

## The Lead Film Electrode Prepared with Use of the Combination of *Ex-situ* and *In-Situ* Methods in Stripping Analysis of Folic Acid

Katarzyna Tyszczyk-Rotko \*

Department of Analytical Chemistry and Instrumental Analysis, Faculty of Chemistry,  
Maria Curie-Skłodowska University, 20-031 Lublin, Poland

**Abstract:** In this article, elaboration of a “hybrid” lead film electrode is reported. The strategy to create such an electrode is based on the combination of *ex-situ* and *in-situ* plating methods and also the use of a reversibly deposited metal mediator (Cd) for the lead film formation. Various plating conditions, which influenced the response of the “hybrid” lead film electrode to folic acid, were thoroughly optimized and discussed. The results have indicated that the sensitivity of the “hybrid” lead film electrode prepared with use of the metal mediator was remarkably improved compared to the *in-situ* and *ex-situ* plated lead film electrodes, and the “hybrid” lead film electrode prepared without use of the metal mediator could be applied to the determination of folic acid in tablets (preparative *Folovit*<sup>®</sup>) with satisfactory results.

**Keywords:** “Hybrid” lead film electrode; Reversibly deposited metal mediator; Pre-plating; *in situ* plating; Stripping voltammetry, Folic acid.

\*) Author to whom correspondence should be addressed. E-mail: ktyszczyk@poczta.umcs.lublin.pl

### Introduction

Stripping voltammetry is a well established electroanalytical technique, providing an efficient, versatile, and highly sensitive method of detecting a wide range of inorganic and organic substances to concentration as low as  $10^{-10}$  mol L<sup>-1</sup> [1,2]. The success of voltammetric sensing procedure depends mainly on the proper choice of the working electrode. The ideal working electrode should offer effective preconcentration, a favorable redox reaction of the target metal or organic substances, reproducible and renewable surface, and a low background current over a wide potential range [3].

In the stripping voltammetry, a whole range of the working electrodes are used. Among them, a special place is held by metal film electrodes. The most commonly used examples are mercury film electrodes [4-6], bismuth film electrodes [3,7-12] and recently, also antimony film electrodes [13-18].

The properties and analytical utility of metal film electrodes depend strictly on the method of coating the support with the metal deposit. In the literature, three general methods of coating the substrate surface with a metal film are described [3-18]. These are:

- *in-situ* plating, in which the metal ions (e.g. Hg(II), Bi(III), Sb(III)) are added into the sample solution and deposited on the electrode surface during the analysis;
- preplating or *ex-situ* plating, where the metal film is plated before the analysis from a solution containing metal ions and then the electrode is transferred to the sample solution;
- method based on modifying the heterogeneous electrodes (carbon paste electrodes, screen-printed electrodes) with a metal precursor.

In 2005, a new type of metal film electrode, the lead film electrode was introduced to voltammetric measurements [19]. From the time of the first work on lead film electrodes they have been successfully applied to the adsorptive stripping voltammetric determinations trace amounts of inorganic ions and biologically active compounds in various matrices [20-23]. So far, lead films have been deposited onto the surface of the support (usually glassy carbon) by an *in situ* plating method. Recently, an *ex situ* plated lead film electrode prepared with the use of a reversibly deposited mediator metal (Zn) was introduced [24].

In this work, a “hybrid” lead film electrode was prepared by combining *ex-situ* and *in-situ* plating methods [25, 26]. In this approach, *ex-situ* plating of the substrate surface with a lead film is based on co-deposition of the metal of interest (Pb) with a reversibly deposited metal mediator (Cd) and, then, on an oxidation of cadmium and further deposition of lead by the appropriate potential. Such an electrode was then re-plated with Pb *in situ* with the sample. The “hybrid” lead film electrode was tested by adsorptive stripping voltammetry of folic acid. The results were compared to those obtained at an *in-situ* plated lead film electrode according to the procedure earlier described in literature [20], an *ex-situ* plated lead film electrode prepared without use of the metal mediator and to those obtained at a “hybrid” lead film electrode prepared without use of the mediator metal.

## Experimental

### *Chemicals, Reagents, Stock and Standard Solutions*

An acetate buffer, used as a supporting electrolyte, was prepared from  $\text{CH}_3\text{COOH}$  and  $\text{NaOH}$  obtained from Merck.  $0.01 \text{ mol L}^{-1}$  solutions of  $\text{Pb}(\text{NO}_3)_2$  and  $\text{CdCl}_2$  were prepared from reagent obtained from Sigma-Aldrich. Folic acid was obtained from Fluka. A stock standard solution of folic acid ( $10^{-2} \text{ mol L}^{-1}$ ) was prepared in  $0.02 \text{ mol L}^{-1}$   $\text{NaOH}$  and stored in a refrigerator until used. Working solutions were prepared daily by dilution of the stock solution. All solutions were prepared in deionized water obtained by passing through a laboratory cartridge purifier (Milli-Q system; Millipore, USA).

