

Research Article

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Application of screen-printed carbon electrode modified with lead in stripping analysis of Cd(II)

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Abstract: In the work presented, a lead film electrode was prepared in situ on a screen-printed carbon support using a reversibly deposited mediator (Zn) and applied to the determination of Cd(II) by anodic stripping voltammetry. The electrochemical method for lead film formation is based on a co-deposition of a metal of interest (Pb), with a reversibly deposited zinc mediator, followed by oxidation of zinc, with additional deposition of lead at the appropriate potential. It serves to increase the density of lead particles, promoting lead film growth, and consequently helps to improve the electrochemical properties of the electrode. This was confirmed by microscopic and voltammetric studies. The obtained detection limit of Cd(II) is equal to $6.6 \times 10^{-9} \text{ mol L}^{-1}$ (-1.6 V for 180 s and then -0.95 V for 5 s). The presented procedure was successfully applied to cadmium determination in Bystrzyca River water samples.

Keywords: stripping voltammetry, cadmium determination, screen-printed lead film electrode, zinc mediator

1 Introduction

Stripping analysis is considered to be the most sensitive electroanalytical technique and highly suitable for the task of field monitoring of toxic metals. The sensitivity of stripping analysis is attributed to its preconcentration step, in which trace metals are accumulated onto the working electrode surface [1,2]. A great variety of electrodes have been employed in metal determination,

but screen-printed electrodes (SPEs) have low unit costs and are capable of undergoing mass production while still maintaining adequate levels of reproducibility. Moreover, SPEs have the advantage of miniaturization. SPEs have been developed as single-use sensors for a variety of applications in environmental, industrial and clinical analyses [3,4]. Among numerous variants of SPEs, screen-printed carbon electrodes (SPCEs) have attracted a great deal of attention because of their easy-to-make modifications, either by immobilizing a modifier on the electrode surface or adding it to the carbon ink before the electrode is made.

Cadmium is a heavy metal which is extremely toxic to animals. Although the mechanisms of cadmium toxicity are poorly understood, it has been speculated that cadmium causes single-strand DNA damage and disrupts the synthesis of nucleic acids and proteins [5]. Cadmium ions are relatively soluble in water and are readily absorbed in plant tissues and in animal organs such as the liver and kidneys. Many kinds of screen-printed electrodes have been used as electrochemical sensors of Cd(II), however, the most common in the literature are: mercury-coated SPEs [6-10], bismuth-coated SPEs [11-17], gold SPEs and gold and/or carbon nanostructured SPEs [18,19]. In the case of voltammetric procedures of Cd(II) determination employing screen-painted electrodes, the lowest detection limit of $8.9 \times 10^{-10} \text{ mol L}^{-1}$ (for a preconcentration time of 360 s) was obtained using sputtered Bi SPE [17].

In 2005 the lead film electrode (PbFE) was introduced for the first time for adsorptive stripping voltammetric determinations of inorganic ions such as Co(II) and Ni(II) [20]. This electrode has several attractive properties that include simple preparation, good reproducibility and electrochemical surface renewal, mechanical stability, ability to operate in a wide range of media with varying pH, effective preconcentration in stripping procedures, well-defined and separated stripping signals for several metal ions and organic compounds [20-23].

In the present article, we report the first utilization of screen-printed carbon electrode as the support for an

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in situ plated lead film electrode prepared with the use of a reversibly deposited mediator [24]. In this approach, a metal of interest (Pb) is co-deposited with a mediator (Zn), followed by the subsequent oxidation of zinc and further deposition of lead at the appropriate potential. The investigated electrode was tested as a sensor for the anodic stripping voltammetric determination of Cd(II) traces. It is worth noting that, to date, our studies have confirmed the usefulness of the mediator for enhancing the electrochemical properties of the PbFE applied to folic acid and Ni(II) determination and the bismuth film electrode for Sn(IV) determination [25-27].

