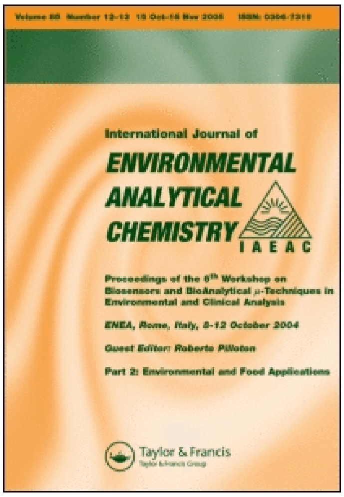

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Determination of cadmium by stripping voltammetry at a lead film electrode

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A procedure for trace cadmium determination by stripping voltammetry at a lead film electrode is presented. Measurements consist of three steps: simultaneous *in situ* formation of lead film and a deposition of metallic cadmium at a lead film electrode, oxidation of cadmium for 1 s and in the last step registering the current corresponding to Cd(II) reduction. The calibration graph was linear from 2×10^{-9} to $1 \times 10^{-6}\,\mathrm{mol\,L^{-1}}$ for a deposition time of 300 s. A detection limit for cadmium following deposition time of 300 s was $6 \times 10^{-10}\,\mathrm{mol\,L^{-1}}$. The relative standard deviation at cadmium concentration $2 \times 10^{-8}\,\mathrm{mol\,L^{-1}}$ was 3.6%. The measurements were carried out from undeaerated solutions. The procedure proposed was validated by analysis of rain water certified reference material.

Keywords: lead film electrode; stripping voltammetry; cadmium; determination

1. Introduction

Cadmium occurs widely in nature, and in addition, substantial amounts of its compounds are present in soil, water and air as a consequence of human pollution. Cadmium is regarded as an extremely toxic element. Prolonged intake of cadmium, even of very small amounts, leads to severe dysfunction of the kidneys. At high doses it is known to produce health effects on the respiratory system and has been associated with bone disease. For this reason the measurements of Cd(II) are important in industrial, clinical and toxicological laboratories [1].

Several methods have already been described for the determination of cadmium. Spectrometric techniques for cadmium determination were recently reviewed in [2,3]. For on-site monitoring of cadmium concentration electrochemical techniques are preferable. Among electroanalytical techniques, anodic stripping voltammetry and adsorptive stripping voltammetry have commonly been used for cadmium determination. Comparison of stripping techniques proposed recently for Cd(II) determination using mercury and non-mercury based electrodes was given in [4]. Only in a few procedures with non-mercury based electrodes the detection limit below $1 \times 10^{-9}\,\mathrm{mol\,L^{-1}}$ was reported [4–8]. In these procedures less accessible electrodes such as edge plane pyrolytic graphite [4], carbon nanotube nanoelectrode array [5], Nafion-coated bismuth film electrode [6], bismuth film zeolite doped carbon paste electrode [7], bismuth nano-powder electrode [8] were used. A low-detection limit for Cd(II) was also reported for silver and gold electrodes [9]. However, in these measurements, a low-detection limit was obtained

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due to application of subtractive anodic stripping voltammetry. Recently, antimony [10] and stannum [11] film electrodes were proposed for Cd(II) determination. However, the detection limits reported were higher than that obtained for the proposed lead film electrode. At carbon paste electrode modified with bismuth powder, a detection limit for Cd(II) of $1 \times 10^{-8}\,\mathrm{mol\,L^{-1}}$ was reported [12]. Such an electrode can be exploited in particular in those cases where the preparation of pre-plated bismuth film electrodes or the introduction of bismuth ions into the solution is undesirable or impossible. To obtain low detection limit in stripping analysis, an increase in the rate of mass transport during the deposition step by sonication of the sample solution [13], heating the solution [14] or activation of the electrode by microwaves [15] were also recommended.