### *Electrochemical Apparatus and Other Instrumentation*

All voltammetric measurements were performed using a  $\mu\text{Autolab}$  analyser made by Eco Chemie, the Netherlands. A classical three-electrode quartz cell of volume 10 mL was used throughout, consisting of a lead film modified glassy carbon working electrode, with an  $\text{Ag}/\text{AgCl}$  reference electrode and a platinum wire as an auxiliary electrode. The glassy carbon electrode was polished using  $0.3 \mu\text{m}$  alumina slurry on a Buehler polishing pad and then was washed and sonicated for 2 min.

### *Preparation of “Hybrid” Lead Film Electrode Using the Combination of Ex-situ and In-situ Plating Procedures.*

The *ex-situ* plated lead film electrode was prepared by an electrochemical method with the use of a reversibly deposited mediator metal. The lead film was deposited from a solution with  $0.1 \text{ mol L}^{-1}$  acetate buffer (pH 3.5),  $5 \times 10^{-5} \text{ mol L}^{-1}$  of  $\text{Pb}(\text{II})$  and  $2.5 \times 10^{-5} \text{ mol L}^{-1}$  of  $\text{Cd}(\text{II})$ . Before each deposition experiment the electrode was cleaned electrochemically at 0.5 V for 30 s. In the course of electrodeposition the potential of the electrode was changed in the following sequence: -1.4 V for 30 s and -0.65 V for 30 s. In the first step Pb (metal of interest) and Cd (reversibly mediator metal) were deposited simultaneously on a glassy carbon surface. During the second step Cd atoms were stripped from surface as Pb continued to deposit resulting in islands of lead atoms growth. During both steps the solution was stirred using a magnetic stirring bar.

Next, the electrode was carefully rinsed with water and transferred into the solution to continue the deposition of lead and the determination of folic acid. Such determinations were performed by preconcentration at -0.88 V vs. ref. (for 120 s) in a solution of 0.1 M acetate buffer (pH 5.6) with  $c(\text{Pb}) = 7.5 \times 10^{-5} \text{ mol L}^{-1}$ . During this step the lead film was deposited and folic acid was accumulated simultaneously. Then after 5 s equilibration time, the square wave voltammograms were recorded between -0.88 and -1.2 V with a frequency of 200 Hz and amplitude of 50 mV.

The potential step of choice was 4 mV. All voltammetric measurements were carried out in undeaerated solutions. By pre-plating Pb on the glassy carbon surface and then plating it again under conditions suitable for analyte (according to the procedure earlier described in literature [20]), the resultant configuration was the “hybrid” lead film electrode.

### ***Sample Preparation***

The pharmaceutical preparation analysed was *Folovit*<sup>®</sup> tablets (Polfarmex; Kutno, PL) containing 0.4 mg of folic acid per tablet. The pharmaceutical was prepared by the following procedure. Ten tablets were weighed and then the average mass per tablet determined. The tablets were carefully grounded to a fine powder, and then a quantity of homogeneous powder equivalent to 0.4 mg of folic acid was dissolved in 10 mL of 0.02 M NaOH by sonication for 5 min. The desired concentration of folic acid was obtained by accurate dilution with deionized water. The sample solution so prepared was added to the supporting electrolyte in voltammetric cell and adsorptive stripping voltammetric measurements at the “hybrid” lead film electrode prepared with use of the mediator metal were carried out under the optimal conditions.