2 Experimental procedures

2.1 Preparation of screen-printed carbon electrodes

The screen-printed carbon electrodes were prepared by screen-printing of commercial carbon ink (C10903D14, Gwent Electronic Materials Ltd., Pontypool, UK) onto the ceramic supports (each 40×10 mm). Thick layers of the carbon ink were formed by brushing the ink through an etched stencil (thickness $100 \mu\text{m}$, electrode printing area 105 mm^2) with the aid of the spatula provided with the screen-printing device (UL 1505 A, Tesla, Czech Republic) onto the ceramic substrates. The printed electrodes were dried at $60 \text{ }^\circ\text{C}$ for 30 min and then covered with a layer of PVC insulator, leaving a defined rectangular shaped (5×3 mm) working area and a similar area on the other side for electrical contact.

2.2 Determination of Cd(II) at the lead film electrode prepared with and without a mediator

The screen-printed carbon electrode was modified by the lead film using an in situ plating method with and without the use of a reversibly deposited zinc mediator. The lead film coating and the voltammetric determinations of cadmium under the optimized conditions were carried out in a solution containing 0.1 mol L^{-1} acetate buffer (pH 4.6 ± 0.1), $2 \times 10^{-5} \text{ mol L}^{-1}$ Pb(II), 0 or $1 \times 10^{-5} \text{ mol L}^{-1}$ Zn(II) and variable concentrations of Cd(II). The potential of the electrode was changed in the following sequence: 0.5 V for 30 s, -1.6 V for 180 s and -0.95 V for 5 s. The first step (the potential of 0.5 V for 30 s), was applied to clean the electrode from the lead remaining after the preceding measurement. In the next step (the potential of -1.6 V

for 180 s), Zn, Pb and Cd were deposited simultaneously onto a screen-printed carbon surface. During the third step (the potential of -0.95 V for 5 s), zinc was stripped from the surface, while lead and cadmium continued to be deposited. During both steps the solution was stirred using a magnetic stirring bar. The stirring was stopped and after 5 s equilibration time, the anodic square wave voltammograms were recorded between -1.6 and 0.5 V with frequency of 10 Hz, amplitude of 50 mV and scan rate of 10 mV s^{-1} . The oxidation peak of lead was much larger than that of cadmium, so the recorded voltammograms were cut in the potential range from -1.2 to -0.6 V . Solutions were not deaerated before voltammetry measurements.

2.3 Reagents and water samples

1 mol L^{-1} acetate buffer (pH = 4.5 ± 0.1), was used as a supporting electrolyte for the proposed voltammetric method and it was prepared from CH_3COOH and NaOH obtained from Sigma-Aldrich and Merck, respectively. The stock standard solutions of Pb(II), Zn(II) and Cd(II) (1 g L^{-1}) were purchased from Merck. The working solutions of Pb(II), Zn(II) and Cd(II) were prepared by appropriate dilution of the stock standard solutions in 0.1 mol L^{-1} HNO_3 (Merck). All solutions were prepared using ultra-purified water ($>18 \text{ M}\Omega \text{ cm}$) supplied by a Milli-Q system (Millipore, UK).

The natural water samples were collected from Bystrzyca River (Lublin, Poland). This material was filtered using a $0.45 \mu\text{m}$ Millipore filter, acidified to pH = 2 using concentrated HNO_3 (Merck) and then UV-irradiated for 3 h.

2.4 Apparatus

The electrochemical experiments were carried out using a $\mu\text{Autolab}$ analyzer (Eco Chemie, Netherlands) in conjunction with a three-electrode system. The electrochemical cell consisted of the silver/silver chloride/potassium chloride ($\text{Ag}/\text{AgCl}/\text{KCl}$ 3 mol L^{-1}) reference electrode, platinum wire as the counter electrode, and the modified screen-printed carbon electrode as the working electrode.

High-resolution microscope FEI DualBeam™ Quanta™ 3D FEG (a/the scanning electron microscope (SEM) with focused ion beam (FIB)) equipped with an energy dispersive X-ray spectrometer (EDS) was used for the electrode surface characterization.

The water samples were mineralized using a UV-digester made by Mineral (based in Poland).

3 Results and Discussion

3.1 Comparison of electrodes

In order to improve the sensitivity of Cd(II) determination at an in situ plated screen-printed lead film electrode a reversibly deposited mediator was applied. Such an application of a mediator in the lead film electrode preparatory step was recently described for the determination of folic acid and Ni(II) [25,26]. This experimental work confirmed that employing a mediator during lead film formation brings about changes in the structure of the lead film and increases the surface coverage of glassy carbon by lead particles. Since this practice facilitated the adsorption of folic acid or the Ni(II) complexes with nioxime, and consequently provided a significant enhancement of voltammetric responses, it was decided to apply this technique to Cd(II) determination.

