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Bismuth-Trifluoride Modified Carbon Paste Electrode for Electrochemical Stripping Analysis of Heavy Metals

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In this article, a novel type metal-film based electrode, bismuth trifluoride-bulk-modified carbon paste electrode (BiF_3-CPE), is for the first time reported and examined in electrochemical stripping analysis for determination of selected heavy metals at the ppb ($\mu g \cdot L^{-1}$) concentration level. Optimal amount of bismuth trifluoride, as the source *of in-nascenti* generated bismuth film, was 10% (w/w). All important experimental and instrumental parameters have been optimized in the square-wave anodic stripping voltammetric mode when using Cd(II) and Pb(II) as the model ions. As found, BiF_3-CPE has exhibited a linear response in several concentration ranges tested, starting from the low ppb level (2–12 $\mu g \cdot L^{-1}$) *via* a mid level (10–150 $\mu g \cdot L^{-1}$), up to rather high concentrations in the range of 200–1200 $\mu g \cdot L^{-1}$; the repeatability of $_{(10\%)}BiF_3$-CPE, expressed by the RSD, being ±1.7 % (for n=10) for Cd(II) and ±1.4% for Pb(II). Interferences from selected heavy metals were also studied and no serious negative effects revealed. Finally, the $_{(10\%)}BiF_3$-CPE has been examined in analysis of certified reference material (sewage sludge with extremely high content of Pb) with a satisfactory agreement with the declared value (2233.2 $\mu g \cdot g^{-1}$ versus 2290 ± 110 $\mu g \cdot g^{-1}$ Pb in the CRM).

Keywords: Bismuth film electrode, carbon paste, bismuth trifluoride, stripping analysis, heavy metals

1. INTRODUCTION

Since the discovery of bismuth-coated electrode and its suitability for electrochemical stripping analysis (ESA) at the dawn of the new millennium [1,2], bismuth film electrodes (BiFEs) and, in general, bismuth-based electrodes (BiEs) or related sensors have become soon one of the most progressive areas within modern electroanalysis (see [3-6] and refs. therein).

Nowadays, already respected category of the so-called non-mercury metallic (film) electrodes covers the scientific activities reported in several hundreds of publications, becoming also the "hot" topic in some brand new monographs [7,8]. The prominent position is held by the bismuth-based configurations, generally considered as environmentally friendly — or "green" [7] — detection units.

It can be expected that, in a period of 2000-2012, (i) bismuth-based electrodes, BiEs, have been the subject of interest in more than 300 papers appearing in both international and local journals (see [5,6] and *e.g.* [9,10]). Nevertheless, also further non-mercury metals came rapidly to the fore, giving rise to various attractive configurations and having enriched the field with rather specific features. Namely, a hypothetic chart continues with (ii) antimony electrodes, SbEs (firstly recommended for ESA in the late 2000s [11], and hitherto being published in nearly 40 reports including *e.g.* [12,13]), (iii) lead film electrodes, PbFEs (with a debut in [14] and then described in 25 reports, most recently in [15]); the remaining ones, namely (iv) *SnFEs, GaFE, CoFE, PtFE*, and *PdFE,* having been examined either occasionally or even in a single attempt (see *e.g.* [8]).

Regarding the bismuth electrodes, there are various arrangements from which the bismuth film-plated configurations are far most popular, considered by some as a new classic among the working electrodes of the new generation [5]. According to special reviews [3-7], the film can be prepared in different ways, when one particular approach utilises Bi^{III}-compounds added directly into the electrode material and purposely transformed into the bismuth film at the electrode surface within the ESA procedure. Up until now, these substances are represented by the following compounds: Bi_2O_3 (firstly proposed in [16], then chosen by [17-23] or even integrated in commercially marketed sensors [24], and newly also in the form of special micro-, nano- or polycrystalline substrates [25-30]); $Bi_2O_3 \cdot 2TiO_2$ and $Bi_2(Al_2O_4)_3 \times H_2O$ [29]; $Bi(NO_3)_3$ (due to solubility in water stabilised inside a composite [31]); $(BiO)_2CO_3$ [30]; and, finally, NH_4BiF_4 [32].

The last named, ammonium tetrafluorobismuthate, proposed by our group [32] had proved itself to be so reliable Bi-precursor that its use motivated us to test also the native bismuth trifluoride, BiF_3; especially, if its antimony analogue, SbF_3, was recently found fairly applicable [33]. The results of the respective study are summarised in the following sections.

2. MATERIAL AND METHODS

2.1. Chemicals, Reagents, Stock and Standard Solutions

All chemicals used for the preparation of stock solutions were of analytical grade and purchased from Merck, Sigma-Aldrich, and Lachema (Brno, Czech Republic). The stock solutions of acetate buffer, ammonia buffer, HNO_3, H_2SO_4, $HClO_4$, and HCl were made 1M in concentration from the respective chemicals by using doubly distilled water and diluted as required.

The AAS-standard solution of Cd(II), Pb(II), Tl(I), In(III), Sn(II), Zn(II), and Cu(II) were used throughout. Water was obtained by double distillation of deionised water though a laboratory made distillation apparatus. All the measurements were carried out at room temperature (24±1 °C).

2.2. Instrumentation

An electrochemical analyzer AUTOLAB equipped with PGSTAT12 (Metrohm) controlled by NOVA software (version 1.8, the same manufacturer) was used for all measurements. This assembly was connected to an external electrode stand incorporating the standard three-electrode cell with the working electrode (see par. 2.3), a Ag/AgCl reference electrode with double junction, and a Pt-plate auxiliary electrode. Stirring was devised with a magnetic bar rotated at 400 rpm.

2.3. Working Electrodes

Carbon Paste. The proper mixture was prepare by thoroughly hand-mixing of 70% (w/w) graphite powder ("CR-5", Maziva Týn, Czech Republic) with 30% (w/w) highly viscous silicone oil ("LUKOIL MV 800", Lučební závody Kolín, Czech Republic) using a porcelain pestle and mortar.