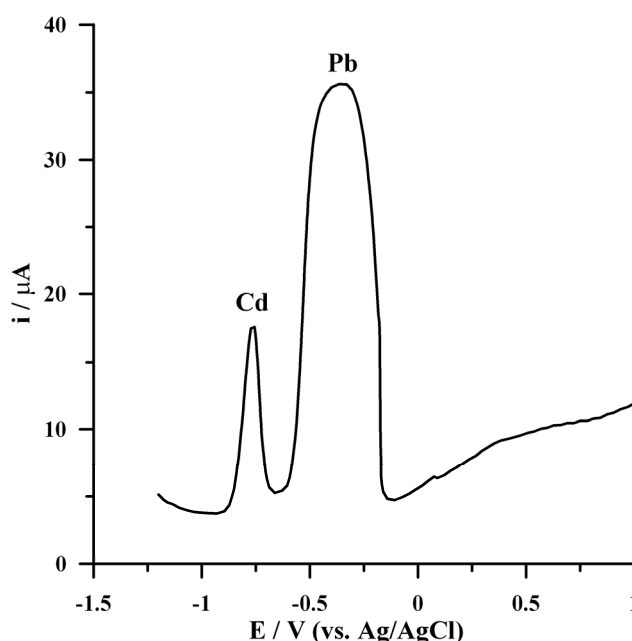
## **Results and Discussion**

The aim of this paper was the application of combination of pre-plating with use of the mediator metal and *in-situ* plating methods, in order to improve properties of the lead film electrodes prepared using *in-situ* method and *ex-situ* method without use of the mediator metal. Due to this fact, various the lead film plating parameters, which influenced the response of a lead film electrodes to folic acid, were optimized and discussed.

### **Selection of the Appropriate Conditions for Pre-plating of Lead Film with the Use of a Reversibly Deposited Metal Mediator**

The metal used as a reversibly deposited mediator must be less noble than the metal of interest, and hence cadmium was used as mediator for further studies. Initially, the deposition behaviour of the Cd(II) and Pb(II) plating solution in acetate buffer was studied. The cadmium and lead were deposited at -1.2 V for 30 s. Fig. 1 shows the stripping voltammogram of a solution containing 0.1 mol L<sup>-1</sup> acetate buffer (pH 3.5), 7.5 × 10<sup>-5</sup> mol L<sup>-1</sup> of Pb(II) and 1 × 10<sup>-5</sup> mol L<sup>-1</sup> of Cd(II).

As seen in Fig. 1, the anodic peaks of Cd and Pb were observed with peak potential values at -0.77 V and -0.35 V, respectively. It must be noted that cadmium and lead can be deposited simultaneously at a potential more negative than -0.9 V vs. ref. and at potential in the range from -0.6 to -0.7 V, whilst cadmium will be stripped from the surface, lead will continually be deposited. Consequently, in further experiments, a potential of -1.2 V and time of 30 s were used for plating cadmium and lead, and a potential of -0.65 V and time of 30 s for the stripping of cadmium and further deposition of lead.



**Fig. 1:** Stripping voltammogram obtained from the solution containing  $7.5 \times 10^{-5} \text{ mol L}^{-1}$  of Pb(II) and  $1 \times 10^{-5} \text{ mol L}^{-1}$  of Cd(II). Experimental conditions: supporting electrolyte / 0.1 M acetate buffer (pH 3.5); SWV: deposition potential -1.2 V vs. ref., deposition time 30 s, frequency 200 Hz, step height 4 mV, and amplitude 50 mV.

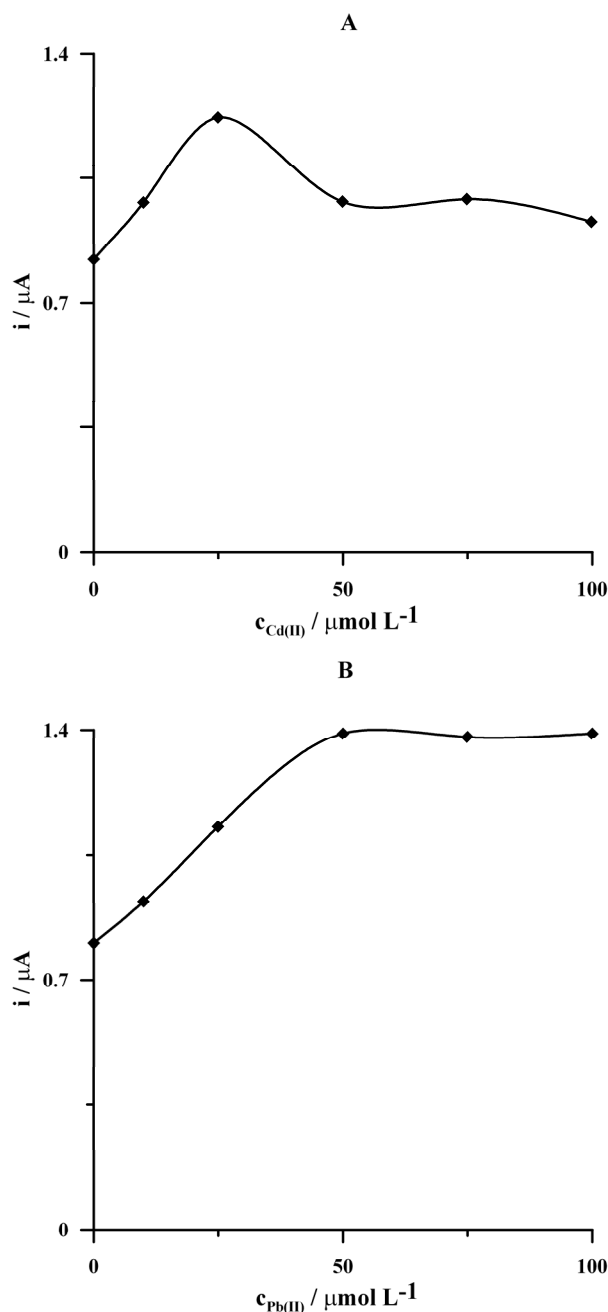
***Effect of pH of the Pre-plating Solution and the Concentration of Cd(II) and Pb(II).*** The influence of pH of the pre-plating solution on the peak current of folic acid at a “hybrid” lead film electrode was studied. In these experiments the lead film was pre-plated from a solution containing 0.1 M acetic acid or 0.1 M acetate buffer with pH in the range from 3.5 to 6.1 and with  $7.5 \times 10^{-5} \text{ mol L}^{-1}$  of Pb(II) and  $1 \times 10^{-5} \text{ mol L}^{-1}$  of Cd(II). In the first step, Pb and Cd were deposited simultaneously on a glassy carbon surface at a potential of -1.2 V for 30 s. During the second step, elemental Cd was stripped off from surface and Pb continued to deposit at a potential of -0.65 V for 30 s.

