlar B., Vytřas K.: Collect. Czech. Chem.

Commun. **65**, 1035 (2000).
[19] Švancara I., Vytřas K.: Chem. Listy **88**, 138 (1994).
[20] Xie Y. Q., Huber C. O.: Anal. Chem. **63**, 208 (1991).
[21] Jagner D., Sahlin E., Renman L.: Talanta **42**, 1447 (1995).
[22] Wang J., Tian B.: Anal. Chim. Acta **274**, 301 (1993).