Modified Carbon Paste. Into a 0.2 g portion of the bare carbon paste the appropriate amounts of bismuth trifluoride were added in order to obtain a series of modified carbon pastes containing from 1 to 13% (w/w) BiF_3. The individual mixtures were homogenized in the same way as described above.

Carbon Paste Electrodes (CPEs). Freshly prepared bare and modified carbon paste mixtures were packed into identical piston-driven carbon paste holders (with the same diameter, d = 3 mm) of our own design and manufactured in our workshops [34,35]. Each completed CPE assembly was checked with respect to the ohmic resistance; all values falling into an interval of 10-30 Ω. Furthermore, each CPE was renewed by extruding *ca.* 0.5 mm of carbon paste out from the body and then smoothed with a wet filter paper. Typically, this mechanical renewal was made before new experiment or a sequence of experiments, respectively.

2.4. Voltammetric Measurements

Square-wave anodic stripping voltammetry (SWASV) was the technique of choice in accordance with our previous experimentation. Unless stated otherwise, the typical measurement had consisted of three fundamental steps: (i) time-controlled electrochemical deposition under stirring (i.e., convective transport), (ii) the rest period in quiet solution, and (iii) positively-going voltammetric scan ("stripping step"). Each measurement also included electrochemical conditioning / cleaning step as an additional procedure. The individual experimental conditions and instrumental parameters are specified directly in the text; usually, in the caption of the corresponding figure(s).

2.5. Sample Preparation

For a demo-analysis of real sample, the certified reference material (CRM) of sewage sludge was selected (a specimen from a municipal water-cleaning station). A precisely weighted portion of 0.1g CRM was decomposed by microwave-assisted digestion in a medium of 6 mL HNO_3 + 1 mL HF + 2 mL H_3BO_3 and subsequently diluted with distilled water to 50 mL, yielding thus a sample stock solution. For proper determination, 250 μL of this solution was pipetted into 20 mL 0.2 M acetate buffer and the whole quantification made by means of the multiple standard-addition method.

3. RESULTS AND DISCUSSION

3.1. Bismuth Trifluoride as the Bi-precursor of Choice

Bismuth trifluoride, BiF_3, is a very stable chemical compound and the most stable among bismuth(III) halides. It is insoluble in aqueous solutions and does not undergo any incidental hydrolysis in water, which is advantageous and, in fact, conditional if this substance is to be used as the bulk modifier in a mixture with the proper electrode material [8]. BiF_3 dissolves only under extreme conditions; *e.g*., in a hot mineral acid or concentrated potassium fluoride; in this case, forming the $KBiF_4$ complex. This further underlines the above-stated benefit – the high chemical stability of BiF_3; nevertheless, this compound can be reduced electrolytically, being transformed into the (*in nascendi*) generated bismuth layer onto the electrode surface during the ESA procedure (see next section). Similarly as during the synthesis, bismuth trifluoride seems to exist also as a complex hydrofluorobismuthic acid, H_3BiF_6 or $BiF_3 \cdot 3HF$, which is in accordance with the well-known behaviour and typical configuration of the fluoride anion – the occurrence as a complex species [36].

NOTE: Thanks to a special position of fluorine among the elements of the VII. group in the periodical system and due to its extreme electronegativity, as well as coordination ability, this halogen can also form bismuth pentafluoride, BiF_5 [36-38]. It is an extremely reactive compound decomposing energetically water (when yielding a mixture of $O_3 + O_2F_2$), representing one of the most effective fluorinating agents and, reportedly [36], being capable to fluorinate also paraffin (above 50 °C). In this context, this substance seems to be a very interesting candidate for special studies whether or not such fluorination of paraffin would be feasible also in the case of mineral oils in the carbon paste mixtures; thus, giving rise to qualitatively new fluorinated binders with potentially attractive properties [8]. The first investigations of this kind are now in consideration [39] and the respective report given.

For comparison, some basic characteristics of solid BiF_3 are confronted with those of the other bismuth(III) halides and, in this way, surveyed in Table 1. As seen, among others, the BiF_3 differs in a typical ionic crystalline structure, occurring in two various forms (α-BiF_3 and β-BiF_3).

Again, strongly electronegative fluoride ensures the ionic character of chemical bonds in BiF_3, whereas the other halogens form covalent chemical bond; both these features being reflected in completely different properties of BiF_3 with respect to the remaining bismuth(III) trihalides.

Concerning the two crystalline structures of bismuth trifluoride, the first one, α-BiF_3, has a cubic structure, whereas the second, β-BiF_3, forms a YF_3-like structure (see Fig. 1) that can be described as a nine-coordinate BiF_9 tri-capped trigonal prism with eight nearly equal Bi–F bond lengths and one longer Bi–F interaction [39].

Table 1. Selected characteristics of bismuth trihalides

	BiF_3	$BiCl_3$	$BiBr_3$	BrI_3
Colour and phase [1]	light-grey crystal	colourless crystal	yellow crystal	greenish black crystal
Melting point[1] (°C)	649	233.5	219	408.6
Boiling point[1] (°C)	900	441	462	540
ΔH_r [1] (kJ/mol)	-900	-379	-276	-150
Ionicity[2] (%)	63	36	22	9
Covalenticity[2] (%)	37	74	78	91
Qualitative solubility[1]	*ins.* H_2O, EtOH	*sol.* Acid, EtOH, *react.* H_2O	*sol.* diluted acid, *sol.* EtOH *react.* H_2O	*ins.* H_2O *slightly sol.* EtOH

Abbreviations & symbols used: ΔH_r ... enthalpy, sol. ... soluble; 1,2) Lit. [37,38]