In the present article, a simple procedure for determination of nanomolar concentrations of Cd(II) by stripping voltammetry at a lead film electrode was proposed. In the proposed procedure, lead film and cadmium were deposited simultaneously at a glassy carbon electrode, then cadmium was stripped at −0.6 V for 1 s and an analytical signal of Cd(II) reduction was recorded by square wave voltammetry. Such a procedure was successfully applied previously for manganese determination at a hanging mercury electrode as reported in [16]. Herein, it should be mentioned that the recently introduced lead film electrode has already been successfully applied to the determination of inorganic ions such as Ni(II), Co(II) [17,18] and Mo(VI) [19] or organic compounds such as folic acid [20], testosterone [21] and trimethoprim [22].

2. Experimental

2.1 *Apparatus*

The measurements were performed using a μAutolab analyser made by Eco Chemie, The Netherlands. A classical three-electrode quartz cell of volume 10 mL was used. A glassy carbon electrode of diameter 1 mm was polished daily using 0.3 μm alumina slurry on a Buehler polishing pad. Platinum wire and Ag/AgCl were used as an auxiliary and reference electrode, respectively.

2.2 *Reagents*

Acetate buffer ($0.5\,\mathrm{mol\,L^{-1}}$) of pH 4.6, used as a supporting electrolyte, was prepared from CH_3COOH purified by subboiling distillation and Suprapure NaOH obtained from Merck. KNO_3 was prepared from an analytical grade reagent (Merck). It was purified additionally by recrystallisation. A standard solution of cadmium at concentration $1\,\mathrm{g\,kg^{-1}}$ was obtained from Aldrich. Certified reference material TMRAIN-95 rain water was obtained from the National Research Council, Canada. Other reagents were obtained from POCh Poland, and used as received. All solutions were prepared using triply distilled water.

2.3 *Standard procedure of measurement*

An aliquot of the analysed sample was pipetted into the electrochemical cell and triply distilled water was added to the volume 8.245 mL. Then 0.5 mL of $0.5\,\mathrm{mol\,L^{-1}}$ acetate buffer at pH 4.6, 0.25 mL of $1\,\mathrm{mol\,L^{-1}}$ KI, 1 mL of $3\,\mathrm{mol\,L^{-1}}$ KNO_3 and 5 μL of $10^{-3}\,\mathrm{mol\,L^{-1}}$ $Pb(NO_3)_2$ were added. Before each measurement, lead film from the preceding measurement was removed electrochemically. For this purpose the electrode was polarised alternatively at potentials −1.25 and 0.5 V for 2 s five times in the stirred analysed solution. In the course of Cd(II) determination, the potential of the electrode was changed in the following sequence: −1.3 V for 310 s; −0.6 V for 1 s. At potential −1.3 V lead and cadmium were deposited simultaneously on the glassy carbon electrode. The solution was stirred for 300 s using magnetic stirring bar. Then after an equilibration period of 10 s cadmium was stripped at potential −0.6 V. Next the analytical signal corresponding to Cd(II) reduction was recorded by square wave voltammetry. The selected parameters were: stripping potential ramp from −0.6 to −1.0 V, frequency 200 Hz, step height 4 mV, square wave amplitude 25 mV. The measurements were carried out from undeaerated solutions.

3. Results and discussion

The proposed procedure of cadmium determination by stripping voltammetry consists of three steps:

- simultaneous formation of lead film on the glassy carbon electrode and cadmium deposition,
- oxidation of deposited cadmium at potential −0.6 V for 1 s and
- recording of a square wave voltammogram corresponding to the reduction of Cd(II).

The procedure is not typical of stripping voltammetry. The reason for modification of the procedure can be explained in the following way. In the presence of a large excess of zinc it is accumulated simultaneously with cadmium and in the course of the stripping step undergoes oxidation at a potential close to that corresponding to the oxidation of cadmium. As a result the signal corresponding to cadmium oxidation overlaps with that of zinc oxidation and interference is observed. To overcome this interference, cadmium and eventually deposited zinc were stripped at −0.6 for 1 s and then the peak of Cd(II) reduction without interference of Zn(II) was recorded. Acceptable results of preliminary measurements were obtained at an *in situ* plated lead electrode so the optimisation of parameters of determinations was performed to obtain a low-detection limit of Cd(II) determination.

