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The simultaneous voltammetry determination of cadmium(II) and lead(II) at bismuth film glassy carbon electode prepared with the use of mediator

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This paper shows a novel, simple and rapid voltammetric procedure, which enables Cd and Pb determination at traces concentrations. All measurements were carried out by differential pulse anodic stripping voltammetry (DPASV) with total time of analysis of 210 s. The obtained detection limits were $8.46 \cdot 10^{-10}$ mol/dm^3 and $2.57 \cdot 10^{-10}$ mol/dm^3 for Cd(II) and Pb(II), respectively. This procedure was successfully applied for the quantification of mentioned metal ions in water samples collected from the Vistula River.

1. INTRODUCTION

The contamination of heavy metals in the environment has dramatically increased during last 50 years [1]. The main reasons for this are industrial development including the extensive use of heavy metals in technological processes and anthropogenic activities [2, 3]. The presence of heavy metal ions in natural environment (in the air, water and soil) causes that they get to the food chain and they are easily collected by organisms [2]. Furthermore, they are hazardous because they are hardly biodegradable and difficult to remove [4]. Heavy metals constitute particular threat for living organisms especially due to their high toxicity and tendency to bioaccumulation in animal and human organisms [5].

Two of the most toxic heavy metals are cadmium and lead [6]. Cadmium causes pulmonary and stomach irritation especially when it is taken in high dose. Then the following symptoms appear: vomiting, vertigo, muscle cramps, abdominal pain and loss of consciousness [7]. Cadmium is able to accumulate in some organs such as the kidneys, the liver and the bones. Long-term exposure to Cd(II) lead to morphological changes in the kidneys, skeletal demineralization (osteoporosis), cardiovascular diseases and it contribute to the tumor formation in the kidneys, the lungs and the prostate [8, 9]. Lead has dangerous influence especially on the nervous system. Lead poisoning causes irritability, headache and memory deterioration [10, 11]. It also has hazardous effect on the liver, the kidney, the brain, endocrine, reproductive and hematopoietic system [7, 12]. Probably, it is associated with the lungs cancer, gliomas, the prostate and the stomach cancer [13, 14]. Especially susceptible to lead effects are children under 6 years old, because their blood-brain barrier is not fully developed and lead impacts on nervous and circulatory at lower threshold levels in comparison to adult [15]. Due to high toxicity and easy circulation it is needed to develop analytical method for trace determination of heavy metal ions in environmental and food samples [16].

Electrochemical methods', especially stripping voltammetry, is an appropriate technique for trace heavy metal ions detection [17]. It is a convenient method due to a low cost, an easy operation and high sensitivity [18]. One of the most important in voltammetry is selection of a suitable electrode material. It has influence on reproducibility, selectivity and sensitivity of the measurement [19]. For many years mercury electrodes for the determination of heavy metal ions were widely used [20]. However, their toxicity caused that scientists began to look for environmentally friendly modifier of the electrodes [21]. Bismuth complies with these requirements. Bismuth-modified electrodes have a lot of advantages. It includes a simple preparation, very low toxicity, high sensitivity, well separated analytical signals and simple electrode preparation [22]. Likewise, bismuth-based electrodes are able to form „fused" alloy with other metals, what is similar to mercury [18]. In this study, a simple, fast and sensitive procedure for Cd(II) and Pb(II) determination at a bismuth film glassy carbon electrode prepared with the use of a reversible deposited mediator (Zn) is shown.

2. EXPERIMENTAL

2.1 Apparatus and electrodes

Differential pulse anodic stripping voltammetric (DPASV) measurements were carried out with the use of µAutolab analyzer (Eco Chemie, Netherlands) connected to a computer equipped with USB electrochemical interface and driven via a GPES 4.9 software package (Eco Chemie, Netherlands). The classic quartz cell with the volume of 10 cm^3 was used. The electrochemical cell comprised three-electrode system includes a silver/silver chloride/potassium chloride (Ag/AgCl/KCl 3 mol/dm^3) as the reference electrode, a platinum wire as the counter electrode and the bismuth film glassy carbon electrode as the working electrode. The glassy carbon surface was polished daily with the use of 0.05 µm, 0.3 µm, 1 µm and alumina slurry on a Buehler polishing pad with following washing and sonication for 1 min.