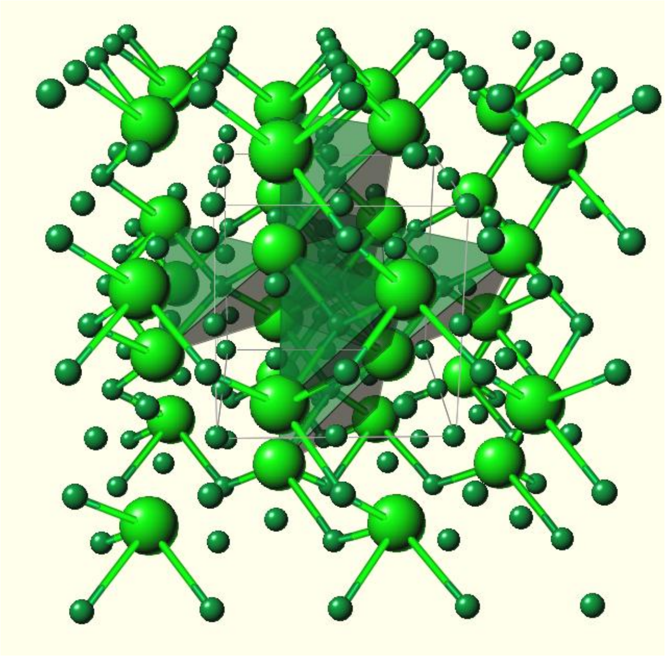

Figure 1. Structure of β-BiF_3.(after [40])

3.2. The Choice of Suitable Amount of Modifier in the Carbon Paste Mixture

Analogically to the experiments with bulk-modified CPE containing Bi_2O_3 [16-23] or NH_4BiF_4 [32], it can be deduced that the bismuth film is formed (*in nascendi*) during electrolytical reduction within the pre-concentration step in ESA according to the following reaction:

$$\mathrm{Bi^{III}F_3} \; + \; 3\,\mathrm{e^-} \longrightarrow \mathrm{Bi^0} \; + \; 3\,\mathrm{F^-} \qquad (1)$$

Also, in this case, it can be assumed that the quality and resultant electroanalytical properties of the generated Bi-film would depend on the conditions of deposition; mainly, upon the composition of the supporting electrolyte (i.e., the main constituents and its concentration together with actual pH) and the parameter set-up for the voltammetric technique of choice (mainly, deposition potential and time). Thus, the individual relations were examined to optimize the experimental procedure and to define the electroanalytical performance of BiF_3-CPE.

At first, the amount — as the mass percentage (w/w) — of modifying agent in the carbon paste was of interest and the results of the respective study are depicted in Fig. 2. As seen, the highest signal and the most favourable signal-to-noise ratio were obtained with the CPE modified with 10% BiF_3, taken thus for all further measurements. (In the figure, this particular electrode is denoted as "10% BiF_3", in the text below as $_{(10\%)}BiF_3$-CPE.)

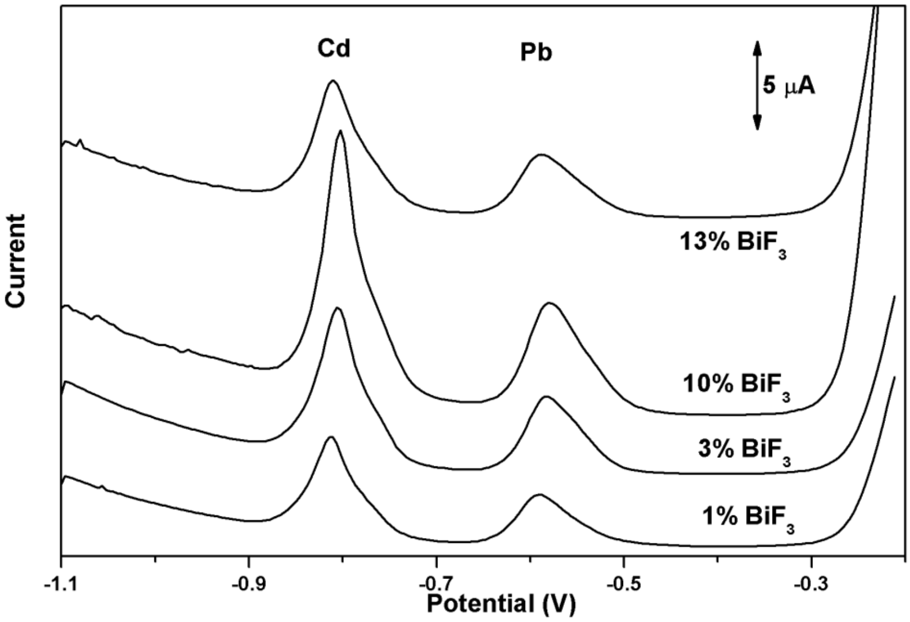

Figure 2. Effect of amount of BiF_3 in the carbon paste mixture upon the response for Cd and Pb. Experimental conditions: 0.2 M acetate buffer (pH 4.5), $c_{(Cd)} \equiv c_{(Pb)} = 90\ \mu g{\cdot}L^{-1}$; deposition step: potential, E_{dep} = -1.2 V vs. ref., time, t_{dep} = 120s; equilibrium period, t_{eq} = 10 s; stripping step: initial potential, $E_{init} \equiv E_{dep}$, final potential, E_{fin} = -0.1 V; conditioning potential, E_{cond} = +0.3 V, t_{cond} = 30 s; SWASV ramp: frequency, f_{sw} = 25 Hz; pulse height, ΔE_{sw} = 50 mV; step increment, s_i = 4 mV.

3.3. Optimisation of Experimental and Instrumental Parameters for the Determination of Pb + Cd

3.3.1. Supporting Electrolyte ... In measurements with $_{(10\%)}BiF_3$-CPE, a wide range of different supporting electrolytes was tested (see Fig. 3 and the corresponding inscriptions), when the most suitable was acetate buffer, which is traditionally used supporting medium for bismuth-based electrodes [5,7,8]. However, the use of $_{(10\%)}$BiF$_3$-CPE was not limited to acetate solutions only.