A comparative study of the in situ plated lead film electrodes prepared with and without the use of a zinc mediator for measuring $5 \times 10^{-7} \text{ mol L}^{-1}$ Cd(II) is presented in Fig. 1. Well-defined and sharp cadmium signals were obtained using the two studied electrodes, however, as can be seen from Fig. 1, the use of a zinc mediator caused an increase of the Cd signal and a decrease of the background current. To better illustrate the role of a zinc mediator, the influence of Zn(II) concentration on the peak currents of Cd(II) ($5 \times 10^{-7} \text{ mol L}^{-1}$ and $2 \times 10^{-6} \text{ mol L}^{-1}$) are presented in Fig. 2. The relative standard deviations of five replicate determinations of Cd(II) for each concentration of Zn(II) were in the range of 3.3 to 4.9%. The Cd(II) peak current increased with increasing the mediator zinc concentration up to $1 \times 10^{-5} \text{ mol L}^{-1}$. Since the peak current of Cd(II) slightly decreased at $5 \times 10^{-5} \text{ mol L}^{-1}$ Zn(II), the Zn(II) concentration of $1 \times 10^{-5} \text{ mol L}^{-1}$ was chosen for subsequent experiments. The microscopic observation (Fig. 3) correlated well with the results of the electrochemical study. The improvement in electrode electrochemical properties with the use of a mediator is connected with the increase of the electrode active surface area, where Cd(II) ions can be reduced to a metallic state. The presence of lead particles on the electrode surface was confirmed using EDS analysis.

3.2 Optimization of voltammetric procedure, calibration graph and analytical application

The influence of different voltammetric conditions and parameters on the peak height of $5 \times 10^{-7} \text{ mol L}^{-1}$ Cd(II) was investigated. The obtained results are presented in Fig. 4

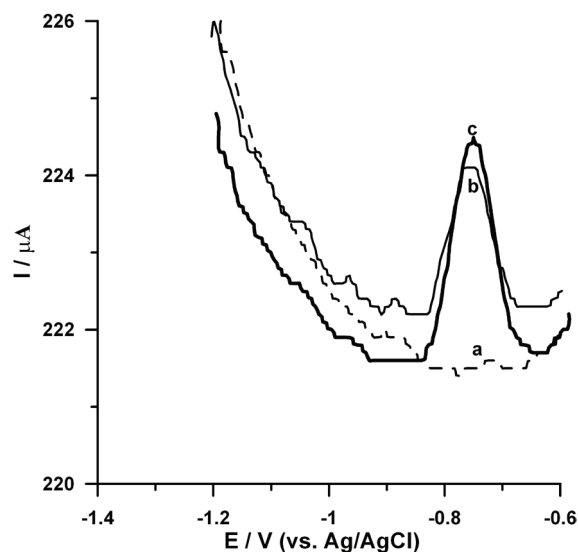


Figure 1: Square wave voltammograms obtained at the in situ plated lead film electrode prepared without (a and b) and with (c) the use of a zinc mediator. The solution for electrode preparation and Cd(II) determination contained 0.1 mol L^{-1} acetate buffer $\text{pH} = 4.6 \pm 0.1$, $5 \times 10^{-6} \text{ mol L}^{-1}$ Pb(II), 0 (a) or $5 \times 10^{-7} \text{ mol L}^{-1}$ Cd(II) (b and c) and 0 (a and b) or $1 \times 10^{-5} \text{ mol L}^{-1}$ (c) Zn(II). Zn, Pb and Cd were deposited at -1.5 V for 120 s. The potential and time of zinc oxidation and further deposition of lead and cadmium were -0.95 V and 120 s, respectively.

