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Heavy metals determination using various *in situ* bismuth film modified carbon-based electrodes

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Abstract: The proposed work deals with the utilization of three carbon-based electrode substrates such as boron-doped diamond, glassy carbon and carbon paste for the preparation of *in situ* bismuth film modified electrodes. Such modified electrodes were subsequently used for the differential pulse anodic stripping voltammetric determination of heavy metal cations (Zn^{2+}, Cd^{2+} and Pb^{2+}) individually and simultaneously using similar experimental conditions (0.1 mol l^{-1} acetic buffer solution of pH 4.5 as supporting electrolyte with the addition of 0.1 mmol l^{-1} Bi^{3+}, deposition potential of –1.4 V and deposition time of 120 s). The results showed that the modification step mostly enhanced the deposition and stripping process of studied cations when compared to the bare electrode substrates. A boron-doped diamond electrode was selected as the substrate for modification and the procedure was applied to the real sample analysis including water sample (certified reference material) and wastewater sample. Using the standard addition method the concentrations of particular heavy metals were quantified and the determined values were in a good agreement with those obtained by the reference method — high resolution atomic absorption spectroscopy with electrothermal atomisation and continual radiation source. This fact highlights that the developed *in situ* bismuth film modified boron-doped diamond electrode is a suitable electrochemical sensor to be applied to routine analysis of water samples containing heavy metals.

Keywords: *in situ* bismuth film modified electrode, heavy metals determination, boron-doped diamond, limit of detection, anodic stripping voltammetry, water sample

Introduction

The task of green electroanalytical chemistry is to search for new possibilities in constructions and applications of non-toxic electrode materials. The cooperation of several scientific divisions has led to the one of environmental friendly candidates — bismuth. It is an attractive electrode material for electroanalysis of reducible species and a good substitution for toxic mercury electrodes. In addition, the toxicity of Bi is significantly lower than in the case of Hg (Wang, 2005).

The basic bismuth electrode (BiE) is a metallic rod of pure Bi (Armstrong et al., 2010). Another advanced preparation of BiEs includes the pre-plating of various electrode substrates with bismuth film or bulk modification of carbon paste. These modifications usually give rise to better sensitivity and selectivity than solid-states electrodes (Baś et al., 2015).

The Bi film (BiF) can be usually prepared by *in* or *ex situ* electrodeposition processes. Both ways require a solution containing Bi^{3+} salts. While in the case of *ex situ* preparation BiF is deposited on substrate from external Bi^{3+} source solution and then the modified electrode is used for measurement in sample solution. Concerning the *in situ* modification, the Bi^{3+} ions (in a sufficient concentration excess) are present directly with the analytes in tested solution (de Lima and Spinelli, 2013; Gerent et al., 2015; Kokkinos et al., 2008; Toghill et al., 2008; Yi et al., 2012). The bulk modification including Bi precursor of the pure Bi powder is possible only in the case of carbon paste electrode (Hočevar et al., 2005; Królicka et al., 2002).

The chemical and electrochemical properties of Bi are comparable to those for Hg. BiEs exhibit a wide cathodic potential range due to high hydrogen overpotential, but not as wide as for Hg owing to the stripping potential of Bi, which is more negative than that of Hg. In addition, BiEs are less susceptible to oxygen background interferences than Hg electrodes. Dissolved oxygen has a more profound effect upon potentiometric stripping measurements, with the stripping signals increasing upon deaerating the sample. Nevertheless, highly reproducible results may be obtained in non-deaerated media (Guzsvány et al., 2011; Wang, 2005). The use of BiEs in various electrolytes is limited by the hydrolysis of Bi^{3+} in alkaline media that creates bismuth hydroxide capable of precipitating and forming an inactive thin film. In very alkaline media (pH > 12) precipitates are re-solubilized due to formation of hydroxo-complexes which may be used for deposition of Bi film (Arduini et al., 2010; Bobrowki et al., 2010; Kapturski and Bobrowski, 2008).