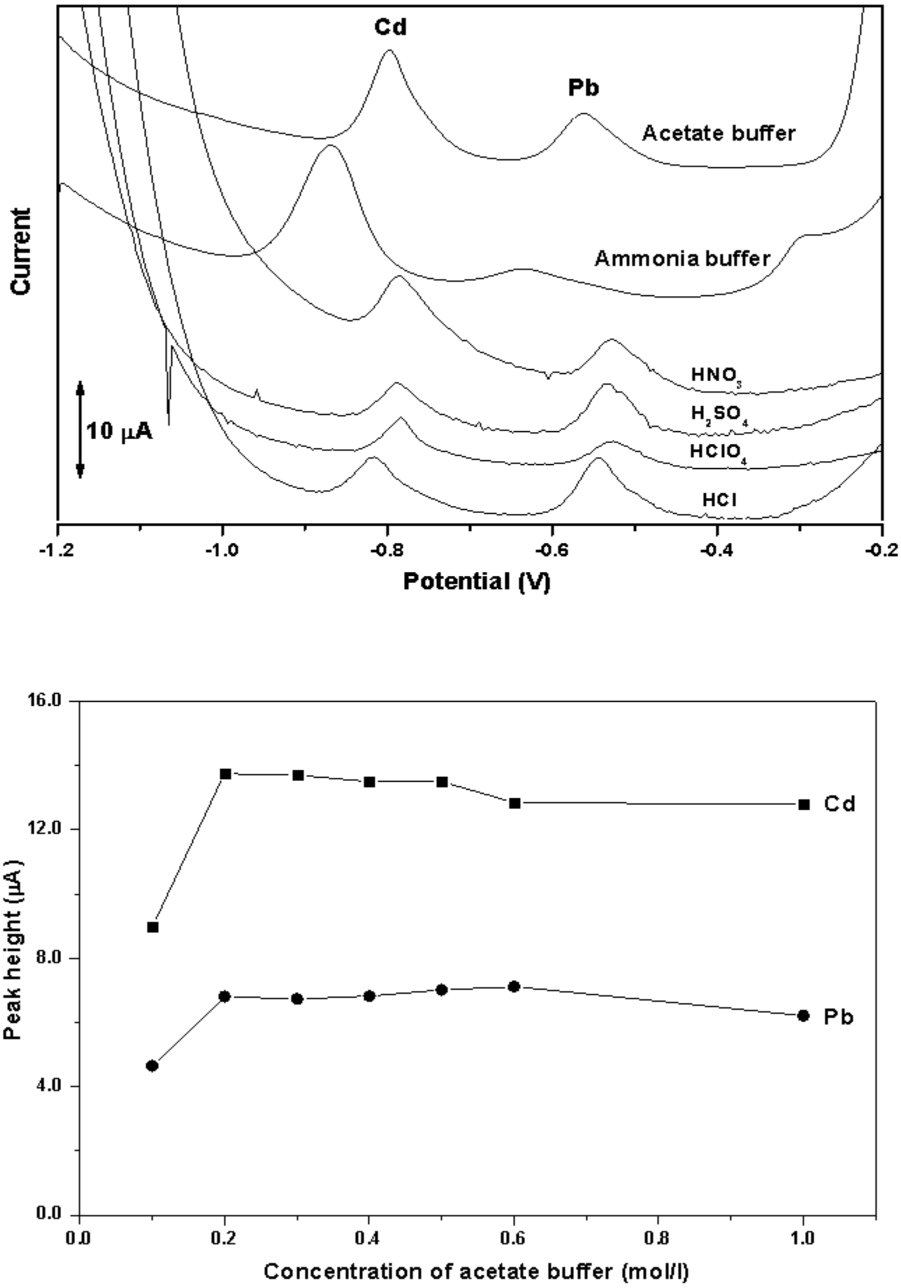

Figure 3. Effect of various supporting electrolytes (above) and effect of acetate buffer concentration on the SWASV response for Cd and Pb (below).

Experimental conditions: $c_{(Cd)} \equiv c_{(Pb)} = 90$ μg·L^{-1}; $E_{dep} = -1.2$ V vs. ref., time, $t_{dep} = 120$s; $t_{eq} = 10$ s; $E_{init} \equiv E_{dep}$, $E_{fin} = -0.1$ V; $E_{cond} = +0.3$ V, $t_{cond} = 30$ s; $f_{sw} = 25$ Hz; $\Delta E_{sw} = 50$ mV; $s_i = 4$ mV.

The set of the individual voltammograms suggests one that there are also other media with possible applicability. For instance, to control the uneven sensitivity of the electrode towards Cd and Pb in favour of the latter, a diluted hydrochloric acid can be used. Or, *vice versa*, to “adjust” the $_{(10\%)}$BiF$_3$-CPE towards the determination of Cd(II) when even certain concentration excess of Pb(II) would not interfere, the medium of choice is then an ammonia buffer (with pH *ca*. 9); by the way, quite an interesting alternative in electroanalysis with BiEs as shown some years ago [41].

3.3.2. The Peak Height(s) vs. Pre-concentration Time ... Another usually tested relation gave rise to gradually increasing current responses for both Cd and Pb with prolonged deposition time. In both cases, no significant saturation of the electrode surface was noticed even for very long depositions and the dependence had remained almost linear up to 30 min (not shown).

3.3.3. The Peak Height(s) vs. Deposition Potential ... Similarly, the dependence of the peak current(s) upon the deposition potential tested in a potential range from −0.9 to −1.4 V vs. ref. had to be optimised finding that pre-concentration at a potential of −1.2 V yielded the most satisfactory results with reasonably suppressed hydrogen evolution (not shown).