Afterwards, the electrode surface was re-plated with Pb *in situ* with the sample. The lead film was deposited and folic acid was accumulated at -0.88 V for 120 s in a solution containing 0.1 M acetate buffer (with pH 5.6),  $7.5 \times 10^{-5}$  M Pb(II) and folic acid at a concentration of  $1 \times 10^{-7}$  mol L<sup>-1</sup>. At a pH equal to 3.5, the peak current of folic acid attained maximal and stable value, being well reproducible. Consequently, the following experiments were carried out in a pH 3.5 acetate buffer solution.

The Cd(II) concentration used for *ex-situ* formation of the lead film electrode has been shown to influence the peak height for folic acid. The concentration of Cd(II) added to the preplating solution was changed from 0 to  $1 \times 10^{-4}$  mol L<sup>-1</sup>. The obtained results are presented in Fig. 2A. It was found that the folic acid peak current increases as the concentration of Cd(II) increases to  $2.5 \times 10^{-5}$  mol L<sup>-1</sup>, so for further study this concentration was chosen. On the basis of the results obtained, it can be stated that the lead film prepared by the *ex-situ* procedure without using the reversibly deposited metal “mediator”, exhibiting worse adsorptive properties than those of the film prepared by reversibly deposited metal “mediator”.

Then the influence of concentration of Pb(II) added to the pre-plating solution on the folic acid signal was studied. These experiments were done at a constant concentration of Cd(II) equal to  $2.5 \times 10^{-5}$  mol L<sup>-1</sup>, while the concentration of Pb(II) was changed in the range from 0 to  $1 \times 10^{-4}$  mol L<sup>-1</sup>. The obtained results are presented in Fig. 2B. At a concentration range from  $5 \times 10^{-5}$  to  $1 \times 10^{-4}$  M Pb(II), the reduction peaks of folic acid attained maximal and stable values and were well reproducible. On the basis of these results, the Pb(II) concentration of  $5 \times 10^{-5}$  mol L<sup>-1</sup> was chosen for further study. The increase of the peak current of folic acid with the increase concentration of Pb(II) added to the pre-plating solution probably is connected with the increase the active surface area of the lead film. It has to be noted that the lead was further deposited in the second step of pre-plating and then plated again *in situ* with the sample.

**Optimization of Deposition Conditions.** In order to estimate the influence of the deposition potential of cadmium and lead directly on the analytical results, the adsorptive stripping voltammetric response of folic acid at a concentration of  $1 \times 10^{-7}$  mol L<sup>-1</sup> was studied. The deposition potential of cadmium and lead was changed in the range from -1.1 to -1.45 V for 30 s. The potential and time of the cadmium oxidation and further deposition of lead were equal to -0.65 V and 30 s, respectively. The results indicate that the peak current of folic acid attained maximal value as the deposition potential of cadmium and lead was -1.4 V, so for further study this potential was chosen.

