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ELECTROANALYSIS WITH BISMUTH- AND ANTIMONY-FILM PLATED CARBON PASTE ELECTRODES IN COMPLEX-FORMING AND MIXED MEDIA

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In this paper, a new study is presented, concerning the possibilities and limitations of bismuth- and antimony-film plated carbon paste electrodes, BiF-CPE and SbF-CPE, in combination with stripping voltammetry and mixed supporting electrolytes containing various complex-forming constituents. The experiments with both BiF-CPE and SbF-CPE in solutions containing halides (F^-, Cl^-, Br^-, I^-), pseudohalides (SCN^-, CNO^-, CN^-), EDTA, or organic anions (tartrate, citrate) were focused on electroanalytical performance of both electrodes for the determination of Cd^{2+} and Pb^{2+} as model ions. Their behaviour was observed and discussed via the effects of the individual media upon the peak characteristics, base-line, as well as the dissolution peak of Bi/Sb. The results obtained have confirmed numerous relations and typical features that can be utilised in practical measurements.

Introduction

During the last summertime, the rapidly growing group of *non-mercury metallic film electrodes* (MeFEs) celebrated its first decade in modern electroanalysis [1]. Since the introduction of bismuth-coated glassy carbon electrode (BiF-GCE [2]) and its first major successor — carbon paste variant (BiF-CPE [3]), the newly established field comprises now more than 200 scientific papers devoted to various types and configuration of bismuth-based electrodes (BiEs [1,4-7]), when other twenty contributions is going to come soon from on-line presentations [8]. Somewhat "younger" antimony film electrodes (SbFEs [9,10]) and related sensors then represent close alternatives to BiEs, occupying now — with 25 reports — the second position among all hitherto existing non-mercury metallic electrodes and sensors.

At present, electroanalysis with BiFEs and SbFEs is in rather paradox situation [7]. On one side, there are still more sophisticated constructions where the fundamental electrode configurations are combined with additional components (modifiers, stabilisers, contact catalysts etc.); on the other hand, many users conventionally rely on the already recommended experimental conditions that may not be necessarily the optimum for some special applications. A typical example of such sophisticated approach is the choice of the supporting electrolytes whose spectrum is surprisingly narrow if one considers, e.g., experience and inspiration from traditional polarographic and voltammetric measurements where the functioning and effects of various complex-forming constituents were well known and widely utilised (see, e.g., Refs [11-13]).

In electroanalysis with BiFEs and other bismuth-based detection systems, the dominating supporting electrolyte has always been the acetate buffer (AcB), with equimolar concentration of both constituents, $CH_3COOH + CH_3COONa$ (1:1), varying in an interval of 0.01-0.5 mol l^{-1} and most frequently containing 0.1 M AcB. It can be estimated [1] that ca. 70 % of all supporting media in measurements with BiEs are of this kind.

Otherwise, the authors have occasionally reported on the use of diluted mineral acids (HCl, $HClO_4$, HNO_3, and H_2SO_4; see, e.g., [6] and refs therein), alkaline hydroxides (NaOH and KOH [14-16]) or various buffering media, such as ammonia and borate buffers or phosphate and Britton-Robinson mixtures, all being usable for measurements with *ex-situ* operated BiFEs (see, e.g., [17,18]) or for experimentation with Bi-powder containing CPE [19]. Typical complex-forming agent used in electroanalysis with BiFEs was EDTA; mainly, during the determination of Tl^{I} in the presence of Pb^{II} and Cd^{II} [14,20]. Other frequent complexants were chloride and especially bromide, used in mixtures with HCl and tested for enhancement of the detection sensitivity [21], selective accumulation of less common metals (e.g., Sn^{II} [22]) or for improvement of the bismuth deposition itself [23-25]. Occasionally used complexing media were then iodide, tartrate, and citrate [26-31]. Regarding the SbFEs and their sub-variants, the solution of preferential choice is diluted hydrochloric acid; usually, 0.01 M HCl [9,10], but higher concentrations can also be the case (see [31] and refs. therein). Among complexing reagents, again, halide anions Cl^- and Br^- were chosen [27], other substances (like thiocyanate [31], or hydrogen tartrate [29]) being in the stage of initial testing.

Within our research group, bismuth- and antimony-based electrodes — in particular, the carbon paste-based variants, BiF-CPEs [2] and SbF-CPEs [10] — have repeatedly been of interest with respect to their applicability in various mixed and complex media, which can be documented on our activities in the early era of both non-mercury electrodes [14,15], in the period of their advanced characterisation [16,19], as well as recently [27-32], including valuable contributions from other collaborating scientists [29,30].