2.2 Reagents and water sample

1 mol/dm^3 acetic buffer was prepared from $CHCOONH_4$ and HCl (30%, Suprapur) obtained from Sigma-Aldrich. The stock standard solutions of Bi(III), Zn(II), Pb(II) and Cd(II) (1 g/dm^3) were purchased from Merck. The working solutions of Bi(III), Zn(II), Pb(II) and Cd(II) were prepared from stock standard solution with appropriate dilution in 0.1 mol/dm^3 HNO_3 (Merck). Ultra-purified water (> 18 MΩ cm) supplied by a Milli-Q system (Millipore, UK) was applied for all solutions preparation.

The river water sample was collected from the Vistula River (Pulawy, Poland) and it was filtered using a 0.45 µm Milipore filter. Then it was acidified to pH = 2 using concentrated HNO_3 and mineralized by 3 h with the use of UV-digester (Mineral, Poland).

2.3 The voltammetric procedure

All measurements were performed in a solution contained 0.05 mol/dm^3 acetic buffer (pH = 3.8) as a supporting electrolyte, $7.5 \cdot 10^{-6}$ mol/dm^3 Bi(III) and $2.5 \cdot 10^{-6}$ mol/dm^3 Zn(II) and increasing concentration of Cd(II) and Pb(II). The glassy carbon electrode was the bismuth film in situ plated with the use of a reversibly deposited mediator (Zn). In the first step, at a potential of –1.5 V for 180 s Bi, Zn, Cd and Pb were simultaneously deposited onto the glassy carbon surface. Then, the potential was changed to the value of –1.05 V for 30 s. In this step, zinc was stripped from the surface, while bismuth, lead and cadmium continued to be deposited. Within the both steps, the solution was stirring with the use of a stirring bar. Afterwards, the stirring was stopped for 5 s and the differential pulse voltammograms were recorded in the range from –1.05 to –0.2 V. The measurements were carried out utilizing non-deaerated solutions.

3. RESULTS AND DISCUSSION

3.1 The comparison of electrodes

The effect of electrode modification on the analytical signal of 2 · 10^{-7} mol/dm^3 Cd(II) and 5 · 10^{-8} mol/dm^3 Pb(II) was performed. Two types of electrodes were investigated: (a) bismuth film glassy carbon electrode modified without, and (b) with the use of a zinc mediator.

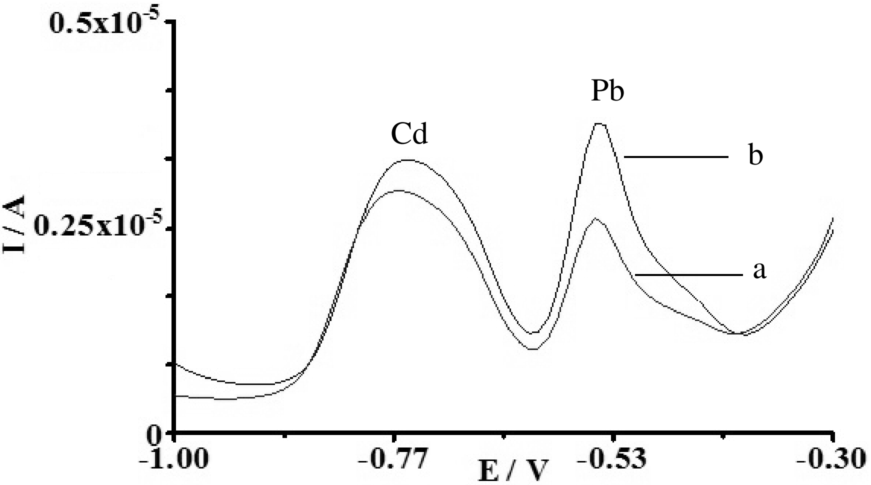


Fig. 1. Square wave voltammograms obtained at: bismuth film glassy carbon electrode modified without (a) and with (b) the use of a zinc mediator. Concentrations of Cd(II) and Pb(II) were 2 · 10^{-7} and 5 · 10^{-8} mol/dm^3, respectively and were determined in solution contained 0.05 mol/dm^3 acetate buffer solution (pH = 3.8), 2 · 10^{-5} mol/dm^3 Bi(III) and 0 (a) or 2 · 10^{-5} mol/dm^3 Zn(II) (b). Bi, Zn, Cd and Pb were deposited at –1.65 V for 180 s and oxidizing of Zn were conducted at potential of –0.95 V for 10 s. Square wave woltammograms were registered from –1.65 to 0.5 V.