3.3.4. Model Calibrations for Cd + Pb and the Repeatability of the Signal(s) ... Fig. 4 overleaf demonstrates a very good linearity of calibration curves for both Cd and Pb investigated with $_{(10\%)}BiF_3$-CPE over a wide concentration range. A selected range, a calibration at the mid μg-per- litre concentration level (namely: 10–130 $\mu g \cdot L^{-1}$ Me^{2+}) is shown in Fig. 4A; the inset specifying the corresponding correlation coefficients: r^2(Cd) = 0.998 and r^2(Pb) = 0.999. Otherwise, the $_{(10\%)}BiF_3$-CPE could be calibrated at the low μg-per-litre level (down to 2–12 $\mu g \cdot L^{-1}$ Me^{2+}) with the correlation coefficients: r^2(Cd) = 0.998 or r^2(Pb) = 0.998 (see inset in Fig 4B), and with the LOD (estimated as "3:1 signal-to-noise ratio") to be about 0.7 $\mu g \cdot L^{-1}$ Cd and 1.0 $\mu g \cdot L^{-1}$ Pb.

Oppositely, at a high concentration level, the performance of $_{(10\%)}BiF_3$-CPE was tested in the range of 200–1200 $\mu g \cdot L^{-1}$ Me^{2+}, where the electrode signal did not exhibit any notable deviation(s) from linearity, which can be documented again by the respective correlation coefficients: r^2(Cd) = 0.990 and r^2(Pb) = 0.996. Finally, the repeatability of $_{(10\%)}BiF_3$-CPE expressed *via* the RSD (for n = 10) was found to be ±1.6 % for Cd and ±1.4 % for Pb, which is — if one considers that the electrode proper is the carbon paste — indeed excellent results for both metals (see also Fig. 5).

3.3.5. Interferences Studies ... A quintet of heavy metal ions, Zn(II), In(III), Sn(II), Tl(I), Cu(II), and their effect on the Cd- and Pb-signals were investigated at two mutual concentration ratios: c_{Me} vs $c_{Cd(Pb)}$ = 10:1 and 100:1. Due to later practical test with the BiF_3-CPE, the analyte of interest was lead, when the results of the respective interference studies for the determination of Pb(II) are surveyed in numerical form in Table 2 (again, see overleaf).