This contribution — in fact, the publication form of a diploma thesis [28] — is a direct continuation of the above-mentioned studies [14-16,19], gathering the experiments with a substantially wider palette of the supporting electrolytes. The most important results and observations from these investigations are summarised in the following sections.

Experimental

Chemicals and Reagents

All chemicals used were of analytical reagent grade and purchased from Sigma-Aldrich or Merck unless stated otherwise. Two main stock solutions of acetate buffer (“AcB” $CH_3COOH + CH_3COONa$, equimolar mixture) and of hydrochloric acid, HCl, were made 1.0 mol l^{-1} in concentration. Other solutions, including all complex-forming media selected, were $HClO_4$, NaOH, ammonia and phosphate buffers (with c = 0.5 mol l^{-1}), NaF, NaCl, NaBr, NaI, KSCN, NaCNO, NaCN, potassium tartrate and citrate (0.1 mol l^{-1}), plus EDTA (0.01 mol l^{-1}).

Stock solutions of Bi(III) and Sb(III) used for the *in-situ* generation of the respective films were spectroscopic standards with a guaranteed content of 1.0000 ± 0.0001 g l^{-1} (1000 ppm) Bi or Sb; both acidified to prevent hydrolysis in aqueous solutions. Finally, stock standard solutions of two model ions, Cd^{2+} and Pb^{2+}, were both prepared as 1.0 mg l^{-1} (1 ppm) and acidified also to pH 2. All the solutions were made from doubly deionised water.

Apparatus and Instrumentation

All the measurements were performed with an AUTOLAB® electrochemical analyser (model "PGSTAT 30"; Ecochemie, Utrecht, Holland) operated *via* the "GPES 4.9" software (the same manufacturer). A three-electrode cell used comprised the working electrode (see below), Ag|AgCl|3 M KCl as the reference, and a Pt-plate (3×5 mm) as the auxiliary electrode. Where applicable, stirring was performed using a Teflon®-coated magnetic bar rotated at 300 rpm. The pH values were measured on a portable pH-meter (model CPH 52; Elteca, Turnov, the Czech Republic) equipped with a combined glass sensor (OP-0808P; Radelkis, Budapest, Hungary) and calibrated using commercial standard buffers.

Working Electrodes

Carbon Pastes. The bare (unmodified) mixture was prepared by thoroughly hand-mixing of 1.0 g spectroscopic graphite powder ("CR-5" type; Maziva Týn, the Czech Republic) with 0.6 ml highly viscous silicone oil ("LUKOIL MV 8000"; Lučební závody Kolín, the Czech Republic). Both components were homogenised using recommended procedure [33].

Carbon Paste Electrodes. Roughly equal portions of the freshly made carbon paste were packed into two identical piston-driven holders (designed in our laboratory [34], with identical surface diameter, D = 2 mm). Both carbon paste electrodes serving as the electrode substrates / supports for Bi- and Sb-films were checked with respect to their ohmic resistance; the values of about 10 ohms having indicated a sufficient homogeneity [33,35,36].

Procedures

Preparation of Working Electrodes for Measurements. As mentioned above, both antimony and bismuth films were deposited *in situ*, i.e., by potentiostatic electrolysis performed directly in sample solutions containing $\mathrm{Sb^{III}}$ or $\mathrm{Bi^{III}}$ species. The carbon paste surface was renewed mechanically by its smoothing against a wet filter paper [21,22] and this operation was usually made prior to a new set of experiments.

Square-Wave Anodic Stripping Voltammetry (SWASV). Typical experiments comprised a potentiostatic preconcentration ("accumulation step") at –1.20 V vs. ref., followed by a 15 s equilibration period and the anodic scanning ("stripping step") from –1.20 V up to +0.20 V vs. ref. The SWV modulation ramp was set as follows: frequency, f_{SW} = 25 kHz; pulse amplitude, DE_{SW} = +50 mV; and the potential increment, i_{SW} = 5 mV. In some experiments, some parameters (e.g., concentrations of Bi^{III} and Sb^{III}, stripping limits, E_{INIT} and E_{FIN}) could be slightly varied and the actual values are given directly in Results and Discussion; usually, within the legends for the individual figures.

Results and Discussion

Choice of the Supporting Electrolytes

According to the intention in use, the supporting media tested within this study could be divided into three main categories; the third one with two sub-classes:

(I) *0.1 M* $CH_3COOH + CH_3COONa$ (1:1; with pH 4.5) and *0.01 M HCl* (pH 2) ... These solutions served as standards for comparison of the peak characteristics (with Cd^{2+} and Pb^{2+} as model ions), as well as the overall signal-to-to noise ratio; the former one in measurements with *in-situ* prepared BiF-CPE, the latter for the same purposes when experimenting with the analogically operated SbF-CPE.