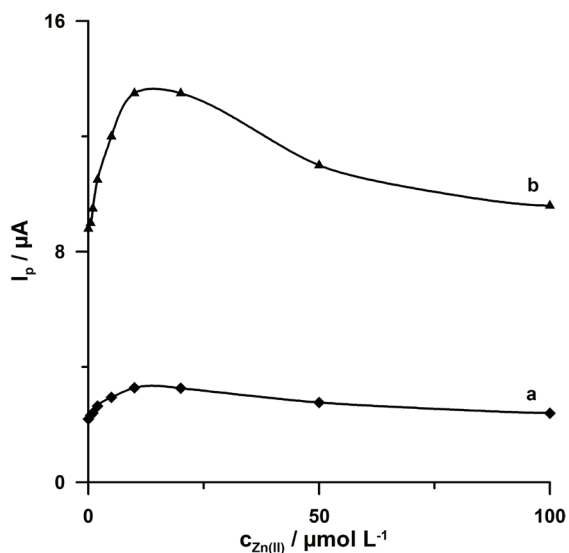


Figure 2: Influence of Zn(II) concentration on the voltammetric signal of Cd(II). The solution contained 0.1 mol L^{-1} acetate buffer $\text{pH} = 4.6 \pm 0.1$, $5 \times 10^{-6} \text{ mol L}^{-1}$ Pb(II), $5 \times 10^{-7} \text{ mol L}^{-1}$ (a) or $2 \times 10^{-6} \text{ mol L}^{-1}$ Cd(II) (b) and increasing concentration of Zn(II). Other parameters were as in Fig. 1.

and Table 1, and they were used for calibration graph construction (Fig. 5). The Cd(II) oxidation peak current attained a maximum and stable value as lead, zinc and

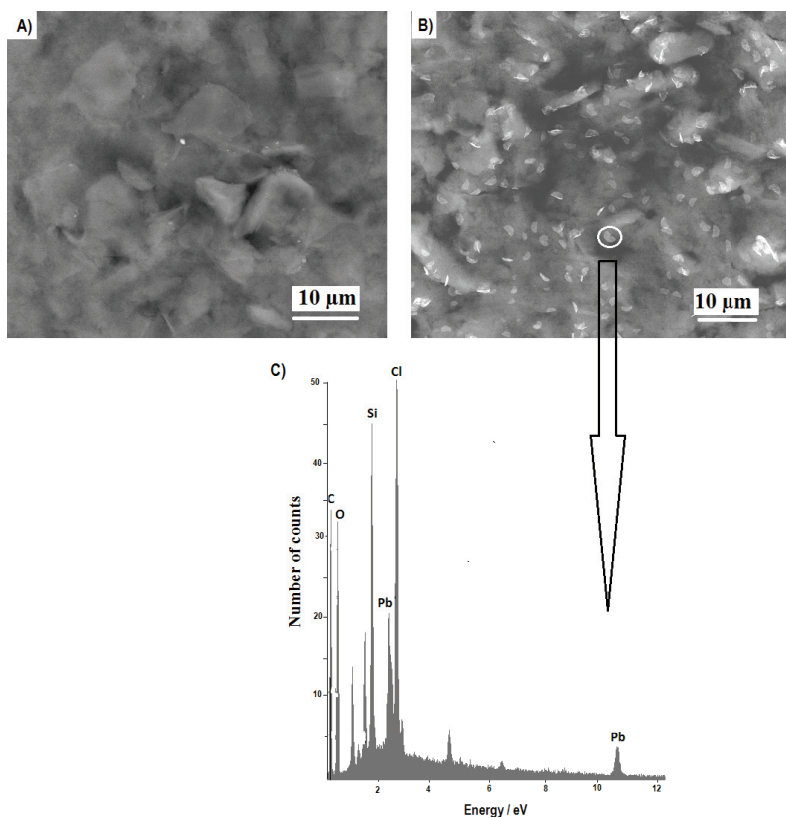


Figure 3. SEM images of lead film electrode surface prepared without (A) and with (B) the use of a zinc mediator. The solution for electrode preparation contained 0.1 mol L^{-1} acetate buffer $\text{pH} = 4.6 \pm 0.1$, $2 \times 10^{-5} \text{ mol L}^{-1}$ Pb(II) and 0 (A) or $1 \times 10^{-5} \text{ mol L}^{-1}$ (B) Zn(II) . Zn and Pb were deposited at -1.6 V for 180 s . The potential and time of zinc oxidation and further deposition of lead were -0.95 V and 5 s , respectively. The EDS spectrum of highlighted fragment of the lead film electrode surface prepared with the mediator (C).