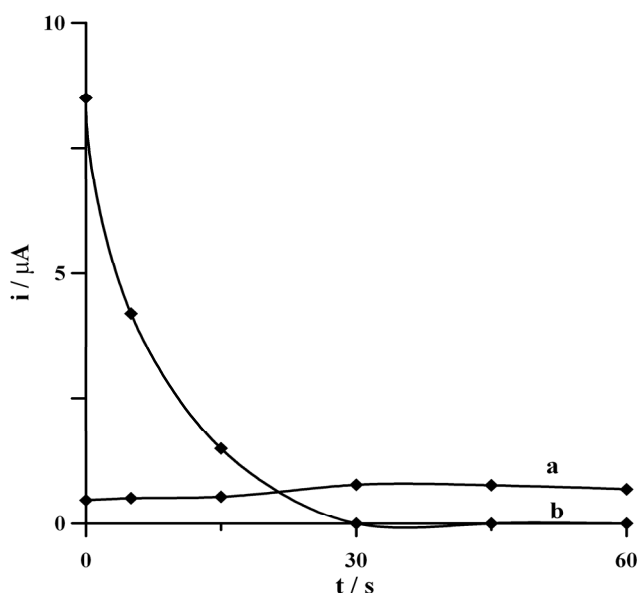


**Fig. 2:** Effect of the concentration of Cd(II) and Pb(II) added to the preplating solution on the peak current of folic acid at a “hybrid” lead film electrode. Legend: **A)** effect of the concentration of Cd(II) at a constant concentration of Pb(II) equal to  $7.5 \times 10^{-5} \text{ mol L}^{-1}$ , **B)** effect of the concentration of Pb(II) at a constant concentration of Cd(II) equal to  $2.5 \times 10^{-5} \text{ mol L}^{-1}$ . Experimental conditions: supporting electrolyte of the preplating solution:  $0.1 \text{ mol L}^{-1}$  acetate buffer (pH 3.5), concentration of folic acid  $1 \times 10^{-7} \text{ mol L}^{-1}$ ; SWV: deposition potential of lead and cadmium  $-1.2 \text{ V vs. ref.}$ , deposition time of lead and cadmium 30 s, potential of stripping of cadmium and further deposition of lead  $-0.65 \text{ V vs. ref.}$ , time of stripping of cadmium and further deposition of lead 30 s, potential of further deposition of lead and accumulation of folic acid  $-0.88 \text{ V vs. ref.}$ , time of further deposition of lead and accumulation of folic acid 120 s. (for other details, see *Experimental*).

Additionally, the results show that prolongation of the deposition time of cadmium and lead from 30 to 120 s did not influence on the peak current of folic acid, so for further study the deposition time of cadmium and lead of 30 s was used.

As mentioned above, at a potential in the range from -0.6 to -0.7 V vs. ref., cadmium will be stripped from the surface as lead will continue in deposition. The experimental results show that the changes of the potential of the cadmium oxidation and further deposition of lead in the range from -0.6 to -0.7 V did not influence on the peak current of folic acid, so for further study the potential of -0.65 V was used.

Next, the time of the oxidation of cadmium and further deposition of lead was studied. The time was changed in the range from 0 to 60 s and its influence on the reduction peak of folic acid at concentration of  $5 \times 10^{-8} \text{ mol L}^{-1}$  and also on the oxidation peak current of cadmium was studied (Fig. 3). It was observed that the reduction peak current of folic acid attained maximal and stable value as the time of the oxidation of cadmium and further deposition of lead was in the range from 30 to 60 s. Additionally, the results show that all cadmium is stripped from the surface of the electrode, while the time of oxidation is equal to 30 s. Consequently, in the following experiments the time of the complete oxidation of cadmium and further deposition of lead of 30 s was used.



**Fig. 3:** Effect of the time of oxidation of cadmium and further deposition of lead. Legend: **a)** the folic acid peak current, **b)** the oxidation peak current of cadmium. Experimental conditions: supporting electrolyte of the preplating solution:  $0.1 \text{ mol L}^{-1}$  acetate buffer (pH 3.5), concentration of folic acid  $5 \times 10^{-8} \text{ mol L}^{-1}$ , SWV: deposition potential of lead and cadmium - 1.4 V vs. ref., deposition time of lead and cadmium 30 s, potential of stripping of cadmium and further deposition of lead -0.65 V vs. ref. (for other details, see *Experimental*).