According to the ability of metal to form the amalgam with Hg, the similar studies with Bi are significantly affected by the presence of Bi^{3+} in the medium for purposes of the speciation analysis. *Ex situ* BiFE offers an advantages in works dealing with complexation reactions of thiol-containing compounds in alkaline and neutral medium, in which hydrolysis of Bi^{3+} does not occur (Bobrowski et al., 2010). On the other hand, *in situ* preparation method provides an experimental simplicity coupled with short analysis time owing to the absence of pre-plating step. In this case, the possible unfavourable chemical reactions between Bi and metals can be problematic (the surface may be fouled or contamined by environment and the undefined formation of intermetallic compounds can be observed) (Serrano et al., 2013). However, it should be taken into consideration that the Bi deposition efficiency may generally depend on particular electrode substrate, thus affecting the analytical performance of heavy metals determination. By exploring various substrates, the Bi deposition can be controlled to construct an effective electrochemical sensor for these purposes. Even though there have been many efforts to utilization of Bi modified electrodes in determination of heavy metals, until now no systematic studies dealing with the effect of several electrode substrates on the analytical performance evaluation at the heavy metals determination have been carried out.

Generally, the heavy metals determination in various types of samples (environmental – air and waters, clinical – body fluids, tissues, and food) is very important due to metal poisoning and accumulation in living organism, which may cause a dysfunction or failure of kidney, liver and other organs (Lee et al., 2015; Naeemullah et al., 2016). A routine analytical method for the determination of heavy metals is atomic absorption spectrometry (Shahbazi et al., 2016; Wang et al., 2016). The use of electroanalytical method for determination of heavy metals allows fast and cheap analyses in contrary with spectral method. In this respect, the use of BiEs is mainly focused on the heavy metals determination (Wang and Lu, 2000) with the dominance for the determination of lead and cadmium (Cerovac et al., 2015; Zhang et al., 2016). Similarly, the BiEs appear to be important also for determination of other metals like Co, Ni, Tl or Cu. The few published papers dealing with determination of organic compounds include an electrochemical reduction of these compounds (Bia et al., 2014; Campestrini et al., 2010; Gerent et al., 2015; Gerent and Spinelli, 2016; Kreft et al., 2012; Sá et al., 2015; Sopha et al., 2012).

In this paper we describe the application of *in situ* bismuth film modified electrodes based on three various carbon-based electrode substrates for individual and simultaneous heavy metals (Zn^{2+}, Cd^{2+} and Pb^{2+}) determination. The analytical usefulness of bare and modified electrodes was compared. The practical feasibility of *in situ* bismuth film modified boron-doped diamond electrode was explored in analysis of water sample (certified reference material) and wastewater sample. In this respect, the proposed advanced strategy may offer a novel insight into searching for the suitable substrates in the issue of bismuth modified electrodes with further monitoring of heavy metals.

Experimental

Metals ions in salts $Zn(NO_3)_2$, $Cd(NO_3)_2$ and $Pb(NO_3)_2$ and other chemicals were obtained from Lachema Brno (Czech Republic) and used without any further purification. All reagents were of analytical grade purity. The acetate buffer solution (AB) was prepared by mixing acetic acid (0.1 mol l^{-1}) with sodium hydroxide (0.1 mol l^{-1}) to the required pH value of 4.5. In regards of *in situ* preparation, a corresponding amount of solid $Bi(NO_3)_3$ was dissolved in AB to reach the concentration of 0.1 mmol l^{-1} Bi^{3+}. All stock solutions of studied metals (1 mmol l^{-1}) were prepared by dissolution of appropriate solid salts in deionized water and then stored in refrigerator. The working solutions of metals with lower concentrations were freshly prepared by diluting particular stock solutions of metals with supporting electrolyte of ABS (pH 4.5) containing Bi^{3+} ions (0.1 mmol l^{-1}).