(II) *0.05, 0,1,* and *0.5 M HCl, 0.05* or *0.1 M* $HClO_4$, and *0.1 M NaOH* ... A trio of strong electrolytes represented by potentially complex-forming hydrochloric acid (at three different concentrations), non-complexing perchloric acid (two concentrations), and decimolar sodium hydroxide (with alkaline pH) had served as the electrolytes of choice for some particular complexants (e.g., $HClO_4$ in a mixture with citrate, $C_6H_5O_7$, and NaOH with cyanide, CN^-).

(IIIa) *0.1 M AcB +* 1×10^{-5}*-0.1 M NaX* (where "*X*" was F, Cl, Br, I, and SCN) for measurements with BiF-CPE, *0.01 M HCl +* 1×10^{-5}*-0.1 M NaX* for the alternate antimony electrode, and *0.05 M NaCl + 0.05 M NaX* for both ... The first set of mixed media with the proper concentration of the main component and optimal pH, where the variation of the individual active constituents enabled to evaluate/highlight some particularly effective compositions. In parallel tests, neutral solutions based on 0.05 M NaCl and the equimolar concentration of the other halide were also prepared and examined.

(IIIb) *0.1 M AcB +* 1×10^{-5}*-0.1 M NaY* (where "Y" was CNO, $C_4H_4O_6$ [tartrate, 2–]; $C_6H_5O_7$ [citrate, 3–], and EDTA) and *0.01 M HCl +* 1×10^{-5}*-0.1 M NaY* ... The second set of mixed media comprised complexants that were found less effective during preliminary assays.

Square-Wave Anodic Stripping Voltammetry of Cd^{2+} and Pb^{2+} Ions at Bismuth- and Antimony-Film-Plated Carbon Paste Electrodes

Measurements with 0.1 M Acetate Buffer and 0.01 M HCl as the Standard Supporting Electrolytes for In-Situ Operated BiF-CPE and SbF-CPE

So far evident preference for decimolar acetate buffer (AcB) as the supporting electrolyte of choice for BiFEs [4-7] and centimolar HCl for SbFEs [1,9,10] had made our selection of the two arbitrary supporting media rather simple, when the respective signal and background characteristics could be set as standards for comparison and interpretation of the relevant parameters for newly tested media. Figure 1 shows a model sequence of experiments with BiF-CPE and a similar set is then given in Fig. 2 for measurements at SbF-CPE. Two sets of voltammograms depict the shape and magnitude of both signals of interest, i.e., Cd- and Pb-peaks,