The obtained results are shown in the Figure 1 and they prove that the use of the zinc mediator causes significant Pb(II) peak current increase from 1.29 μA to 2.70 μA and slight influence on the Cd(II) peak current. Growth of Cd(II) peak height from 2.25 μA to 2.45 μA was observed. Therefore, the bismuth film glassy carbon electrode modified with the use of mediator was chosen for the further studies.

3.2 The optimization of conditions and parameters for Cd(II) and Pb(II) determination

The effect of the working electrode modification with the bismuth film and influence of a zinc mediator on the analytical signal of Cd(II) and Pb(II) were investigated. Moreover, voltammetric technique type, Bi(III) and Zn(II) contaminations, the deposition time and potential of Bi, Zn, Cd and Pb as well as the time and potential of Zn stripping from the electrode surface were checked.

3.2.1 The impact of voltammetric technique type

The influence of voltammetric technique type was investigated. Voltammetric measurements were carried out for concentration of Cd(II) and Pb(II) equal to $2 \cdot 10^{-7}$ mol/dm^3 and $5 \cdot 10^{-8}$ mol/dm^3, respectively. Two voltammetric techniques were compared: differential pulse voltammetry (DPV) and square wave voltammetry (SWV). The Cd(II) and Pb(II) peaks height obtained with the use of SWV were greater, but that obtained with the use of DPV were much better shaped, so for further studies DPV technique was chosen.

3.2.2 The composition of measurement solution

In this part of experiments, the effect of Bi(III) concentration on the analytical signals of Cd(II) and Pb(II) was investigated. The concentration range of Bi(III) from $2.5 \cdot 10^{-6}$ mol/dm^3 to $1 \cdot 10^{-5}$ mol/dm^3 was tested. The results show that the concentration of Bi(III) affects on the peak currents of studied ions and the largest signal of Cd(II) was obtained for $7.5 \cdot 10^{-6}$ mol/dm^3 Bi(III) and for a higher concentration of Bi(III), the lead peak current was still increasing. Due to the decrese of the Cd(II) peak current and the fact that obtained analytical signals of cadmium had worse quality, the concentration $7.5 \cdot 10^{-6}$ mol/dm^3 of Bi(III) was considered as optimal (Fig. 2 A).

The use of mediator during the deposition of electrode modifier metal causes the analytical signal enhancement of both metal ions [23, 24] and organic compounds [25]. This effect depends on the mediator concentration, in this case Zn(II). The concentration of Zn(II) was changed from 0 to $2 \cdot 10^{-5}$ mol/dm^3 and for $2.5 \cdot 10^{-6}$ mol/dm^3 the cadmium(II) peak was the highest. For higher concentration of Zn(II) the peak current of Pb(II) was still increasing, but the peak current of Cd(II) was decreased (Fig. 2 B). Werefore, $2.5 \cdot 10^{-6}$ mol/dm^3 was chosen as an optimal concentration of Zn(II).