The potentiostat/galvanostat Autolab PGSTAT-101 (Metrohm Autolab B.V., The Netherlands) controlled with the NOVA 1.8 software was used for all electrochemical measurements. The three-electrode cell system was equipped with platinum wire as a counter electrode and an Ag/AgCl/3 mol l^{-1} KCl as a reference electrode. As a working electrode three different carbon-based substrates were used such as follows: boron-doped diamond (BDDE, 3 mm diameter, resistivity of 75 mΩ cm, B/C ratio of 1000 ppm, Windsor Scientific Ltd, United Kingdom), glassy carbon (GCE, 3 mm diameter, Metrohm, Czech Republic) and carbon paste (CPE). CPE was prepared by mixing of 1 g carbon glassy spherical powder (2–12 µm, Sigma Aldrich) and 0.5 ml mineral oil (Sigma Aldrich) inserted in a Teflon tube. pH values of supporting electrolyte were measured by pH meter Model 2015 (Denver Instrument, USA) with a combined electrode (glass-reference electrode). All potentials mentioned in this paper were referred against Ag/AgCl/3 mol l^{-1} KCl reference electrode. The spectral measurements were performed using high-resolution continuum source atomic absorption spectrometer contrAA 700 (HR CS ETAAS, Analytic Jena, Germany) and used as a reference method.

Prior to starting measurements, dissolved oxygen was eliminated by bubbling of gaseous nitrogen for 10 min. All electrode substrates were treated mechanically with alumina slurry (0.3 µm α alumina, Bioanalytical systems Inc.) and electrochemically under the condition of Bi stripping (potential of +0.5 V) in 0.1 mol l^{-1} AB medium during 5 min. In the case of BDD, sonication in the mixture of methanol:water (1:1, v/v) for 5 min was used instead of polishing. Differential pulse anodic stripping voltammetry (DPASV) was performed using following instrumental parameters of DPASV: potential step of 5 mV, modulation amplitude of 25 mV and modulation time of 50 ms. All calibration curves were obtained by successive addition of aliquots of the stock solution of metal into the electrochemical cell already containing required volume of doped supporting electrolyte. The calibration modes were based on addition of the aliquots of particular stock solution either with the presence of all metals with similar concentrations or with the presence of only one of the metals. Each solution was tested six-fold. The limit of detection (LOD) was calculated as the treble of standard deviation for the blank solution divided by the slope of the calibration curve.

The two water samples were considered to be analyzed such as the sample of the certified reference material (Trace elements in water, No. 12-3-10) from Slovak Institute of Metrology and the wastewater sample from a Taiwan metal-processing factory. Aliquot volumes of reference material (10 µl) and wastewater (1 ml) were placed into the electrochemical cell and filled up with 20 ml of supporting electrolyte containing Bi^{3+} ions (0.1 mmol l^{-1}). Analysis of all samples was performed by the standard addition method with respective volumes of 10, 20 and 30 µl ($n = 6$).

In the case of spectral analysis (reference method) the samples were stabilized with addition of ultrapure HNO_3 and analyzed without any dilution by the standard addition method. The concentrations of all metals in standard solution were 1 g l^{-1}. Quantification was carried out with standard additions of 2, 4 and 10 µl using respective wavelength maximum of 213.8 nm (Zn), 217.3 nm (Pb) and 228.8 nm (Cd).

Results and Discussion

Based on literature survey, the AB (pH 4.5) was chosen as a suitable supporting electrolyte (without any Bi hydrolysis) to prepare *in situ* bismuth film modified electrodes for determination of heavy metals. Firstly, the Bi deposition process on each electrode substrate was examined in order to find the optimum values of deposition potential and time. Fig. 1 illustrates the dependences of Bi stripping current versus deposition potential (E_{dep}) in the studied range from –1.5 to –0.4 V. It was

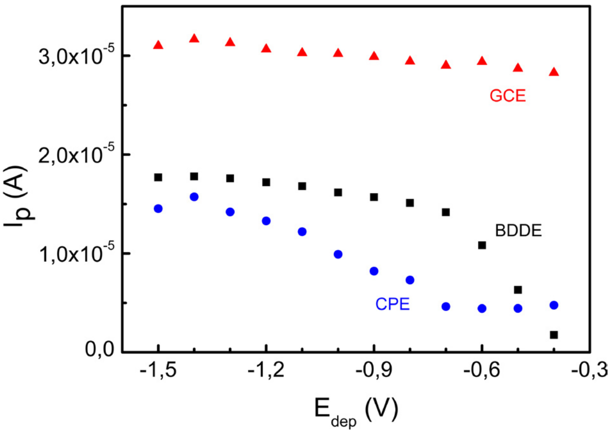

Fig. 1. Optimization of deposition potential for the preparation of Bi modified electrodes using BDDE (■), CPE (●) and GCE (▲) substrates.