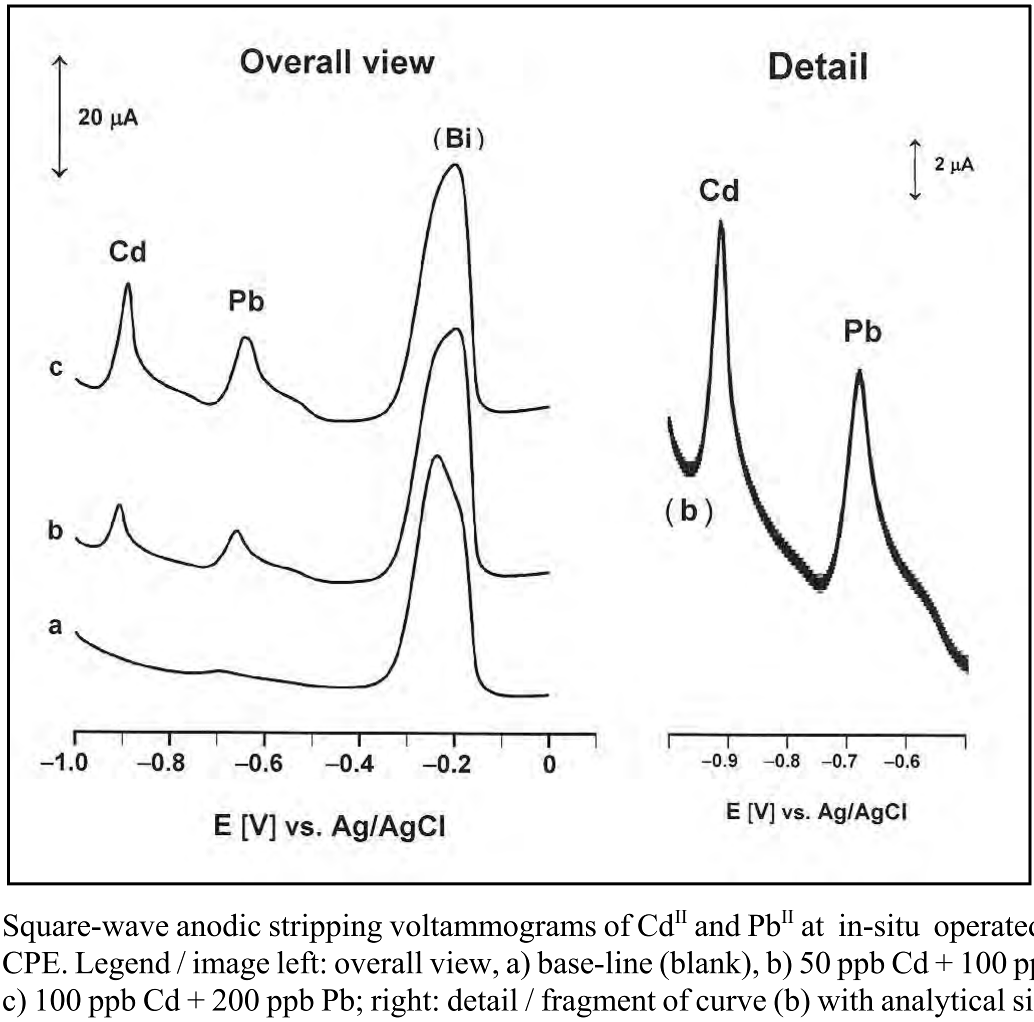

Fig. 1 Square-wave anodic stripping voltammograms of Cd^{II} and Pb^{II} at in-situ operated BiF-CPE. Legend / image left: overall view, a) base-line (blank), b) 50 ppb Cd + 100 ppb Pb, c) 100 ppb Cd + 200 ppb Pb; right: detail / fragment of curve (b) with analytical signals. Experimental conditions: supporting electrolyte (s.e.): 0.1 M AcB + 1 ppm Bi^{III} (pH 4.61); Accumulation parameters: potential, $E_{ACC} = -1.0$ V vs. Ag/AgCl/3 M KCl (ref.); time, $t_{ACC} = 30$ s; Equilibrium period, $t_{EQ} = 10$ s; Stripping limits: $E_{INIT} = -1.0$ V, $E_{FIN} = +0.2$ V vs. ref.; SWV-modulation ramp: $f_{SW} = 25$ kHz, $\Delta E_{SW} = +50$ mV, $i_{SW} = 5$ mV

as well as the overall character of the stripping curves recorded from the initial potential, E_{INIT}, up to the final potential, E_{FIN}. (The latter is given by the dissolution peaks of Bi or Sb, indicating the electrochemical oxidation of the film and its stripping out of the carbon paste surface.)

