SCIENTIFIC PAPERS
OF THE UNIVERSITY OF PARDUBICE
Series A
Faculty of Chemical Technology
3 (1997)

VOLTAMMETRIC DETERMINATIONS AT POLYMERIC COLLOIDAL GOLD PASTE ELECTRODES - PRELIMINARY COMMUNICATION

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Received September 12, 1997

A new method of preparation of polymeric paste electrodes containing metallic gold colloid is described and their applications for the determination of mercury(II) in water samples are preliminarily tested. The main goal of the use of these electrodes lies in the simple renovation of their active surface. However, the reproducibility of the voltammetric records still depends on the way of the electrode pretreatment and, from this point of view, the development of a general procedure for some determinations, e.g. of mercury(II), still represents a real challenge with many problems which have to be solved.

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Introduction

Gold electrodes are very often used in various applications in analytical electrochemistry, mostly when the measurements at more positive potentials are required [1]. However, the surface of the solid electrodes more easily undergoes oxidation, which gives rise to an increase in background currents and other undesirable responses, resulting in some complications during practical measurements. In the case of solid gold electrodes, their surface has to be regenerated by a mechanical procedure requiring some experience and manual skill, however, such operations may complicate the determination desired.

To overcome the behaviour of the solid electrodes and, at the same time, to avoid their positives, carbon paste electrodes plated with a gold film were introduced and applied for the voltammetric determination of mercury(II) [2]. These electrodes were represented by a thin layer of metallic gold deposited onto a carbon paste support and were recommended because of the simple renovation of their surface.

In this paper, a new method of preparation of polymeric paste electrodes containing colloidal gold is described and their applications are tested. Such electrodes have not yet been reported. Our preliminary experiments showed that these may be applied to voltammetric determinations, e.g., for trace amounts of mercury in water samples.

Experimental

Apparatus

An Eco-Tribo-Polarograph, Polarosensors, Prague, equipped with the electrodes of the holder type Mini-on-Microelectrode system; a Crytur RAE11J reference and an auxiliary Crytur PPE electrode (both Monokrystaly, Turnov) were connected to, and controlled by a PC DX386 with graphic exit through a FUTURE laser printer A4. The polymeric colloidal gold paste electrode (PCGPE) was made of a mixture of polypropylene and Teflon and was connected to the measuring apparatus *via* a stainless steel piston (Fig. 1). A small electromechanic stirrer TRIBO II consisting of a glass pneumovalve rod (for bubbling of nitrogen) completed the arrangement.

The procedure used for the preparation of the colloidal gold was as follows: Gold(III) chloride (6.4 g) was dissolved in ethanol and the solution was reduced with ethanolic solution of hydroxylamine hydrochloride, and ammonia was added to achieve the pH 7.0 value. The colloidal gold formed was diluted with diethyl ether and completed with diethylether solution of polypropylene (relative molecular mass of about 12-26 thousands). After evaporation, the resulting paste was rubbed down and filled into the electrode body.

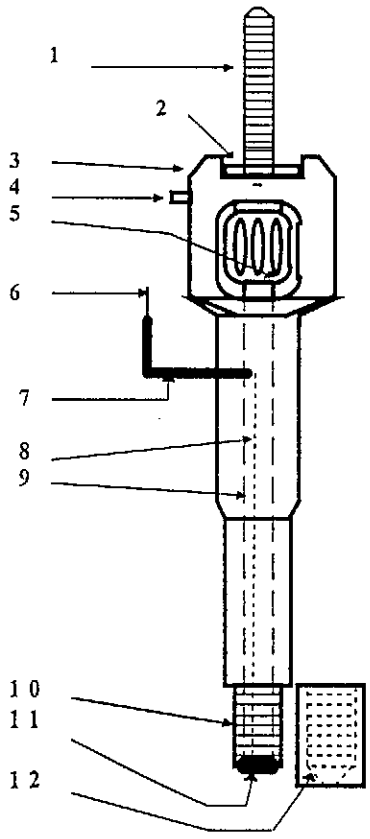

Fig. 1 Construction of the working electrode (PCGPE): 1 - A vertically sliding piston with an external thread; 2 - a leading bed of the piston; 3 - a box head with a bearing of the piston; 4 - an element ensuring the vertical shifting of the piston without any rotation; 5 - a matrix for the vertical shift of the piston; 6 - an output contact for a signal; 7 - a screening of the conductor; 8 - an inner part of the conductor; 9 - an inner wall of the electrode body; 10 - a bottom ending of the electrode body with external thread for a Teflon jet; 11 - a platinum contact with the active part of the electrode filling; 12 - a Teflon jet with internal thread serving for completion with the electrode body