Tab. 1. The comparison of LOD values for individual and simultaneous heavy metals determination.

Electrode substrate	Modification	LOD (nmol l^{-1})					
		Individual determination			Simultaneous determination		
		Zn^{2+}	Cd^{2+}	Pb^{2+}	Zn^{2+}	Cd^{2+}	Pb^{2+}
BDDE	–	3425	49	14	417	65	13
	BiF	1000	9	45	130	12	34
GCE	–	905	64	43	1058	209	15
	BiF	1566	17	26	17	4	34
CPE	–	896	895	936	273	129	69
	BiF	1162	382	772	70	74	109

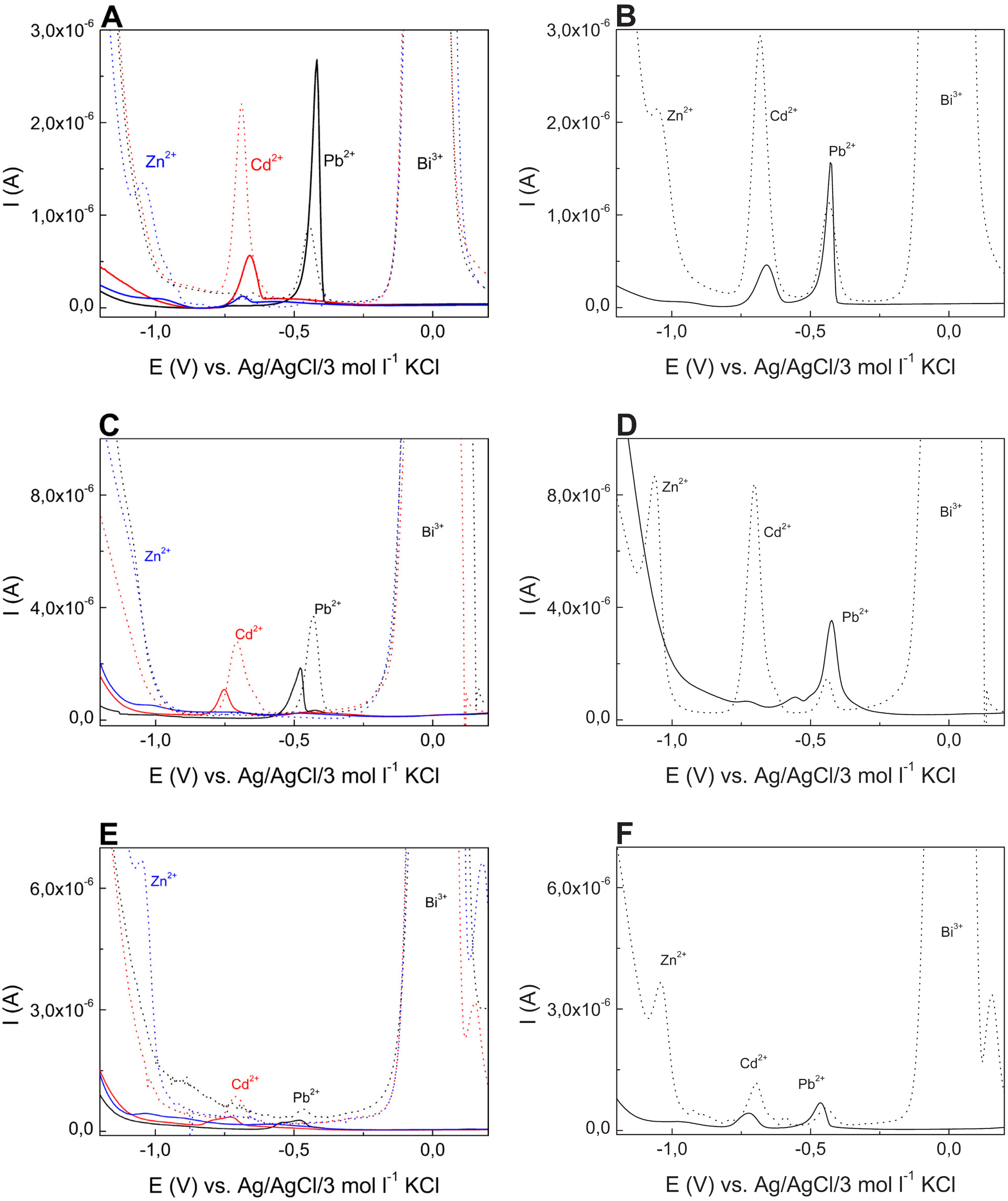

Fig. 2. DPAS voltammograms of modification effect for determination of heavy metals on bare electrode substrate (solid line) and modified electrodes (dotted line). The heavy metals were evaluated in individual (left) and simultaneous mode (right) with BDDE (A, B), GCE (C, D) and CPE (E, F) substrate under experimental conditions: c(Zn^{2+}, Cd^{2+}, Pb^{2+}) = 1 μmol l^{-1}; c(Bi^{3+}) = 0.1 mmol l^{-1} in 0.1 mol l^{-1} AB (pH 4.5), t_{dep} = 120 s, E_{dep} = –1.4 V, potential step 5 mV, modulation amplitude 25 mV, modulation time 50 ms.

observed that the height and width of re-oxidation peak increased as the deposition potential had more negative values. All stripping currents yielded the highest value at –1.4 V, therefore this potential was chosen as optimal value for Bi deposition. The deposition time (t_{dep}) was investigated in the range from 30 to 600 s for each substrate and the effect was found to be different when stripping current responses reached a maximum in 120 and 100 s in the case of BDDE and GCE substrates, respectively (not shown here). Concerning the CPE, the stripping current of Bi did not provide any significant effect on deposition time. As an optimal value of deposition time for preparing BiF on all substrates 120 s was chosen.