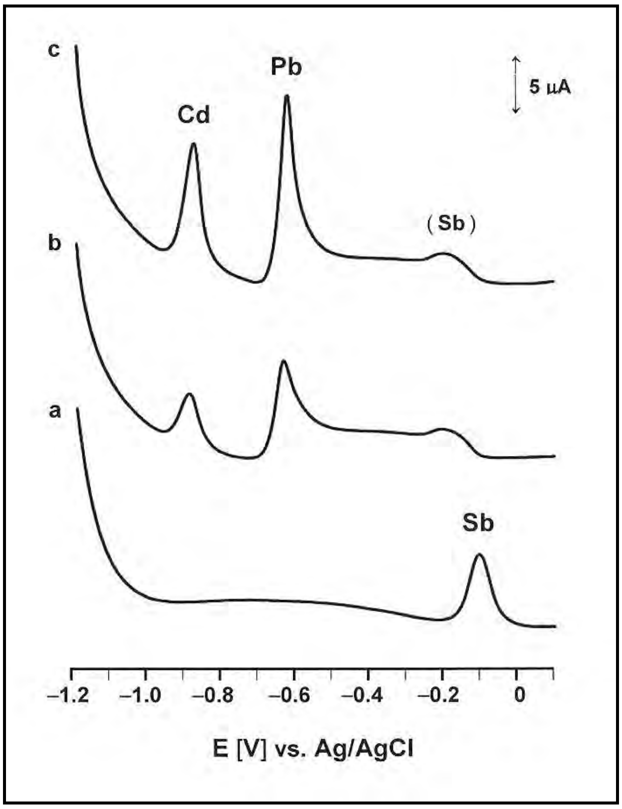

Fig. 2 Square-wave anodic stripping voltammograms of Cd^{II} and Pb^{II} at in-situ operated SbF-CPE. Legend: a) base-line (blank), b) 50 ppb Cd + 100 ppb Pb, c) 100 ppb Cd + 200 ppb Pb. Experimental conditions: s.e.: 0.01 M HCl + 0.5 ppm Sb^{III} (pH 1.42); Accumulation: $E_{ACC} = -1.0$ V vs. ref., $t_{ACC} = 30$ s, $t_{EQ} = 10$ s.; Stripping: $E_{INIT} = -1.0$ V, $E_{FIN} = +0.1$ V vs. ref.; SWV ramp: $f_{SW} = 25$ kHz, $\Delta E_{SW} = +50$ mV, $i_{SW} = 5$ mV

In case of measurements with BiFE, the Bi-signal is normally many-fold larger than stripping peaks for Cd and Pb [4-7] and hence, Fig. 1 also offers a zoom (on the right) with detailed view upon the re-oxidation of both model ions.
This was not necessary for voltammograms obtained with the SbFE, where the Sb-peak is always markedly smaller [9,10] and the overall view could be adjusted appropriately for all the signals depicted in Fig. 2. Furthermore, in order to obtain fine and well-developed responses of Cd and Pb whose detection at both BiFE and SbFE is usually more sensitive for cadmium [4-6,9], the additions of model ions had not been made at a suitable concentration ratio; typically, as a mixture with "c(Cd) : c(Pb) = 1 : 2".

Otherwise, the behaviour of both BiF-CPE and SbF-CPE in two "optimal electrolytes" was also checked with respect to the reproducibility of the corresponding signals for Cd^{II} and Pb^{II}. In all cases, metallic films were always stripped off after each scan and regenerated electrochemically during the subsequent *in-situ* accumulation. For both electrodes and the individual signals evaluated, the reproducibility has been found excellent (about ±1 %), which is also documented by the data in Table I.

Table I Peak intensities evaluated from testing measurements and reproducibility [%] at two different non-mercury metallic film electrodes (data from Ref. [28])

n	BiF-CPE / 0.1 M AcB		BiF-CPE / 0.01 M HCl	
	I_P(Cd), μA	I_P(Pb), μA	I_P(Cd), μA	I_P(Pb), μA
1	3.3	4.3	6.6	2.9
2	3.4	4.2	6.7	3.0
3	3.5	4.3	6.7	3.0
4	3.5	4.4	7.0	3.0
5	3.5	4.4	6.7	3.0
6	3.2	4.2	6.8	3.1
7	3.4	4.5	6.8	3.2
8	3.3	4.3	6.7	3.1
9	3.4	4.3	6.9	3.2
10	3.4	4.4	6.8	3.2
$R_{\%}$	±0.9	±0.9	±1.1	±1.0

Experimental conditions and further data: the same surface of both CPE substrates; For other parameters, see Figs 1 and 2

Herein, however, it should be quoted that the concentrations of both Cd^{2+} and Pb^{2+} ions had been chosen at the higher ppb range, which was the model level chosen for all the supporting media prepared and examined in this study.

The Effect of Complex-Forming Species

Effect of the Halides

Fluoride, F^-: In analytical chemistry, the fluoride anion is known for its specific reactions; especially for the capability to form very stable complexes [37,38]; see also data in Table II with some additional references [39-46]. Because the electrode redox transformations of such strong complexes are difficult to accomplish [11,12], the use of F^- in faradic measurements is quite rare and correspondingly

Table II Chemical equilibria data for selected compounds of metals with halides, pseudohalides, and other complex-forming anions (taken and assembled from [38-46])

Stability / Formation constants [a] [Compounds of Bi^{III}, Sb^{III}, Cd^{II}, Pb^{II}]