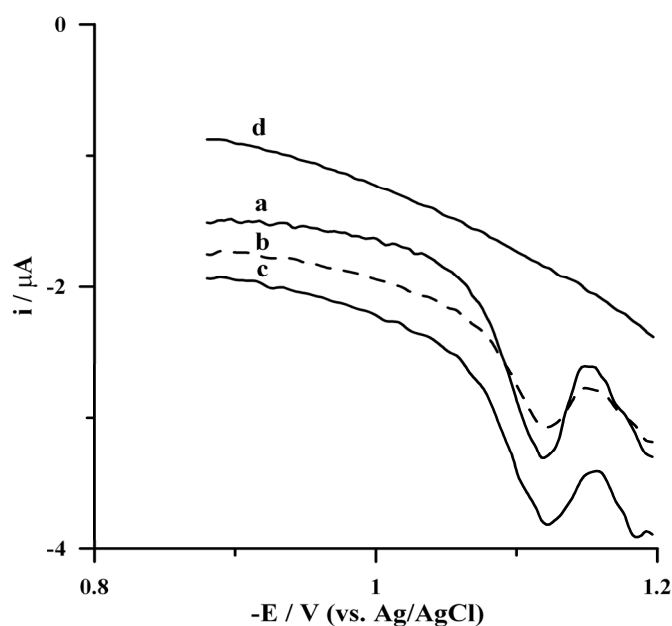


## Comparison of Lead Film Electrodes Prepared with Use of Different Plating Methods

In order to improve the electrochemical performance of the lead film electrode, the combination of *ex-situ* and *in-situ* plating methods and also the use of a reversibly deposited mediator metal were applied. The “hybrid” lead film electrode prepared with use of the mediator metal was tested by adsorptive stripping voltammetry of folic acid. The results were compared to those obtained at an in situ plated lead film electrode according to the procedure earlier described in literature [20], an *ex-situ* plated lead film electrode prepared without use of the mediator metal and to those obtained at a “hybrid” lead film electrode prepared without use of the mediator metal.

Fig. 4 shows typical square wave adsorptive stripping voltammograms for folic acid, present at the concentration of  $6.5 \times 10^{-8}$  mol L<sup>-1</sup>, obtained at the “hybrid” lead film electrode prepared with use of the mediator metal (curve **a**), the in situ plated lead film electrode (curve **b**), the *ex-situ* plated lead film electrode (curve **c**) and the “hybrid” lead film electrode prepared with use of the mediator metal (curve **a**), the “hybrid” lead film electrode prepared without use of the mediator metal (curve **d**). The “hybrid” lead film electrode prepared without use of the mediator metal and the *in-situ* plated lead film electrode yielded wider signal with worse baseline for the folic acid peak than the “hybrid” lead film electrode prepared with use of the metal mediator. From Fig. 4, it is also evident that the signal for folic acid obtained at the “hybrid” lead film electrode prepared with use of the mediator metal (curve **a**) is higher than those obtained for the some concentration of folic acid at the in situ plated lead film electrode (curve **b**) and the “hybrid” lead film electrode prepared without use of the mediator metal (curve **c**) in terms of the peak height (0.96  $\mu$ A, 0.49  $\mu$ A, and 0.71  $\mu$ A, respectively). In addition, in the case of the *ex-situ* plated lead film electrode prepared without use of the mediator metal no signal of folic acid at concentration of  $6.5 \times 10^{-8}$  mol L<sup>-1</sup> was observed.

In overall, the data of Fig. 4 suggest that the sensitivity for folic acid is the lowest on the “hybrid” lead film electrode prepared with use of the mediator metal. It was confirmed that the analytical utility of the lead film electrode depend strictly on the procedure of coating the support with the lead deposit. It has to be quoted that the method of preparation of the “hybrid” lead film electrode with use of the mediator metal lengthens analysis time, yet at the same time it contributes to a decrease of background current, helps improve shape of peak, increases the peak current in comparison with an in situ plated lead film electrode.



**Fig. 4:** Square wave voltammograms obtained in the course of the determination of folic acid at concentration of  $6.5 \times 10^{-8} \text{ mol L}^{-1}$  at the lead film electrodes prepared with the use of different plating methods. Legend: **a**) the “hybrid” lead film electrode prepared with use of the mediator metal, **b**) the in situ plated lead film electrode, **c**) the “hybrid” lead film electrode prepared without use of the mediator metal, **d**) the *ex-situ* plated lead film electrode. Experimental conditions: supporting electrolyte of the pre-plating solution:  $0.1 \text{ mol L}^{-1}$  acetate buffer (pH 3.5); SWV: potential of deposition of lead and accumulation of folic acid  $-0.88 \text{ V}$  vs. ref., time of deposition of lead and accumulation of folic acid 120 s, frequency 200 Hz, step height 4 mV, and amplitude 50 mV (for other details, see *Experimental*).