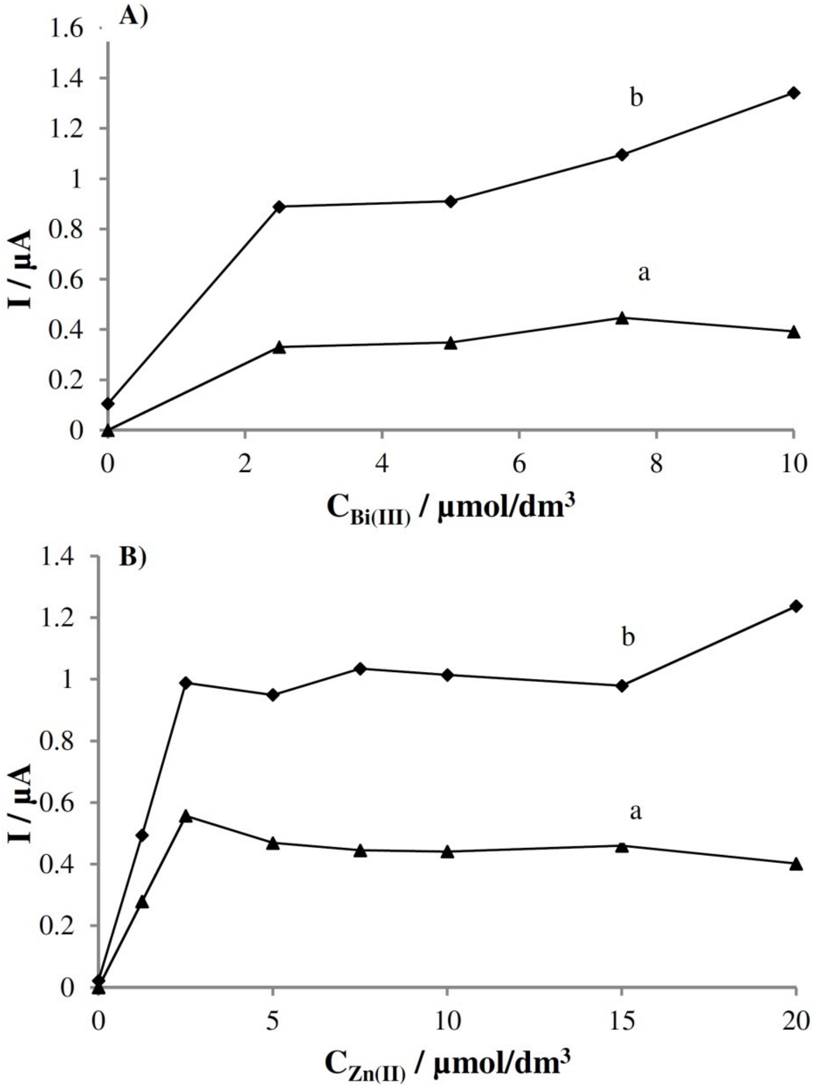


Fig. 2. The influence of: A) Bi(III) and B) Zn(II) concentration on the peak currents of Cd(II) (a) and Pb(II) (b). The solution contained 0.05 mol/dm^3 acetate buffer (pH = 3.8), $2 \cdot 10^{-5}$ mol/dm^3 Zn(II) (A), $7.5 \cdot 10^{-6}$ mol/dm^3 Bi(III) (B), $2 \cdot 10^{-7}$ mol/dm^3 Cd(II) and $5 \cdot 10^{-8}$ mol/dm^3 Pb(II).

3.2.3 The influence of procedure parametres

The influence of bismuth, zinc, cadmium and lead deposition potential was verified in the range from –1.8 to –1.2 V for $2 \cdot 10^{-7}$ mol/dm^3 of Cd(II) and $5 \cdot 10^{-8}$ mol/dm^3 of Pb(II).