Complex	$\beta(MeX_n)$	Complex	$\beta(MeX_n)$	Complex	$\beta(MeX_n)$
BiF_4^-	2.5×10^{1} [h]	SbF_4^-	7.9×10^{15} [h]	CdF_4^{2-}	< 1 [??]
$BiCl_4^-$	3.2×10^{6} [h]	$SbCl_4^-$	1.6×10^{4} [h]	PbF_4^{2-}	≈ 1 [??]
$BiBr_4^-$	4.0×10^{8} [h]	$SbBr_4^-$	1.0×10^{10} [?]	$CdBr_4^-$	7.9×10^{2}
BiI_4^-	1.0×10^{15}	SbI_4^-	-- [k]	$PbBr_4^-$	2.0×10^{2}
$Bi(SCN)_4^-$	2.0×10^{4}	$Sb(SCN)_4^-$	-- [l]	PbI_4^-	3.0×10^{2}
$Bi(CN)_4^-$	... [??]	$Sb(CN)_4^-$	... [??]	$Zn(SCN)_4^{2-}$	3.2×10^{1}
$Bi(OH)_4^-$	1.6×10^{34}	$Sb(OH)_4^-$	1.6×10^{2}	$Cd(SCN)_4^{2-}$	... [??]
Bi−acet [c]	... [??]	Sb−acet [c]	... [??]	$Pb(SCN)_4^{2-}$	... [??]
$Bi(tart)_2^+$ [d]	-- [i]	Sb−tart [d]	3.2×10^{21}	$Cd(CN)_4^{2-}$	7.9×10^{17}
$Bi_2(citr)_2^{2-}$ [e]	2.0×10^{29} [j]	Sb−citr	-- [m]	$Pb(CN)_4^{2-}$	2.0×10^{10}
BiY^- [f]	2.0×10^{27}	CdY^{2-} [f]	2.5×10^{16}	$Cd(OH)_4^{2-}$	4.9×10^{8}
Sb−EDTA [g]	4.0×10^{31}	PbY^{2-} [f]	7.9×10^{17}	$Pb(OH)_4^{2-}$	1.2×10^{32}

Solubility products [b]

Compound	$K_S(Me_aX_b)$
$Bi(OH)_3$ [n]	4.0×10^{-31}
$Sb(OH)_3$ [n]	4.0×10^{-42} [h]
BiF_3	-- [o]
$BiBr_3$	-- [p]
BiI_3	7.7×10^{-19}
$PbCl_2$	1.7×10^{-5}
$PbBr_2$	6.6×10^{-6}
CdI_2	-- [q]
PbI_2	7.1×10^{-9}
$Cd(SCN)_2$	-- [q]
$Pb(SCN)_2$	2.1×10^{-5}
$Pb(N_3)_2$	2.5×10^{-9}

Legend: a) average values if found in more sources; b) t = 25 °C, if not stated otherwise; c) acetate, (1–); d) tartrate (2–), for antimony as adduct $Sb_2(tartrate)_2$ in equilibria with H^+ + tartaric acid + $Sb(OH)_3$, according to [38]); e) citrate, (3–); f) ethylenediaminetetraacetates, (3–) and (2–); g) adduct SbY + ethylenediaminetetraacetate + $Sb(OH)_3$ [38]; h) values obtained at higher ionic strength, I_i; i) moderately stable, structure according to [40,41]; j) structure and data according to [42]); k) moderately stable, according to [43,44]; l,m) minor mentions in [45] and [46] ; n) unclear structure, possible adducts $Me(OH)_3\times n\ H_2O$, $Me(OH)_3$ + MeO(OH) etc.; o) insoluble in water due to the formation of polymeric aggregates of the $(MeF_3)_n$ type; p) sparingly soluble in acidic media, in pure water decomposes *via* hydrolysis to solid BiOBr; q) largely soluble in water (above 500 g l^{-1}); <) less than, ≈) around; both according to [38]; ?) approximate / uncertain data; ??) likely does not exist; --) not given; ...) not found to that, also electroanalysis with BiFEs and SbFEs does not comprise to date any report concerning the use of a system with fluoride [1,8].

By going deeper into the databases comprising also local publications, one can find one mention on a 0.2 M AcB + 0.1 M KF mixture [26] tested without a notable success for separation of Cd, Pb, and In by means of their stripping peaks.

Thus, herein we describe the first experience with the effect of this halide, whose compounds — namely: NH_4BiF_4, BiF_3, and SbF_3 — are already in the centre of interest in our current investigations [47-49] on new types of bulk modifiers — as a stable and very effective source of metallic bismuth and antimony in the respective carbon-paste configurations. Regarding this study and the F^- species, its behaviour was observed in a series of mixed solutions at varied concentrations (in an interval from 1×10^{-5} up to 0.1 M F^-); some typical results are illustrated in Figs 3 and 4.

Figure 3 shows a first interesting effect, when a certain concentration of fluoride has resulted in evident decrease of the dissolution peak of Bi at the BiF/CPE and its response become particularly small for higher concentration level of the co-deposited ions — Cd^{II} and Pb^{II} whose peaks are developed normally, however (see curve “c”). Such a decrease has already been described for the SbFE counterparts [9,10], but not for a bismuth-based electrode [4-7]. By optimising the most effective content of fluoride in the supporting medium (for details, see Ref. [28]), it has been ascertained that the smallest Bi-peaks was obtained in solutions containing 0.001 up to 0.01 M F^-. (Higher concentrations already led to undesirable deformations of signals for both model ions, as well as of the Bi-peak itself, very high concentrations of fluoride, $c(F^-) > 0.1$ mol l^{-1} then caused the split of the latter into two separate peaks.)