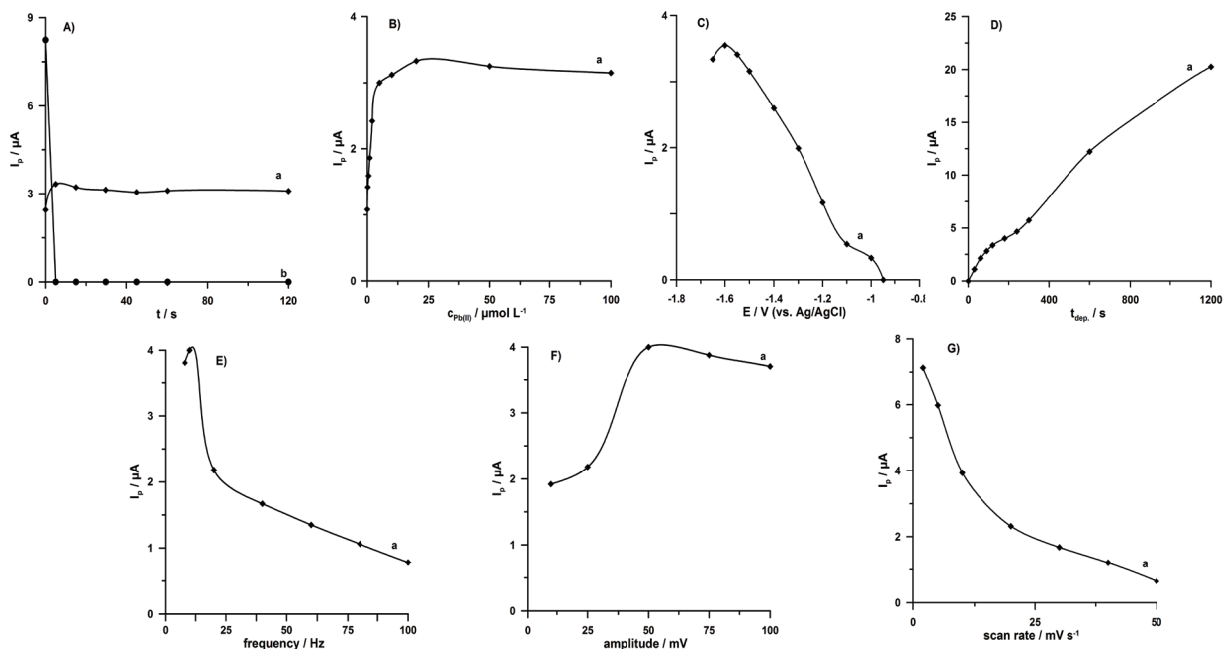


Figure 4. Influence of: A) time of Zn oxidation, B) Pb(II) concentration, C) deposition potential, D) deposition time, E) frequency, F) amplitude, G) scan rate on the voltammetric signal of $5 \times 10^{-7} \text{ mol L}^{-1}$ Cd(II) (A-G, line a) and on the voltammetric signal of $1 \times 10^{-5} \text{ mol L}^{-1}$ Zn(II) (A, line b).