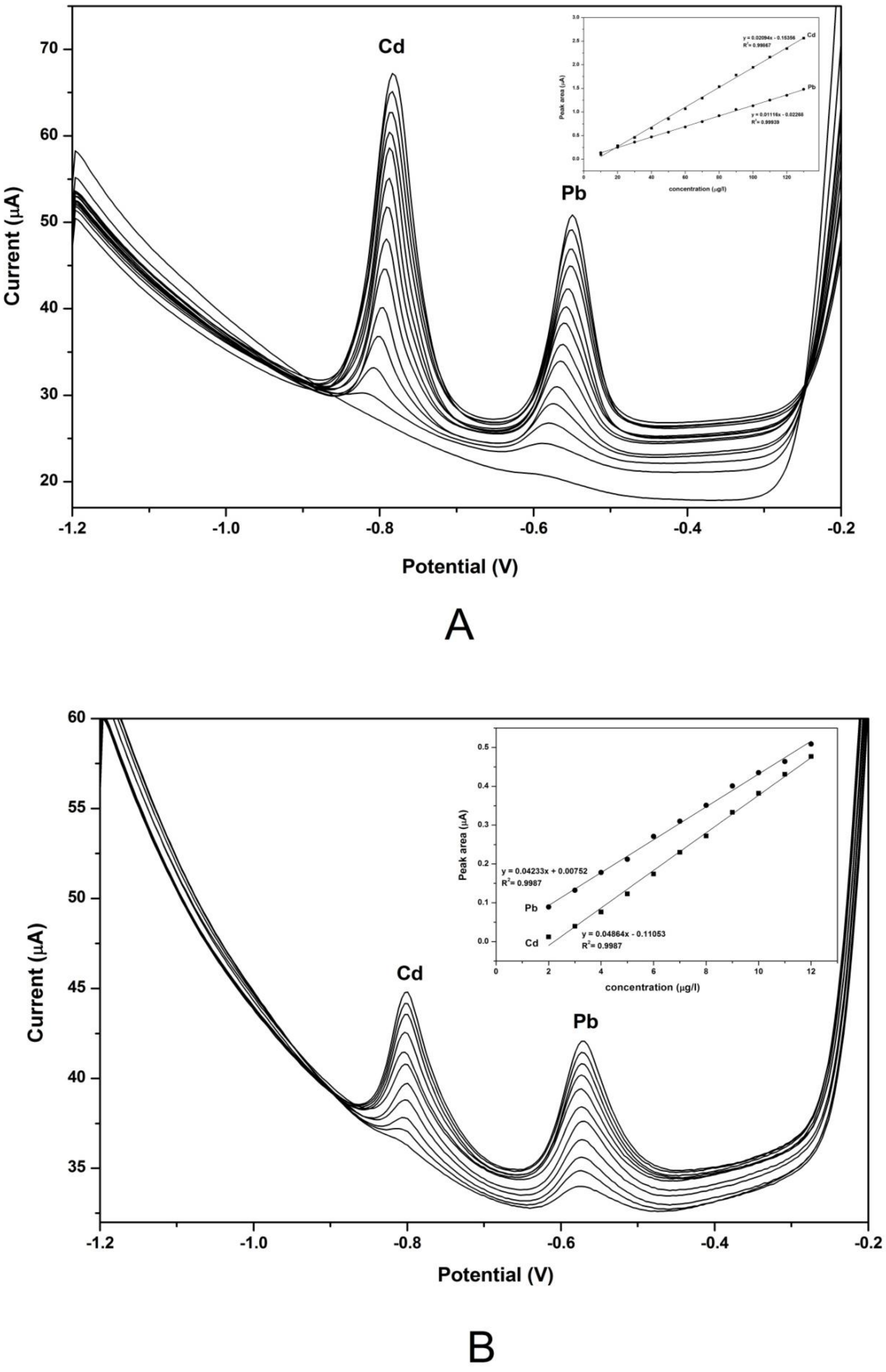

Figure 4. Calibration of Cd(II) and Pb(II) at the μg·L^{-1} level: (**A**) 10 – 130 μg·L^{-1}; (**B**) 2 – 12 μg·L^{-1}. Experimental conditions: E_{dep} = -1.2 V vs. ref., time, t_{dep} (A) = 120s, t_{dep} (B) = 300s; t_{eq} = 10 s; $E_{init} \equiv E_{dep}$, E_{fin} = -0.1 V; E_{cond} = +0.3 V, t_{cond} = 30 s; f_{sw} = 25 Hz; ΔE_{sw} = 50 mV; s_i = 4 mV.

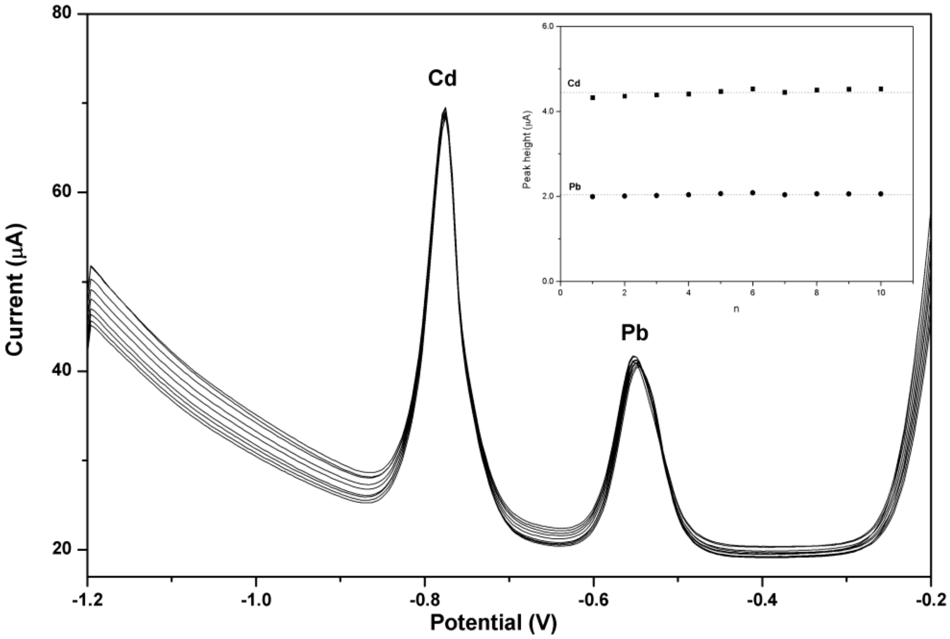

Figure 5. Square-wave stripping voltammograms for ten replicate measurements. Experimental conditions: $c_{(Cd)} \equiv c_{(Pb)} = 90\ \mu g \cdot L^{-1}$; $E_{dep} = -1.2$ V vs. ref., time, $t_{dep} = 120s$; $t_{eq} = 10$ s; $E_{init} \equiv E_{dep}$, $E_{fin} = -0.1$ V; $E_{cond} = +0.3$ V, $t_{cond} = 30$ s; $f_{sw} = 25$ Hz; $\Delta E_{sw} = 50$ mV; $s_i = 4$ mV.

For actual selection of interfering ions, a very negative effect was shown by the Cu(II) ions that had practically disabled the detection of Pb(II) already at the comparable concentrations and required thus the adequate masking in the sample(s) prior to analysis.

Table 2. Influence of selected ions upon the Pb-signal.

Interfering ion / c(Me):c(Pb)	Change of signal (in %)	
	10:1	**100:1**
Zn(II)	–0.9	–0.8
In(III)	–1.3	–21.5
Sn(II)	–1.5	–17.5
Tl(I)	–3.9	–14.1
Cu(II)	–36.9	–61.4

NOTE: The Cu(II) ions were included into the study as to know the effect of one of the most abundant metal elements in natural samples. In ESA with bismuth-film operated electrode, the detection of Cu(II) is not possible because copper is more precious than bismuth and the reoxidation signal of Cu lies out of the working potential range [5,42]. Nevertheless, the effect of Cu(II) upon the Pb- (or Cd-) signals can also be evaluated, but the respective analysis is not a simultaneous determination of Pb(II) and Cu(II) at a BiF-CPE, but the determination of Pb(II) in the presence of Cu(II) and Bi(III), released from the carbon paste bulk.

By testing potentially effective complexing or precipitating agents, the most efficient suppression was achieved by adding the ferrocyanide anion which reacts according to following reaction,

$$2\ Cu^{2+} + [Fe(CN)_6]^{4-} \longrightarrow Cu_2[Fe(CN)_6] \qquad (2)$$

well-known from classic “probe” qualitative analysis [43] as the formation of *Hatchett*'s brown [44]. Fig. 6 illustrates the ability of ferrocyanide to “restore” the Pb-signal *via* the decomposition of an intermetallic adduct of copper (see *e.g.* [45] and refs in) and its consecutive conversion into the highly stable complex-like compound of Hatchett's precipitate.