Comparable relations were also found for the behaviour of SbF-CPE in the fluoride-containing media, which is documented in Fig. 4, showing also an “amplifying effect” of the fluoride at two different concentrations with respect to the response for Cd and mainly for Pb. Again, the optimum was found out in the interval of 0.01-0.001 M F^- (see the set “A”), higher concentrations having led to various peak malformations (not shown), whilst lower concentrations had a lower amplifying effect (set “B”). Finally, as expected, the voltammograms obtained with SbF-CPE exhibited a large dissolution peak of Sb only in the blank solutions, whereas the addition of further metal ions and their co-deposition immediately led to abrupt decrease in the Sb-stripping signal [9,10].

Similarly as for the following complex-forming species, the most important effects and phenomena for F^- are summarised and discussed in Conclusion, often in confrontation with the data given in Table II, due to the finding that many observations shared related features and, apparently, also the same causes and consequences in the individual measurements.

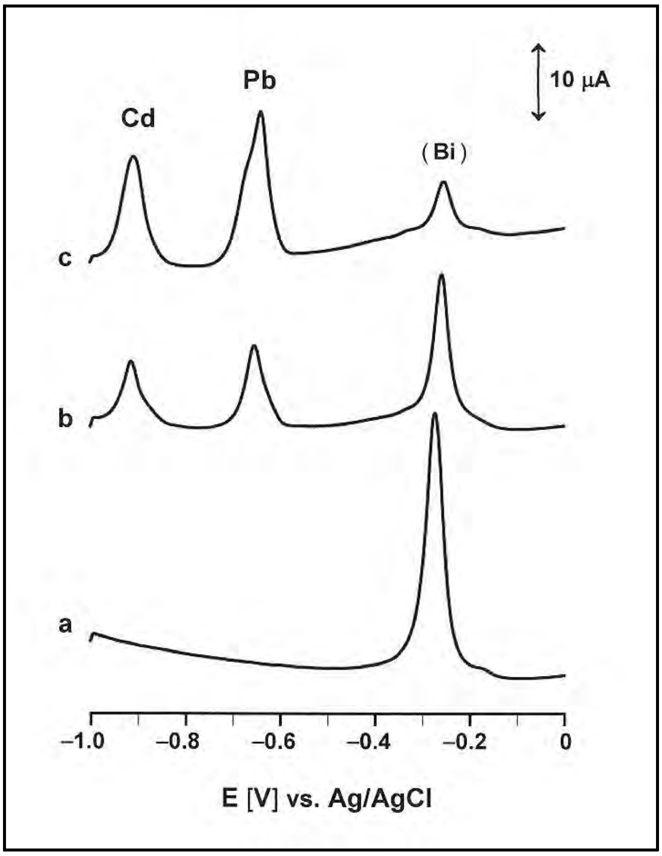

Fig. 3 Square-wave anodic stripping voltammetry of Cd^{II} and Pb^{II} at the BiF-CPE in the presence of fluoride anion. Legend: A) s.e.: 0.1 M AcB + 0.01 M NaF, B) 0.1 M NaCl + 0.01 M NaF; a) blank, b) 50 + 100, c) 100 ppb Cd + 200 ppb Pb. Experimental conditions: see Fig. 1