Chemicals and Reagents

All the chemicals used were of analytical reagent grade and purchased from Lachema, Brno. Stock solutions and buffers for the supporting electrolytes were prepared, redistilled water was used throughout.

The working electrode was subjected to different ways of its pretreatment in order to obtain measurable signals for very low concentration levels of mercury(II). First, a cycling voltammetric procedure was applied between 0 and +1600 mV and back at a rate of 10 $V\,s^{-1}$ (20 cycles) which seemed very useful. After such a pretreatment, the analysis of the model sample was realized using the DPV method. In the supporting electrolyte (0.1 M $HClO_4$), the mentioned DPV stripping gives a voltammetric curve with very low background. However, in a model sample containing 1.0 $\mu g\,l^{-1}$ of mercury(II), the voltammetric curve gave two peaks, at +320 and +550 mV, resp., and the same curve was recorded when another model sample containing 0.5 $\mu g\,l^{-1}$ Hg and the same basic electrolyte was analyzed. When the working surface of the PCGPE was renewed, both the positions and the magnitude of the peaks changed significantly.

After changing numerous operational steps it was observed that only such records are reproducible in which the cycling procedures are always previously applied, either to the sample to be analyzed, or to the sample containing a known addition of the standard. In such a case, the concentration dependence of the signal was linear (see Figs 2, 3).

However, these promising results could not fully be reproduced. When repeating the procedure with the renewed electrode surface, the records for the same standard additions showed smaller and smaller sensitivity. Similarly, after new filling of the electrode body with the rest of the polymeric colloid gold paste (on which the ageing was observable as a greasier consistence), no reproducible results could be obtained.

Conclusion

Although this first attempt at the application of the PCGPEs did not bring sufficient number of positive results, some of the experimental measurements indicate that perhaps this type of the voltammetric sensors has some chance to be developed. The simple renovation of the electrode surface offers some advantages which deserve further attention. However, questions connected to various problems like the optimum ratio of the colloid gold to polypropylene in a paste, the stability and ageing of the resulting paste, the electrode pretreatment, etc. must be thoroughly studied and solved before the PCGPEs are recommended for practical use.