The individual and simultaneous determination of heavy metals was accomplished using DPASV technique on bare and *in situ* BiF modified electrodes (Fig. 2). The two calibration modes were applied for the simultaneous determination: the proportional signal increment of each metal and the signal increment of only one of all studied metals while the concentrations of others were kept constant. The slopes of obtained calibration curves (sensitivities) in almost all cases of this study (individual and simultaneous mode) were significantly higher when the modified electrode was exploited. For the determination of Zn^{2+} and Cd^{2+} the BiF modification of electrode surface was found to be useful for all substrates due to enhanced electron transfer of heavy metals on bismuth film. However, the determination of Pb^{2+} was probably coupled with a tendency of undefined intermetallic compounds formation during deposition process (Yang et al., 2013) which resulted in increase of LODs in certain cases (Table 1). The modification caused the decrease of Pb^{2+} stripping signal on BDDE and CPE, except GCE. Ultimately, *in situ* Bi modification can improve the potential separation of signals contrary to the bare substrates (shown as a shift of signals in Fig. 2). For further experiments, we have chosen BDD

Tab. 2. The influence of trace In^{3+} concentration on stripping signals of heavy metals.

$c(In^{3+})$ / µmol l^{-1}	Zn^{2+}		Cd^{2+}		In^{3+}		Pb^{2+}	
	E / V	I / µA	E / V	I / µA	E / V	I / µA	E / V	I / µA
–	–1.0	1.7	–0.7	4.2	–	–	–0.4	2.3
0.1	–1.1	68	–0.7	1.7	–	–	–0.5	1.5
1	–1.1	67	–0.7	1.6	–0.6	1.4	–0.5	1.2