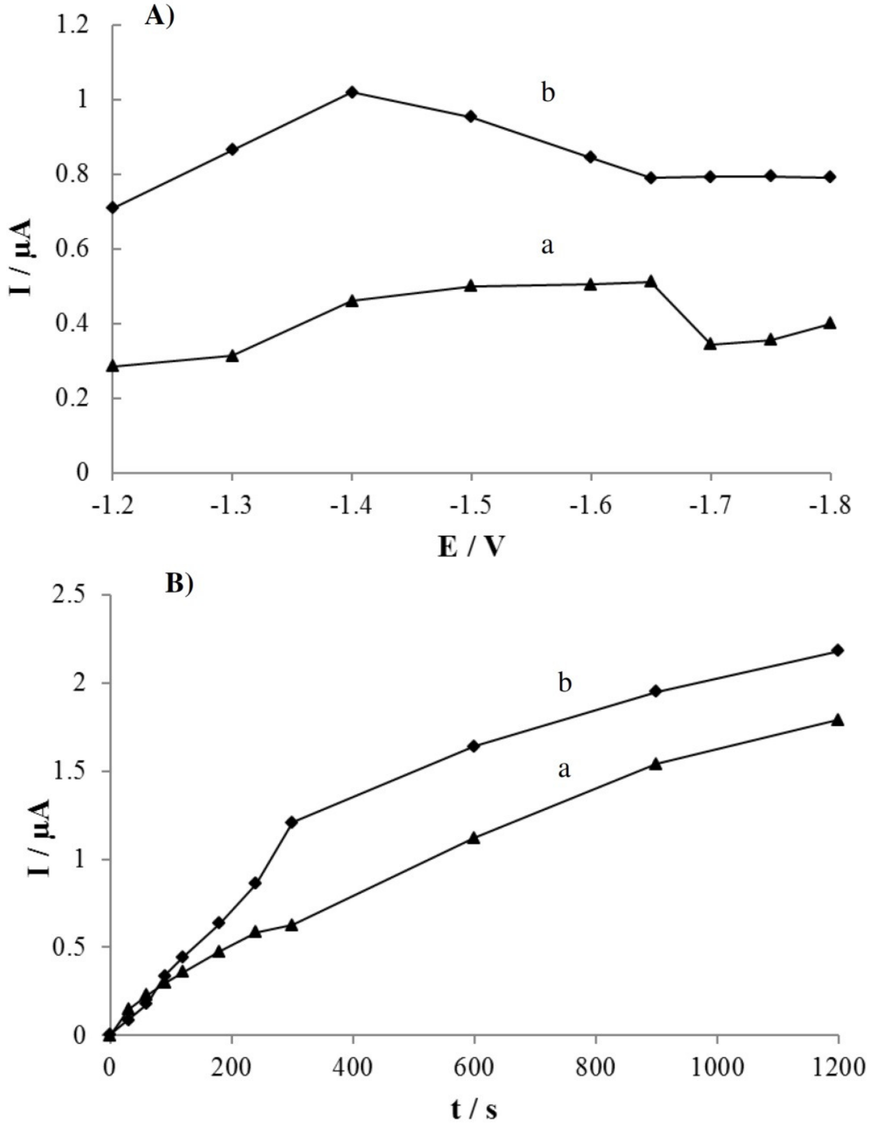
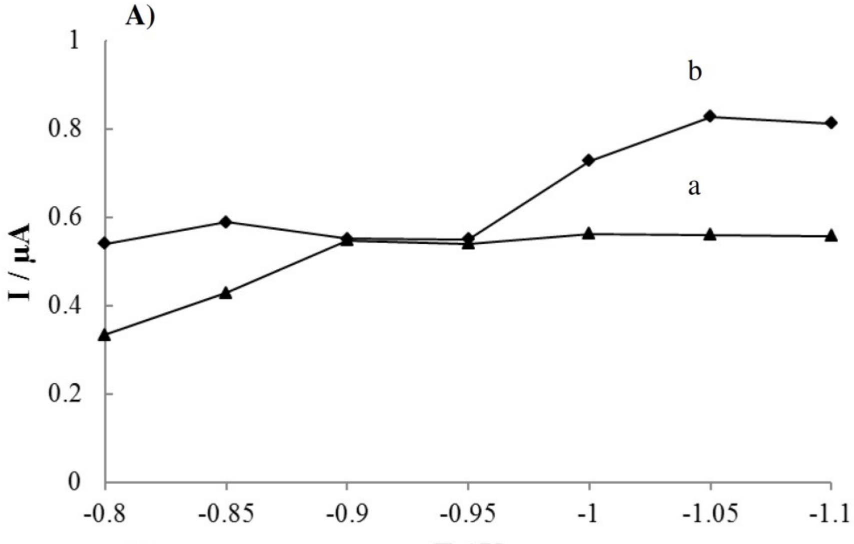


Fig. 3. The influence of Bi, Zn, Cd and Pb deposition potential (A) and time (B) on the analytical signals of Cd(II) (a) and Pb(II) (b). The solution contained 0.05 mol/dm^3 acetate buffer (pH = 3.8), $7.5 \cdot 10^{-6}$ mol/dm^3 Bi(III), $2.5 \cdot 10^{-6}$ mol/dm^3 Zn(II), $2 \cdot 10^{-7}$ mol/dm^3 Cd(II) and $5 \cdot 10^{-8}$ mol/dm^3 Pb(II). The deposition time and potential of Bi, Zn, Cd and Pb were 180 s (A) and –1.5 V (B), respectively.

As it can be seen in Fig. 3A, within the potential range from –1.4 to –1.65 V the lead(II) peak current was decreasing while the increase of cadmium(II) peak height was observed. For this reason, potential of –1.5 V was recognized as the optimal value taking into account the height of both peaks and it was chosen for the further studies. Whereas, the deposition time of Bi, Zn, Cd and Pb was changed from 0 to 1200 s and its influence on the cadmium and lead peaks was studied (Fig. 3 B). The maximum currents were obtained within 1200 s, but in order to reduce the total time of analysis, the time of 180 s was chosen.