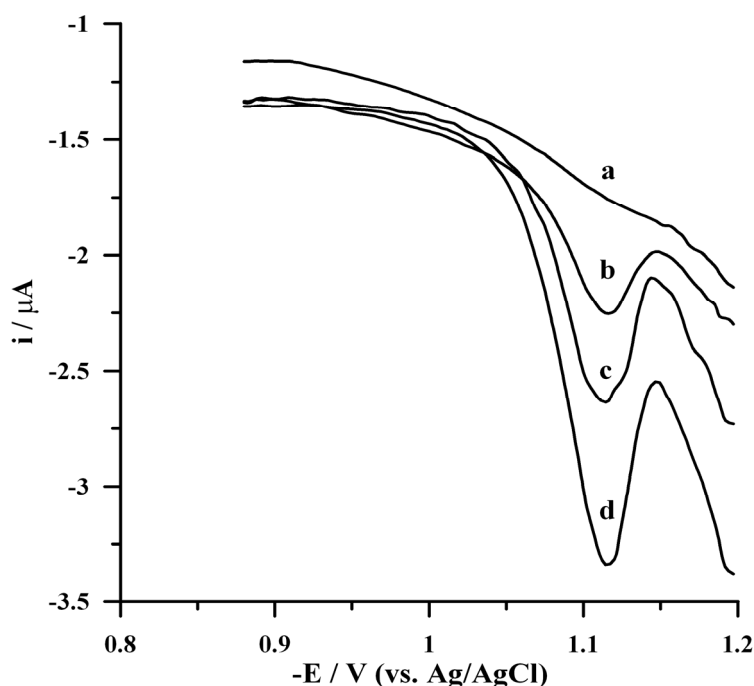
### Calibration Plot, Limit of Detection, and Limit of Quantification

The calibration graph for the accumulation time of 120 s was linear from  $2 \times 10^{-9}$  to  $2 \times 10^{-7} \text{ mol L}^{-1}$  and obeyed the equation  $y = 0.0137x + 0.0125$ , where  $y$  and  $x$  are the peak current ( $\mu\text{A}$ ) and folic acid concentration ( $\text{nmol L}^{-1}$ ), respectively. The correlation coefficient ( $r^2$ ) was 0.9999. The relative standard deviations for a folic acid concentration of  $1 \times 10^{-7} \text{ mol L}^{-1}$  were 3.5% ( $n = 5$ ) and 4.2% ( $n = 20$ ). It has to be noted that before each measurement the electrode was cleaned electrochemically at the potential of  $+0.5 \text{ V}$  for 30 s and the glassy carbon surface was pre-plated with Pb and then re-plated with Pb in situ with the sample. The detection and quantification limits for an accumulation time of 120 s estimated from 3 and 10 times the standard deviation for the lowest determined concentration of folic acid were about  $7 \times 10^{-10}$  and  $2.4 \times 10^{-9} \text{ mol L}^{-1}$ , respectively.

The favorable performance of the “hybrid” lead film electrode prepared with use of the metal mediator is supported by estimating the detection limit to a value of  $7 \times 10^{-10} \text{ mol L}^{-1}$ , almost  $6 \times$  lower than that found for an *in-situ* plated lead film electrode ( $4 \times 10^{-9} \text{ mol L}^{-1}$ ) [20].

### Analytical Applications

The “hybrid” lead film electrode prepared with use of the metal mediator (Cd) was evaluated by carrying out the determination of folic acid in tablets of *Folovit*. The recovery rate of the method proposed was used as a criterion to evaluate the accuracy of the method. The recovery of five independent experiments was 102% with a relative standard deviation (RSD) of  $\pm 3.9\%$ , demonstrating a very good accuracy of the proposed method. The quantitative results obtained for the tablets were in agreement with the data supplied by the manufacturer. based on these results, it can be stated that the proposed procedure can be applied to sensitive determination of folic acid in its pharmaceutical formulations.



**Fig. 5:** Square wave voltammograms obtained in the course of the determination of folic acid in tablets (*Folovit*) Legend: **a**) blank, **b**) as (a) + sample diluted (1:10), **c**) as (b) +  $2 \times 10^{-8} \text{ mol L}^{-1}$  folic acid, **d**) as (b) +  $2 \times 10^{-8} \text{ mol L}^{-1}$  folic acid. Experimental conditions: supporting electrolyte of the pre-plating solution:  $0.1 \text{ mol L}^{-1}$  acetate buffer (pH 3.5); SWV: potential of deposition of lead and accumulation of folic acid  $-0.88 \text{ V}$  vs. ref., time of deposition of lead and accumulation of folic acid 120 s, frequency 200 Hz, step height 4 mV, and amplitude 50 mV (for other details, see *Experimental*).