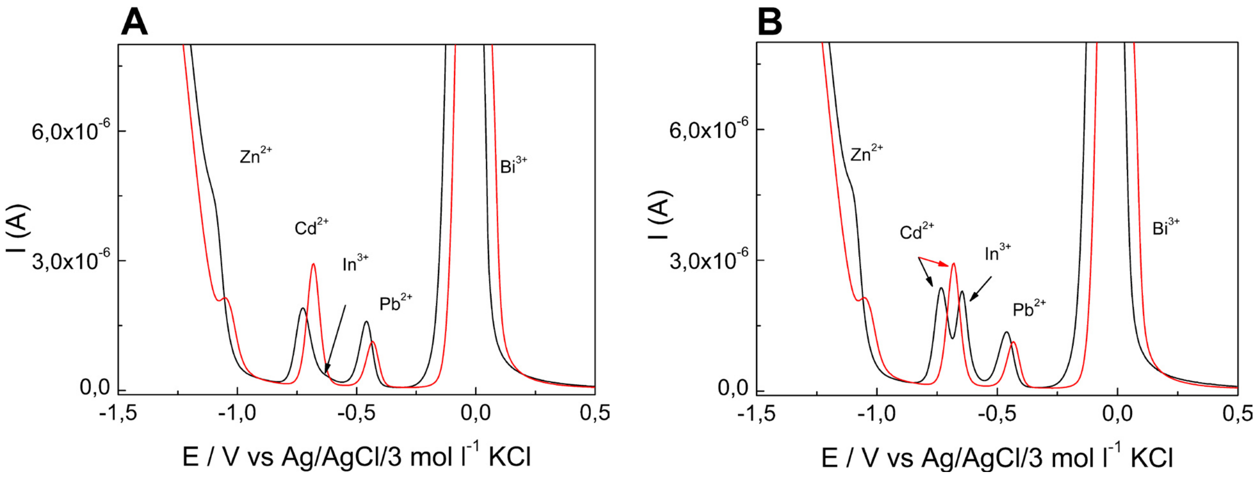

Fig. 3. DPAS voltammograms for interference study before (black) and after (red) addition of 0.1 µmol l^{-1} (A) and 1 µmol l^{-1} (B) of In^{3+} ions under experimental conditions: BiF-BDDE; $c(Zn^{2+}, Cd^{2+}, Pb^{2+})$ = 1 µmol l^{-1}; $c(Bi^{3+})$ = 0.1 mmol l^{-1} in 0.1 mol l^{-1} AB (pH 4.5), t_{dep} = 120 s, E_{dep} = –1.4 V, potential step 5 mV, modulation amplitude 25 mV, modulation time 50 ms.

Tab. 3. Water samples analysis using BiF-BDDE (n = 6).

Sample	Determined cations	Expected value (µmol l^{-1})	Determined value* (µmol l^{-1})	Recovery (%)	Reference method* (µmol l^{-1})
Reference material	Pb^{2+}	0.24	0.23 ± 0.02	95.8	0.24 ± 0.01
Industrial wastewater	Zn^{2+}	–	3.25 ± 0.12	–	3.27 ± 0.03

*Confidence interval calculated according ($\bar{x} \pm t_{n-1,\alpha} \cdot \frac{SD}{\sqrt{n}}$); $t_{5;\,0.05}$ = 2.015.

electrode substrate for Bi modifying since this material is recently very perspective.

In order to evaluate the selectivity of the proposed method for the heavy metals determination and on the basis of literature survey (Charalambous and Economou, 2005) In^{3+} was chosen as a possible interfering metal. Its peak maximum was noticed at –0.63 V on Bi film modified BDDE thus directly influencing the Cd^{2+} signal. The effect of two In^{3+} concentration levels (0.1 and 1 μmol l^{-1}) on the stripping signals of heavy metals was explored (Fig. 3). These experiments revealed that the presence of trace In^{3+} concentration in solution caused a slight shift of all signals to more negative potentials. Moreover, Cd^{2+} signal decreased considerably by 37 % and the changes of signals for Zn^{2+} and Pb^{2+} were slightly lower (Table 2). It is evident that trace amount of In^{3+} can significantly influence the Cd^{2+} determination.

Subsequently, the Bi film modified BDDE (BiF-BDDE) was applied to assess the heavy metals content in two different water samples including sample with declared amount of some heavy metals and industrial waste water sample from Taiwan factory with expected zinc content. The particular sample preparations are described in Experimental section.

In both samples no all heavy metals were determined simultaneously, only the concentration of one expected metal. In order to eliminate the matrix effect the standard addition method was employed. The spectral method was performed to verify the accuracy of the results for the proposed method. The average results of successive measurements under optimal experimental conditions are summarized in Table 3. The recovery value of around 96 % in the case of reference material analysis indicated that the accuracy of the proposed electro-

Tab. 4. The comparison of analytical parameters of *in situ* prepared bismuth film electrode with the previously reported ones for the determination of heavy metals.