3.1 *Composition and pH of the supporting electrolyte*

An acetate buffer was used as a supporting electrolyte. It was observed that the addition of $0.3\,\mathrm{mol\,L^{-1}}$ KNO_3 to the electrolyte assures stability and reproducibility of the cadmium peak current. Taking into account literature data [23], where it was shown that the addition of KI to the electrolyte causes an increase of the cadmium stripping peak, we also added this compound to the supporting electrolyte. The influence of KI concentration on the cadmium reduction peak current was shown in Figure 1. For further measurements $0.025\,\mathrm{mol\,L^{-1}}$ acetate buffer of pH 4.6, containing $0.3\,\mathrm{mol\,L^{-1}}$ KNO_3 and $0.025\,\mathrm{mol\,L^{-1}}$ KI, was chosen as a supporting electrolyte.

3.2 *Influence of deposition potential*

The influence of the deposition potential was studied for Cd(II) concentration of $2 \times 10^{-8}\,\mathrm{mol\,L^{-1}}$. The results obtained are presented in Figure 2. For further study

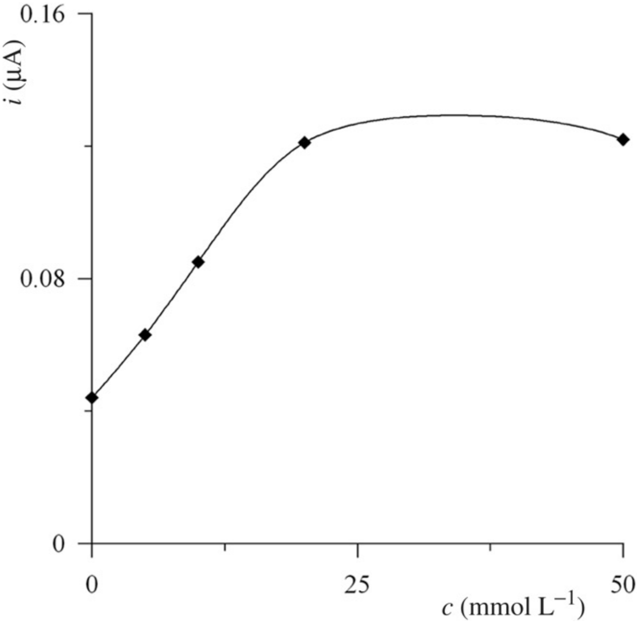

Figure 1. Influence of KI concentration added to supporting electrolyte on the peak current for Cd(II). Concentration of Cd(II) 2×10^{-8} mol L^{-1}. Deposition time 300 s.

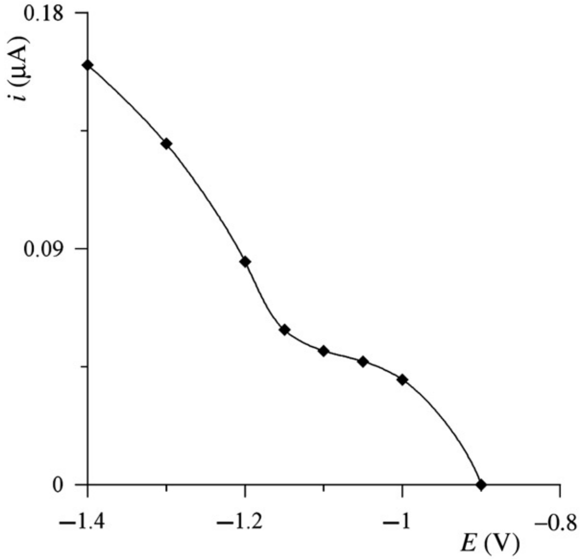

Figure 2. Influence of deposition potential on the peak current for Cd(II). Concentration of Cd(II) 2×10^{-8} mol L^{-1}. Deposition time 300 s.

the deposition potential −1.3 V was chosen. For Cd(II) determination in samples containing over a 1000-fold molar excess of Zn(II) less negative deposition potential is recommended.