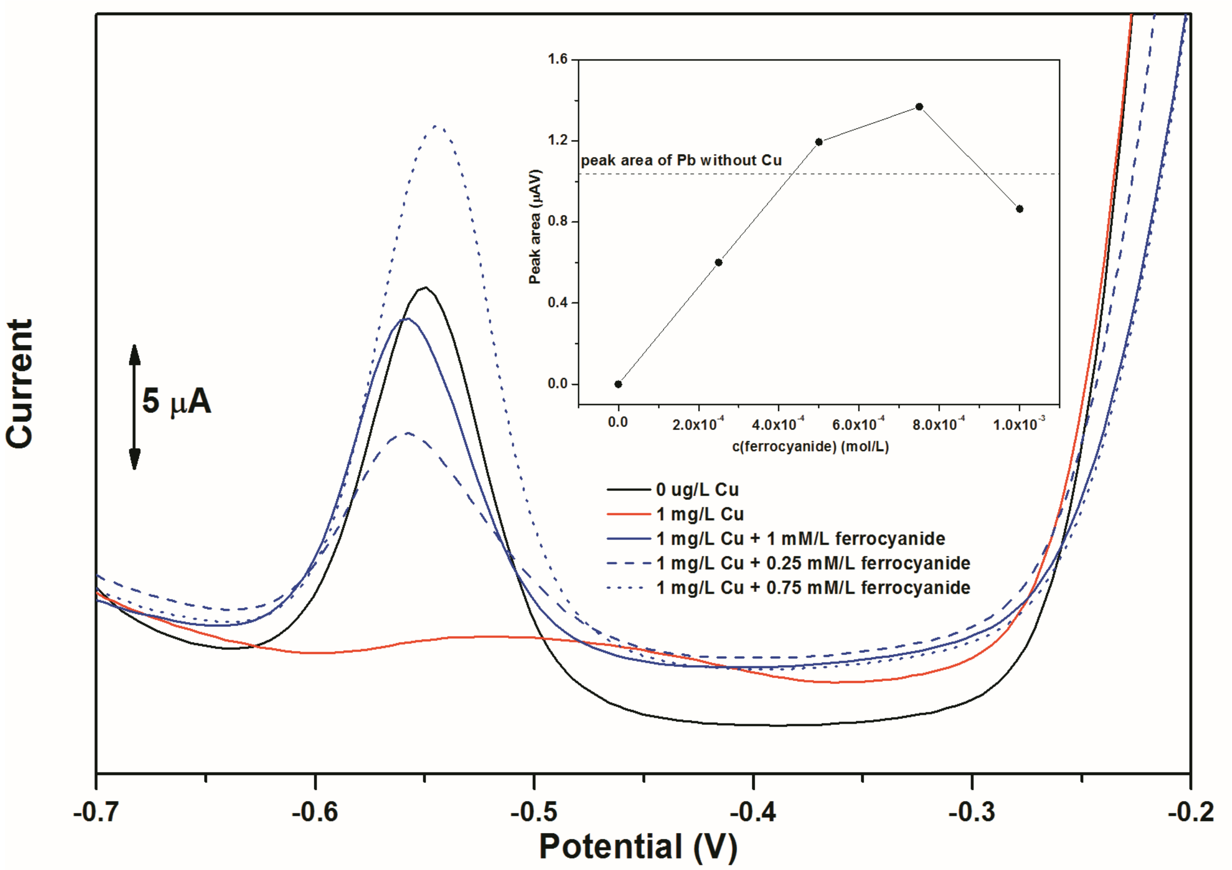

Figure 6. Effect of ferrocyanide on the response of Pb in solution containing Cu. Experimental conditions: black line: $c_{(Pb)}$ = 100 μg·L^{-1}, $c_{(Cu)}$ = 0 mg·L^{-1}, $c_{(Ferr)}$ = 0 mmol·L^{-1}; red line: $c_{(Pb)}$ = 100 μg·L^{-1}, $c_{(Cu)}$ = 1 mg·L^{-1}, $c_{(Ferr)}$ = 0 mmol·L^{-1}; blue dash line: $c_{(Pb)}$ = 100 μg·L^{-1}, $c_{(Cu)}$ = 1 mg·L^{-1}, $c_{(Ferr)}$ = 0.25 mmol·L^{-1}; blue dot line: $c_{(Pb)}$ = 100 μg·L^{-1}, $c_{(Cu)}$ = 1 mg·L^{-1}, $c_{(Ferr)}$ = 0.75 mmol·L^{-1}; blue full line: $c_{(Pb)}$ = 100 μg·L^{-1}, $c_{(Cu)}$ = 1 mg·L^{-1}, $c_{(Ferr)}$ = 1 mmol·L^{-1}; E_{dep} = -1.2 V vs. ref., time, t_{dep} = 120s; t_{eq} = 10 s; $E_{init} \equiv E_{dep}$, E_{fin} = -0.1 V; E_{cond} = +0.3 V, t_{cond} = 30 s; f_{sw} = 25 Hz; ΔE_{sw} = 50 mV; s_i = 4 mV.

A set of of the voltammograms demonstrates pretty well the whole process, when the Cu(II) ions were added into the test solution at a 100-fold concentration excess with respect to Pb(II) and the original Pb-signal (black curve) had totally disappeared (red curve).

Then, addition and the subsequent increase of the ferrocyanide concentration resulted in the re-appearance of the Pb-signal (three blue curves drawn as full, dashed, and dotted lines), which could be made reproducibly had the concentration of $[Fe(CN)_6]^{4-}$ been properly selected as a ratio of "$c_{(Ferr)} : c_{(Cu)} \approx 1: 6$".

3.4. Applicability of $_{(10\%)}BiF_3$-CPE in Analysis of Real Sample

Unlike to a series of previous demo-analyses, where the real samples of choice were always water specimens with relatively simple matrix, the electroanalytical performance of $_{(10\%)}BiF_3$-CPE was tested on the determination of Pb(II) in sewage sludge, containing extremely high content of various potentially interfering elements, including all common heavy metals. The sample was prepared by ordinary mineralisation in a MW-assisted digestion unit (for details, see *Experimental*, par. *2.5*) and after appropriate buffering taken for the SWASV analysis with quantification by means of standard addition method with three aliquots. The determination was carried out with a single sample and the respective voltammograms are shown in Fig. 7, together with the corresponding plot proving a fine linearity of the signal with concentration. In the sample analysed, the total amount of lead was found to be 2233.2 µg Pb / g sample; the certified value being 2290 ± 110 µg Pb / g.