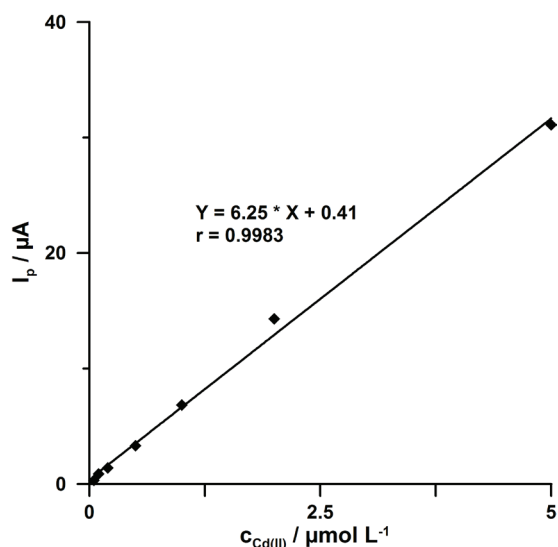


Figure 5: Calibration curve of Cd(II). The solution for electrode preparation contained 0.1 mol L^{-1} acetate buffer $\text{pH} = 4.6 \pm 0.1$, $2 \times 10^{-5} \text{ mol L}^{-1}$ Pb(II), $1 \times 10^{-5} \text{ mol L}^{-1}$ Zn(II) and increasing concentration of Cd(II). Zn, Pb and Cd were deposited at -1.6 V for 180 s. The potential and time of zinc oxidation and further deposition of lead and cadmium were -0.95 V and 5 s, respectively.

cadmium were simultaneously deposited for 1200 s. However, for further measurements a time of 180 s was chosen in order to decrease the total time of analysis. Additionally, in order to decrease the total time of analysis the scan rate of 10 mV s^{-1} was chosen for subsequent experiments. It was found that the calibration graph was linear from 5×10^{-8} to $5 \times 10^{-6} \text{ mol L}^{-1}$ and obeyed the equation $y = 6.25x + 0.41$, where y is the peak current (μA) and x is the Cd(II) concentration ($\mu\text{mol L}^{-1}$). The correlation coefficient (r) was 0.9983. The detection and quantification limits of Cd(II) estimated at 3 and 10 times the standard deviation ($n = 5$) for the lowest determined concentration divided by the slope of the linear regression equation are equal to $6.6 \times 10^{-9} \text{ mol L}^{-1}$ and $2.3 \times 10^{-8} \text{ mol L}^{-1}$ (a total deposition time of 185 s), respectively. The detection limit of the presented procedure is lower than those obtained at the bismuth film screen-printed electrodes [28].

The Cd(II) concentration in the Bystrzyca River samples was below the detection limit of the procedure at the in situ plated lead film screen-printed carbon electrode prepared with a mediator. The analyzed samples were therefore spiked with Cd(II) at concentration levels of 5×10^{-8} and $2 \times 10^{-7} \text{ mol L}^{-1}$ and then the cadmium content was determined using the standard addition method. The recovery values are 102.8% and 99.0% with relative standard deviations of 4.2% and 3.9%, respectively. The obtained results (Table 2) showed satisfactory accuracy and precision of the proposed voltammetric procedure.

Table 1: Optimized voltammetric conditions and parameters for Cd(II) determination at the lead film screen-printed carbon electrode prepared with the use of a zinc mediator.

Conditions and parameters	Studied range	Chosen value
Zn(II) concentration	$0.5 - 100 \mu\text{mol L}^{-1}$	$10 \mu\text{mol L}^{-1}$
Time of Zn oxidation	$0 - 120 \text{ s}$	5 s
Pb(II) concentration	$0.2 - 100 \mu\text{mol L}^{-1}$	$20 \mu\text{mol L}^{-1}$
Deposition potential of Zn, Pb, Cd	$-1.65 - (-0.95) \text{ V}$	-1.6 V
Deposition time of Zn, Pb, Cd	$0 - 1200 \text{ s}$	180 s
Frequency	$8 - 100 \text{ Hz}$	10 Hz
Amplitude	$10 - 100 \text{ mV}$	50 mV
Scan rate	$2 - 50 \text{ mV s}^{-1}$	10 mV s^{-1}

Table 2: Results of Cd(II) determination at an in situ plated lead film screen-printed carbon electrode in Bystrzyca River samples.

Sample	Cd(II) added (mol L^{-1})	Cd(II) found (mol L^{-1})	Recovery (%)	RSD ($n = 5$) (%)
Bystrzyca River	0	0	-	-
	5.0×10^{-8}	5.14×10^{-8}	102.8	4.2
	2.0×10^{-7}	1.98×10^{-7}	99.0	3.9

4 Conclusions

The obtained results show that the in situ plated lead film screen-printed carbon electrode prepared with the use of a reversibly deposited zinc mediator provides a much better electrochemical performance in comparison to the lead film electrode prepared without a mediator. The data confirm the fact that the morphology of lead film significantly influences the active surface area of these electrodes, thus facilitating the deposition of cadmium and providing a significant enhancement of the voltammetric response.

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