3.3 *Influence of deposition time*

The deposition time was changed from 120 to 600 s. The peak currents for Cd(II) increased nearly linearly with the deposition time to 600 s. For further study the deposition time of 300 s was chosen.

3.4 *Calibration graph*

The calibration graph for deposition time of 300 s was linear from 2×10^{-9} to 1×10^{-6} mol L^{-1} and obeyed the equation $y = 7.3x - 5$, where y and x are the peak current (nA) and Cd(II) concentration (nmol L^{-1}). The linear correlation coefficient $r = 0.998$. The relative standard deviation for Cd(II) determination at concentration 2×10^{-8} mol L^{-1} was 3.6% ($n = 5$). The detection limit for Cd(II) following the deposition time of 300 s calculated as a 3σ for the lowest determined concentration of Cd(II) was 6×10^{-10} mol L^{-1}. Figure 3 shows the square wave voltammograms for low determined Cd(II) concentrations. Sensitivity for Cd(II) using the procedure proposed in this article was 1.2 times lower as compared to anodic stripping voltammetry. However, this method allows for minimisation of Zn(II) interference.

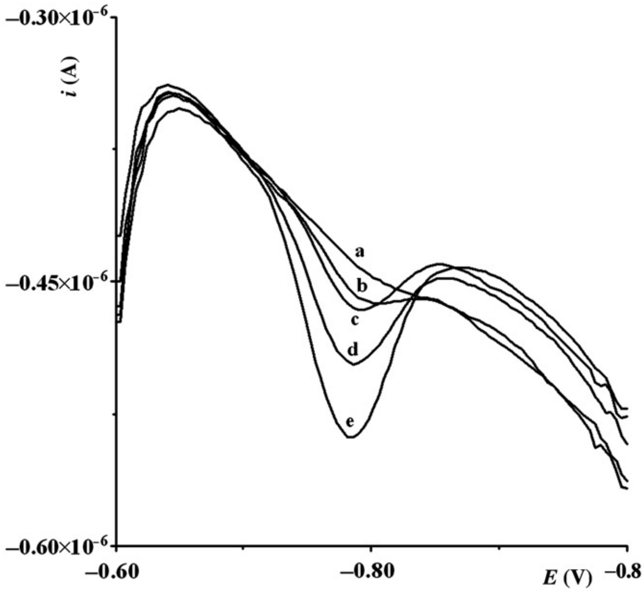

Figure 3. Square wave voltammograms obtained for supporting electrolyte (a) and solutions containing increasing concentrations of Cd(II): (b) 2×10^{-9}; (c) 5×10^{-9}; (d) 1×10^{-8} and (e) 2×10^{-8} mol L^{-1}. Deposition time 300 s.

Table 1. Relative signals obtained for $2 \times 10^{-8}\,\mathrm{mol\,L^{-1}}$ Cd(II) in the presence of interfering ions. Deposition at −1.3 V for 300 s.

Foreign ions	Molar excess of foreign ions	Relative signal
Cu^{2+}	50	0.37
Fe^{3+}	50	0.41
Zn^{2+}	1000	2.20
Ni^{2+}	100	0.83
Ni^{2+}	1000	0.39
Mn^{2+}	100	0.82
Mn^{2+}	1000	0.76
VO_3^-	100	0.91
VO_3^-	1000	0.80
MoO_4^{2-}	100	0.81
Sn(II)	100	0.80
Tl(I)	1	1.02
In(III)	10	1.25

3.5 *Interferences*

The influence of foreign ions on the determination of Cd(II) was studied using a fixed concentration of Cd(II) of $2 \times 10^{-8}\,\mathrm{mol\,L^{-1}}$ and a deposition time of 300 s. Foreign ions were added separately. The results obtained are presented in Table 1. The results obtained indicate that the presence of large excess of foreign ions influence Cd(II) signal, so the determinations of Cd(II) in real samples should be carried out using the method of standard additions. Regarding metal ions with similar electrochemical characteristics, it must be noted that Zn(II) and In(III) did not give the signal at the potential of the Cd(II) peak. Tl(I) did not interfere at comparable concentrations. However, in the presence of a 10-fold excess of Tl(I), its reduction peak appears at more negative potential and interference. In real samples, the concentration of Tl(I) was usually lower than that of Cd(II) and interference cannot be observed.