## Conclusions

In this paper, for the first time, the “hybrid” lead film electrode has been prepared with use of the metal mediator and applied to the determination of biologically active compound by adsorptive stripping voltammetry. In this approach, involving the pre-plating of Pb onto the glassy carbon surface with the use of a reversibly deposited metal mediator (Cd) followed by repeated plating under conditions appropriate for the analyte, *i.e.* folic acid, the configuration of a “hybrid” lead film electrode has been accomplished.

This arrangement combines the properties of both pre-film formation and *in-situ* film formation method sequences and the results obtained have shown that such an film electrode incorporating a reversibly deposited metal mediator may provide a much better electrochemical performance compared to the *in-situ* and *ex-situ* plated lead film variants. This confirms the fact that the plating method applied to the lead film formation influences the active surface area of these electrodes. It has to be noted that, under optimized conditions of the lead film formation, the proposed procedure for the determination of folic acid at the “hybrid” lead film electrode with the metal mediator by and coupled with adsorptive stripping voltammetry offers better electroanalytical performance and a lower detection limit than that obtained at *in-situ* plated lead film electrode.

## References

1. R.G. Compton, C.E. Banks: *Understanding Voltammetry*, World Scientific, Singapore, 2007.
2. J. Wang: *Analytical Electrochemistry*, Wiley-VCH, New York, 1994.
3. J. Wang: *Electroanalysis* **17** (2005) 1341.
4. A. Economou, P.R. Fielden: *Trends Anal. Chem.* **16** (1997) 286.
5. R. Metelka, K. Vytřas, A. Bobrowski: *J. Solid State Electrochem.* **4** (2000) 348.
6. A. Economou, P.R. Fielden: *Analyst* **128** (2003) 205.
7. A. Królicka, R. Pauliukaite, I. Švancara, R. Metelka, A. Bobrowski, E. Norkus, K. Kalcher, K. Vytřas: *Electrochem. Commun.* **4** (2002) 193.
8. R. Pauliukaite, R. Metelka, I. Švancara, A. Królicka, A. Bobrowski, K. Vytřas, E. Norkus, K. Kalcher: *Anal. Bioanal. Chem.* **374** (2002) 1155.
9. A. Królicka, A. Bobrowski: *Electrochem. Commun.* **6** (2004) 99.

10. K.E. Toghill, G.G. Wildgoose, A. Moshar, C. Mulcahy, R.G. Compton: *Electroanalysis* **20** (2008) 1731.
11. L. Baldrianová, I. Švancara, A. Economou, S. Sotiropoulos: *Anal. Chim. Acta* **580** (2006) 24.
12. I. Švancara, C. Prior, S.B. Hočevar, J. Wang: *Electroanalysis* **22** (2010) 1405.
13. S.B. Hočevar, I. Švancara, B. Ogorevc, K. Vytřas: *Anal. Chem.* **79** (2007) 8639.
14. E. Tesařová, L. Baldrianová, S.B. Hočevar, I. Švancara, K. Vytřas, B. Ogorevc: *Electrochim. Acta* **54** (2009) 1506.
15. V. Urbanová, K. Vytřas, A. Kuhn: *Electrochem. Commun.* **12** (2010) 114.
16. A.M. Ashrafi, K. Vytřas: *Talanta* **85** (2011) 2700.
17. A.M. Ashrafi, K. Vytřas: *Electrochim. Acta* **73** (2012) 112.
18. A. Bobrowski, M. Putek, J. Zarebski: *Electroanalysis* **24** (2012) 1071.
19. M. Korolczuk, K. Tyszczyk, M. Grabarczyk: *Electrochem. Commun.* **7** (2005) 1185.
20. M. Korolczuk, K. Tyszczyk: *Electroanalysis* **19** (2007) 1959.
21. K. Tyszczyk, M. Korolczuk: *Comb. Chem. High T. Scr.* **13** (2010) 753.
22. K. Tyszczyk-Rotko, I.H. Taşdemir: *J. Electroanal. Chem.* **670** (2012) 11.
23. K. Tyszczyk-Rotko, J. Maj: *Electroanalysis* **24** (2012) 101.
24. K. Tyszczyk: *Electrochim. Acta* **56** (2011) 3975.
25. A. Economou, P.R. Fielden: *Analyst* **121** (1996) 1903.
26. R. Garcia-Mancó Carra, A. Sánchez-Misiego, A. Zirino: *Anal. Chem.* **67** (1995) 4484.