In the next part of experiments, the influence of Zn oxidation and further Bi, Cd and Pb deposition potential and time on the Cd(II) and Pb(II) peak currents were investigated. It was studied for the concentrations of Cd(II) and Pb(II) equal to $2 \cdot 10^{-7}$ mol/dm^3 and $5 \cdot 10^{-8}$ mol/dm^3, respectively. The potential was changed in the range from –1.2 to –0.8 V and time was extended from 0 to 60 s. In the range from –0.9 to –1.1 V the Cd(II) peak height did not change. The most satisfying results were obtained for the potential of –1.05 V due to the maximum of Pb(II) peak current (Fig. 4 A). Time of 30 s was chosen in order to total remove Zn from the working electrode surface and the largest increase of Pb(II) peak current (Fig. 4 B).



B)

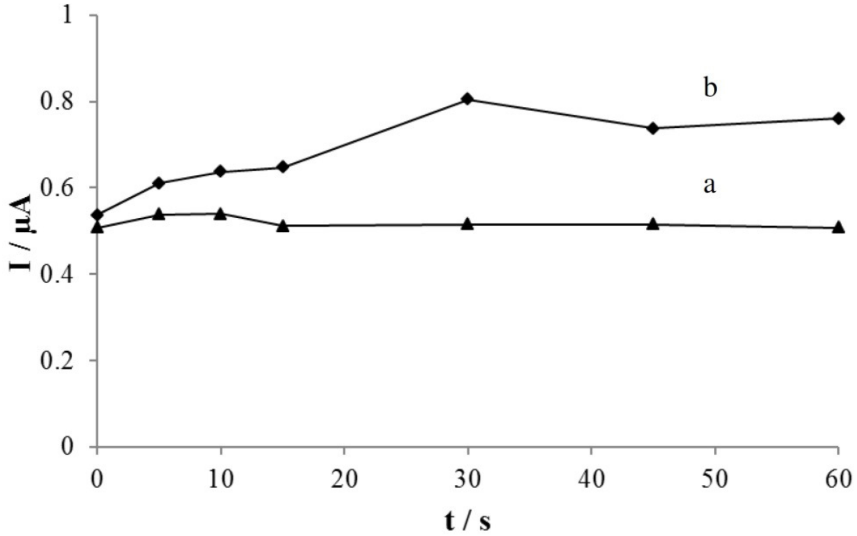


Fig. 4. The influence of potential (A) and time (B) of Zn oxidation and further Bi, Cd and Pb deposition on the analytical signals of Cd(II) (a) and Pb(II) (b). The solution contained 0.05 mol/dm^3 acetate buffer (pH = 3.8), 7.5 · 10^{-6} mol/dm^3 Bi(III), 2.5 · 10^{-6} mol/dm^3 Zn(II), 2 · 10^{-7} mol/dm^3 Cd(II) and 5 · 10^{-8} mol/dm^3 Pb(II). The time and potential of Zn oxidation and further Bi, Cd, Pb deposition were 10 s (A) and -1.05 V (B), respectively.

3.4 Calibration graph

The measurements for calibration graphs for the simultaneous determination of Cd(II) and Pb(II) were performed under optimized conditions at the bismuth film glassy carbon electrode prepared with the zinc mediator. For this purpose, measurements were taken in three cases: (1) constant concentration of Pb(II) and increasing concentration of Cd(II), (2) constant concentration of Cd(II) and increasing concentration of Pb(II) and (3) simultaneous increasing concentration of both metal ions. In the Table 1 the obtained results included linear working range, the linear regression equation, correlation coefficient (r), limits of detection and quantification are shown. The detection and quantification limits of Cd(II) and Pb(II) were calculated on the basis of 3 and 10 times the standard deviation (n = 3) for the lowest determined concentrations of Cd(II) and Pb(II) and divided by the slope of the linear regression equation, respectively.

Table 1. The results obtained at the BiFE during calibration graphs construction for: (1) Cd(II) in the presence of constant concentration of Pb(II) ($5 \cdot 10^{-8}$ mol/dm^3); (2) Pb(II) in the presence of constant concentration of Cd(II) ($5 \cdot 10^{-7}$ mol/dm^3) and (3) increasing concentration of Cd(II) and Pb(II).