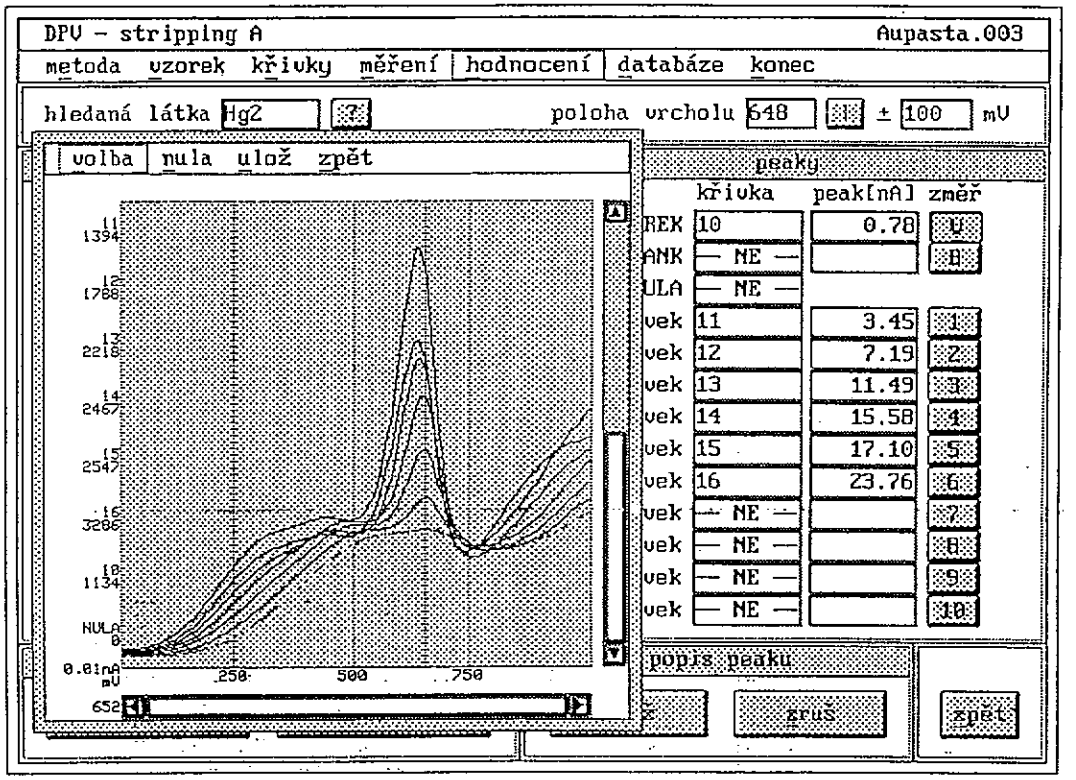

Fig. 2 Differential pulse anodic stripping voltammograms of a sample containing mercury(II) analysed by the method of multiple standard addition using a PCGPE electrode: 10 - A sample; 11–16 - curves recorded after the 1st, 2nd, ... 6th addition of the standard (50 µl containing 20 ng Hg). Volume of the sample 50 ml; E_{acc} = 0 mV; E_{fin} = 1000 mV; t_{acc} = 600 s; scan rate 20 mV s^{-1}; pulse height 50 mV; pulse width 100 ms. Output of the Eco-Tribo-Polarograph

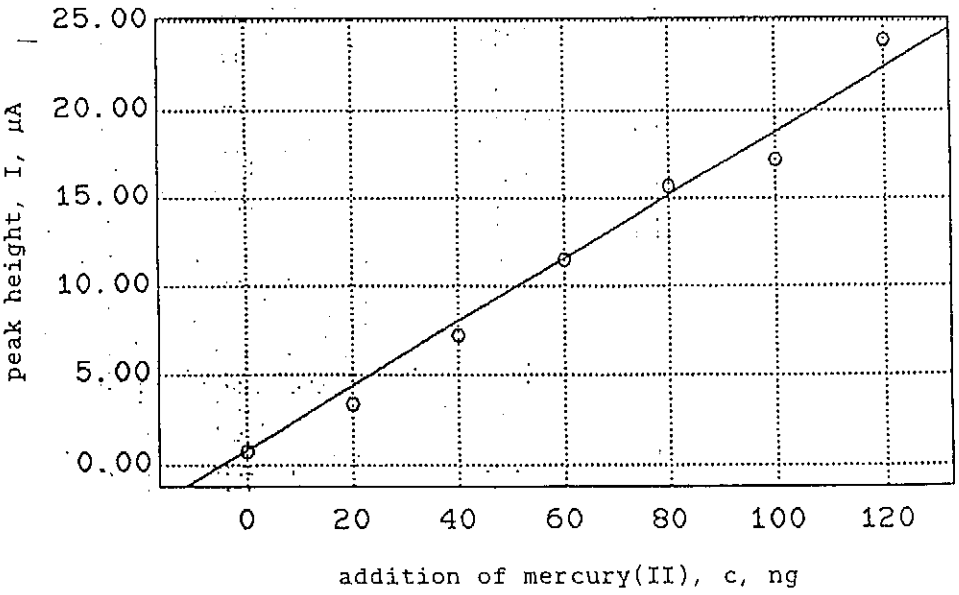

Fig. 3 Determination of mercury(II) using multiple standard addition method. Regression line, $I = 0.180c + 0.780$; correlation coefficient, $r_k = 0.993$. Found, 4.33 ng Hg/50 ml. The numbering of the points corresponds to that of the voltammetric curves given in Fig. 2

References

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