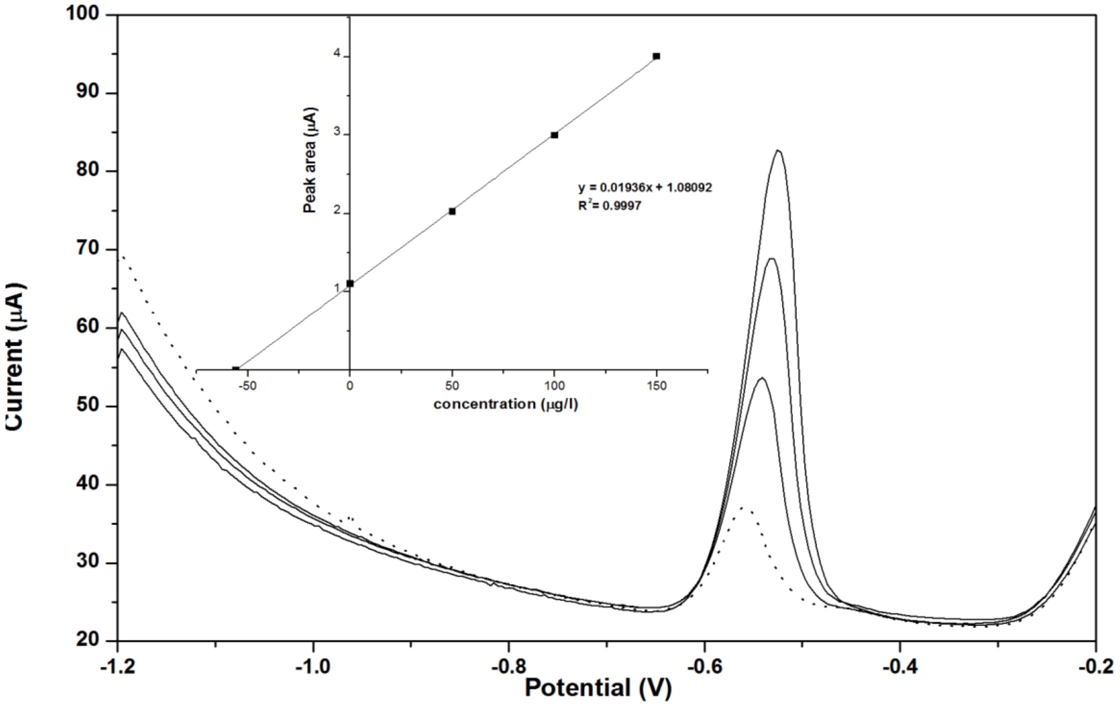

Figure 7. Determination of real sample by the standard addition method. Experimental conditions: E_{dep} = -1.2 V vs. ref., time, t_{dep} = 300s; t_{eq} = 10 s; $E_{init} \equiv E_{dep}$, E_{fin} = -0.1 V; E_{cond} = +0.3 V, t_{cond} = 30 s; f_{sw} = 25 Hz; ΔE_{sw} = 50 mV; s_i = 4 mV.

Otherwise, to examine the performance of $_{(10\%)}BiF_3$-CPE in trace analysis, a series of model solutions was prepared and spiked either with Pb(II) or with Cd(II) at the lower microgram level; in both cases, with 20 and 50 ppb Me(II). The individual analyses were performed again by the standard addition method (with three aliquots) and evaluated *via* the recovery rate (R_R); in all cases having found the "R_R" values between 85-110 % for the spike of Pb and 80-115 % for Cd (see Table 3).

Table 3. Analysis of model water sample spiked with Pb(II) or Cd(II)

Analyte	Spiked	Found
Cd(II)	20 μg·L^{-1}	17 μg·L^{-1}
	50 μg·L^{-1}	55 μg·L^{-1}
Pb(II)	20 μg·L^{-1}	16 μg·L^{-1}
	50 μg·L^{-1}	57 μg·L^{-1}

Note: For analysis of real sample, see text above.

4. CONCLUSIONS

In this article, a new type of a bismuth film-operated and carbon paste-based electrode, $_{(10\%)}BiF_3$-CPE, has been introduced and tested on the determination of Cd(II) and Pb(II); the latter being the analyte of choice in a real sample of sewage sludge. The pros and cons of the electrode proposed, as well as of the corresponding SWASV procedure, are as follows:

(+) another type of BiF-CPE operating *via* the so-far unused Bi-precursor / bulk modifier, BiF_3(s);

(+) non-oxide type of the Bi-precursor whose behaviour seems to be — and has also been proved — as more stable and better reproducible compared to the hitherto most frequently chosen bulk modifier, the bismuth trioxide, Bi_2O_3(s) (see *e.g.* [17] and discussion in);

(+) simple and rapid preparation of the modified electrode material, as well as of the electrode itself;

(+) satisfactory selectivity and sensitivity of the respective SWASV method, in the basic parameters fully comparable to the previous procedures based on identical or related principles;

(–) certain toxicity reported for BiF_3 [37,38] compared to nearly harmless Bi_2O_3; with respect to a minimal solubility and a very limited reactivity of BiF_3 (see above), however, this substance would be harmful at larger amounts, which is not the case of this application;

(–) possible troubles with the presence of fluoride in the sample(s) released from the electrode material during its use; however, an incidental negative effect of the F^- species — *e.g.* undesirable complexation of the analyte — has to be yet confirmed experimentally.

It can be concluded that the already classical concept of bulk-modified carbon paste electrodes [8] can flexibly be combined with the newest trends in modern electrochemistry; one of the most typical examples being “green” [3-5,46] or “greening” [7]) electroanalysis with bismuth-based electrodes, sensors, and detectors, as well as other related configurations.

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