The type of calibration graph		Linear working range [mol/dm^3]	Linear regression equation	Correlation coefficient (r)	LOD [mol/dm^3]	LOQ [mol/dm^3]
1		$1 \cdot 10^{-8}$ – $5 \cdot 10^{-6}$	$y = 4.73x - 0.13$	0.9987	$4.76 \cdot 10^{-9}$	$1.59 \cdot 10^{-8}$
2		$2 \cdot 10^{-9}$ – $2 \cdot 10^{-6}$	$y = 13.50x - 0.13$	0.9998	$2.57 \cdot 10^{-10}$	$8.56 \cdot 10^{-10}$
3	Cd(II)	$1 \cdot 10^{-8}$ – $5 \cdot 10^{-6}$	$y = 5.42x + 0.14$	0.9967	$8.46 \cdot 10^{-10}$	$2.82 \cdot 10^{-9}$
	Pb(II)	$2 \cdot 10^{-9}$ – $2 \cdot 10^{-6}$	$y = 15.08x + 0.088$	0.9998	$6.99 \cdot 10^{-10}$	$2.33 \cdot 10^{-9}$

y – peak current [µA]
x – concentration of Cd and Pb [µmol/dm^3]

3.5 The application of the procedure in real water sample

The optimized procedure was applied to the determination of Cd(II) and Pb(II) in water samples from the Vistula River. The cadmium and lead contents were estimated using the standard additional method. The determined concentration of Cd(II) in water sample was $3.50 \cdot 10^{-8} \pm 0.39 \cdot 10^{-8}$ mol/dm^3 and Pb(II) was $8.09 \cdot 10^{-9} \pm 0.96 \cdot 10^{-9}$ mol/dm^3. The voltammograms obtained during the determination of Cd(II) and Pb(II) in the Vistula River sample are presented in the Figure 5.

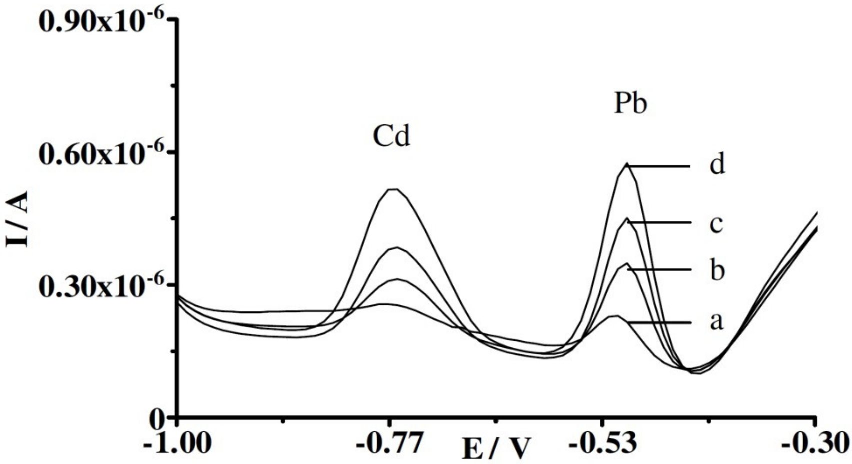


Fig. 5. Differential pulse anodic stripping voltammograms obtained during the determination of Cd(II) and Pb(II) in the Vistula River sample at the bismuth film glassy carbon electrode: a) sample (9.4 cm^3); b) as (a) + $5 \cdot 10^{-8}$ mol/dm^3 Cd(II) + $1 \cdot 10^{-8}$ mol/dm^3 Pb(II); c) as (a) + $1 \cdot 10^{-7}$ mol/dm^3 Cd(II) + $2 \cdot 10^{-8}$ mol/dm^3 Pb(II); d) as (a) + $1.5 \cdot 10^{-7}$ mol/dm^3 Cd(II) + $3 \cdot 10^{-8}$ mol/dm^3 Pb(II).

4. CONCLUSION

The optimized procedure for the simultaneous determination of Cd(II) and Pb(II) at an environmentally friendly bismuth film glassy carbon electrode prepared with the use of a zinc mediator provides low limits of detection and wide linear ranges of the calibration graphs. The application of the zinc mediator contributes an enhancement of cadmium and lead peak currents. Moreover, the application of the procedure gives satisfactory results during the quantification of Cd(II) and Pb(II) in the river water sample.

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