Working electrode	Preparation t_{dep} (s), E_{dep} (V)	Analyte	Electrolyte	LOD (nmol l^{-1})	Reference
BiF/GCE	*in situ*, 120, –1.4	Tl^{+} In^{3+}	AB, pH 4.5	19 17	Wang et al., 2001
BiF/GCE	*ex situ*, 120, –1.2	Cr^{VI}	AB, pH 6.0	0.3	Lin et al., 2005
BiF/NanoSiO$_2$/GCE	*in situ*, 120, –1.1	Cd^{2+} Pb^{2+}	AB, pH 4.5	5.34 0.96	Yang et al., 2014
BiF/Au-GN-Cys/GCE	*in situ*, 800, –1.2	Cd^{2+} Pb^{2+}	AB, pH 4.5	0.89 0.24	Zhu et al., 2014
BiF/MWCNT/pPVC/GCE	*ex situ*, 120, –1.2	Cd^{2+} Pb^{2+}	AB, pH 5.0	1.8 1.9	Chamjangali et al., 2015
BiF/G/IL-SPE	*in situ*, 120, –1.2	Cd^{2+} Pb^{2+}	AB, pH 4.5	3.38 0.48	Wang et al., 2014
BiF-DP-CPE	*ex situ*, 240, –1.0	Cd^{2+} Pb^{2+}	AB, pH 4.5	2.1 1.9	Tian et al., 2012
BiF/NA/AG	*in situ*, 300, –1.4	Zn^{2+} Cd^{2+} Pb^{2+}	AB, pH 4.5	0.24 0.62 8.72	Lee et al., 2015
BiF/SbE	*in situ*, 210, –1.3	Cd^{2+}	HCl, pH 2.0	1.3	Yi et al., 2012
BiF/BDDE	*in situ*, 120, –1.2	Cd^{2+} Pb^{2+}	0.1 mol l^{-1} $HClO_4$	91 21	Toghill et al., 2008
BiF-BDDE	*in situ*, 120, –1.4	Zn^{2+} Cd^{2+} Pb^{2+}	AB, pH 4.5	130 12 34	This work

Abbreviations: AG – activated graphene, CuE – copper electrode, Cys – cysteine, DP – dioctyl phthalate, G – graphene, GN – gold nanoparticle, IL – ionic liquid, MWCNT – multiwalled carbon nanotube, NA – Nafion, pPVC – poly(pyrocatec holviolet), SbE – antimony electrode, SPE – screen printed electrode.

chemical method using BiF-BDDE was considered to be sufficient. In addition, the results of electroanalytical method are in a good agreement with those obtained by spectral method. These values corroborated that there were no significant matrix interferences in the analyzed samples. Thus, the modification of BDD electrode with BiF is effective to reliably determine the trace concentrations of heavy metals in water samples.

The comparison of the basic characteristics between the developed method using *in situ* BiF-BDDE and so far reported electrochemical methods involving other substrates for the heavy metals determination is given in Table 4. It is evident that most of them applied both *in* and *ex situ* prepared bismuth electrodes. The slopes of calibration curves in simultaneous mode with the use of modified electrodes were higher giving rise to the significantly lower LODs. These LODs are slightly higher in comparison with those reported in other papers.

Concurrently the simultaneous mode has proven to be more sensitive for the determination of Zn^{2+}, Cd^{2+} and Pb^{2+} than individual mode. It is assumed that the increasing of signal by mutual influence of metals present in the solution is caused.

Conclusion

In this paper the bismuth film modified electrodes were prepared by *in situ* technique using three substrates (boron-doped diamond electrode, carbon paste and glassy carbon electrode). Such modified electrodes were applied to determine the concentrations of heavy metals cations (Zn^{2+}, Cd^{2+} and Pb^{2+}). Based on the results achieved from individual and simultaneous determination mode, the BDDE was chosen as the perspective substrate. Modification of the substrate by bismuth film leads to an improvement in potential separation of signals and to a more sensitive determination of most studied heavy metals. The simultaneous determination mode has provided lower LODs. The BiF-BDDE was subsequently used for heavy metals determination in different water samples. The concentration levels determined by proposed method were compared with reference spectral method and good agreement was noticed. Based on this fact, the use of bismuth modification can be useful and favourable for sensitive and accurate determination of heavy metals.

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