To study the influence of surface active substances on the analytical signal in the proposed procedure, three types of surfactants: cationic – cetyltrimethylammonium bromide (CTAB), anionic – sodium dodecylsulphate (SDS) and non-ionic – Triton X-100 were used. The results obtained are presented in Figure 4. It was observed that Triton X-100 at concentrations to $5\,\mathrm{mg\,L^{-1}}$ causes an increase of the Cd(II) signal, while SDS and CTAB do not influence significantly Cd(II) signal up to concentration $5\,\mathrm{mg\,L^{-1}}$. The interference of surfactants on Cd(II) signal at the lead film electrode was lower as compared to that observed at Nafion-coated bismuth film electrode [6].

3.6 *Analytical applications*

The proposed procedure was applied to Cd(II) determination in TMRAIN-95 rain water certified reference material. Analyses were performed using the method of standard additions. The result obtained for Cd(II) was $0.52\,\mathrm{\mu g\,L^{-1}}$ with RSD 5.5% ($n = 5$) and was comparable to that certified value $0.48 \pm 0.12\,\mathrm{\mu g\,L^{-1}}$. The results obtained indicate that the proposed method can be applied to the analysis of real samples for Cd(II).

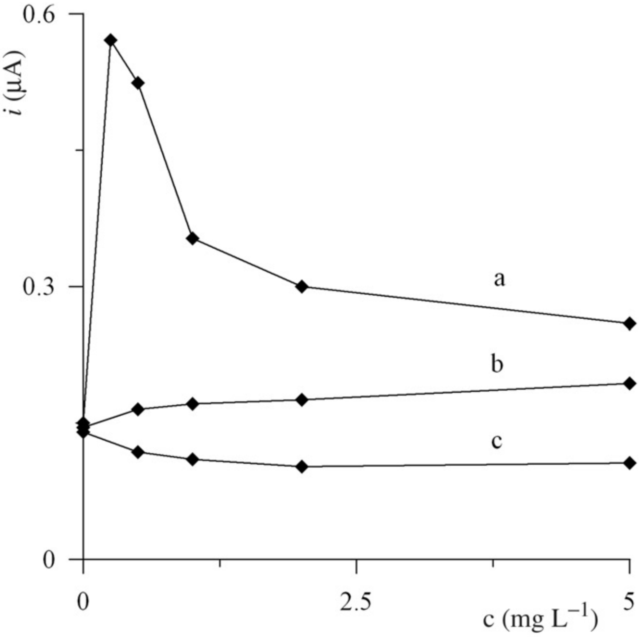

Figure 4. The influence of: (a) Triton X-100; (b) CTAB; (c) SDS concentration on the peak current of $2 \times 10^{-8}\,\mathrm{mol\,L^{-1}}$ Cd(II). Deposition time 300 s.

4. Conclusion

A simple procedure for cadmium determination at an *in situ* plated lead film electrode was proposed. Cadmium was deposited at potential −1.3 V, then it was stripped for 1 s at −0.6 V and the reduction signal of Cd(II) was registered. Such modification of procedure was applied to overcome Zn(II) interference. For amplification of the Cd(II) reduction signal KI was added to the supporting electrolyte [23]. A low-detection limit for Cd(II) of $6 \times 10^{-10}\,\mathrm{mol\,L^{-1}}$ and a wide linear dynamic range of the procedure was obtained following the deposition time of 300 s. The lead film electrode is toxic. However, toxicity and volatility of lead salts used for preparation of this electrode is lower as compared to reagents used for preparation of mercury electrodes. For example, the maximum contaminant level in drinking water recommended by EPA for lead was equal $15\,\mu\mathrm{g\,L^{-1}}$ while for mercury $2\,\mu\mathrm{g\,L^{-1}}$ [24]. A simple procedure of preparation and regeneration of the lead film electrode was proposed. Measurements were carried out from undeaerated solutions.

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