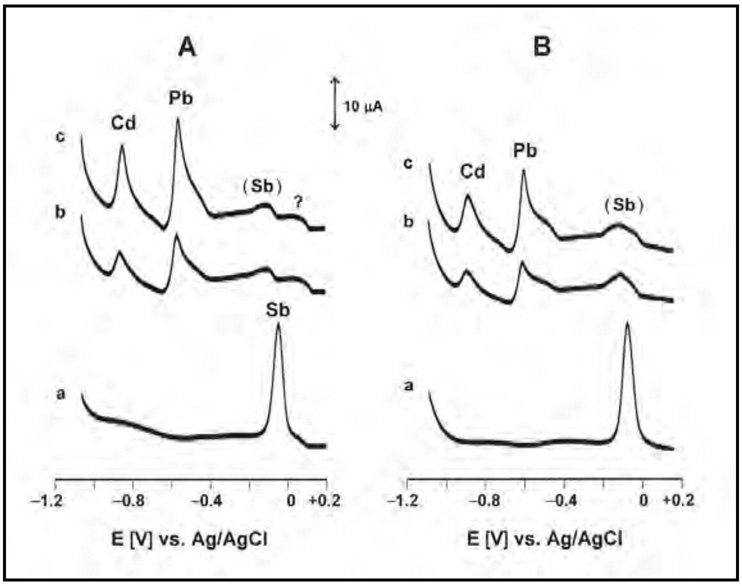

Fig. 4 Square-wave anodic stripping voltammetry of Cd^{II} and Pb^{II} at the SbF-CPE in the presence of fluoride anion. Legend: A) s.e.: 0.01 M HCl + 0.01 M NaF, B) 0.01 M HCl + 1×10^{-5} M NaF; a-c) see Fig. 3. Experimental conditions: see Fig. 2

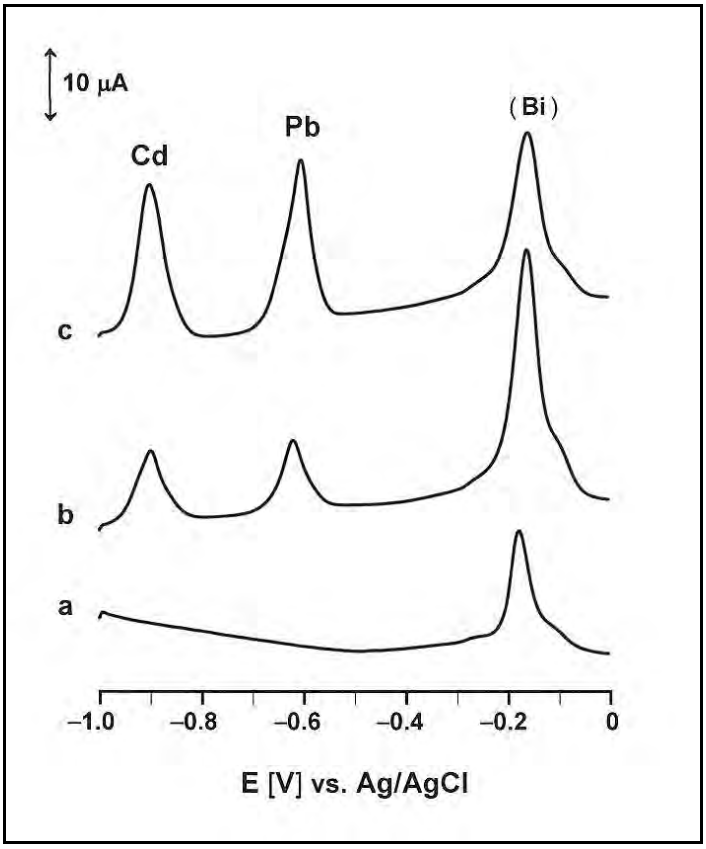

Fig. 5 Square-wave anodic stripping voltammetry of Cd^{II} and Pb^{II} at the BiF-CPE in chloride-based medium. Legend: a-c) see Fig. 3. Experimental conditions: s.e.: 0.1 M NaCl (pH 6.02); for other parameters, see Fig. 1

Chloride, Cl^-: By pursuing some previous studies [21,27], very fine voltammetric records could be obtained with the BiF-CPE in neutral solutions of 0.1 M NaCl whose slightly acidic pH was due to the spike with acidified Bi^{III} ions.
As documented in Fig. 5, also chloride has somewhat equilibrated the different sensitivity towards Cd and Pb (compared to, e.g., equally concentrated acetate buffer); nevertheless, still not enabling the complete equivalence (see legend and the double concentrations of Cd^{2+} with respect to Pb^{2+} ions.)

Finally, in the presence of the Cl^-, a certain decrease in the dissolution Bi-peak can be noticed (see curves “b” and “c”), but the whole effect was less pronounced compared to assays with the F^- ion. Otherwise, the effect of chloride was not studied in more detail because its behaviour is relatively well-described thanks to two previous reports [9,10].

Bromide, Br^-: Also the behaviour of the third halide was mapped quite thoroughly: there are about ten contributions dealing with it (see Ref. [1] and refs therein). Besides pioneering investigations on the effect of Br^- upon the deposition process and the resultant morphology of the Bi-films (see, e.g., [23-25,50]) or some special studies with BiFEs in the framework of advanced optimisations in electrochemical stripping analysis [9,10,26,31], the bromide anion — when present in traces at a concentration of about 10 mM Br$^-$ — was found to ensure a noticeable improvement of the overall stripping process [51].

This is shown in Fig. 6, illustrating a text-book case of well-developed signals of interest, minimal background, as well as the stability of the dissolution

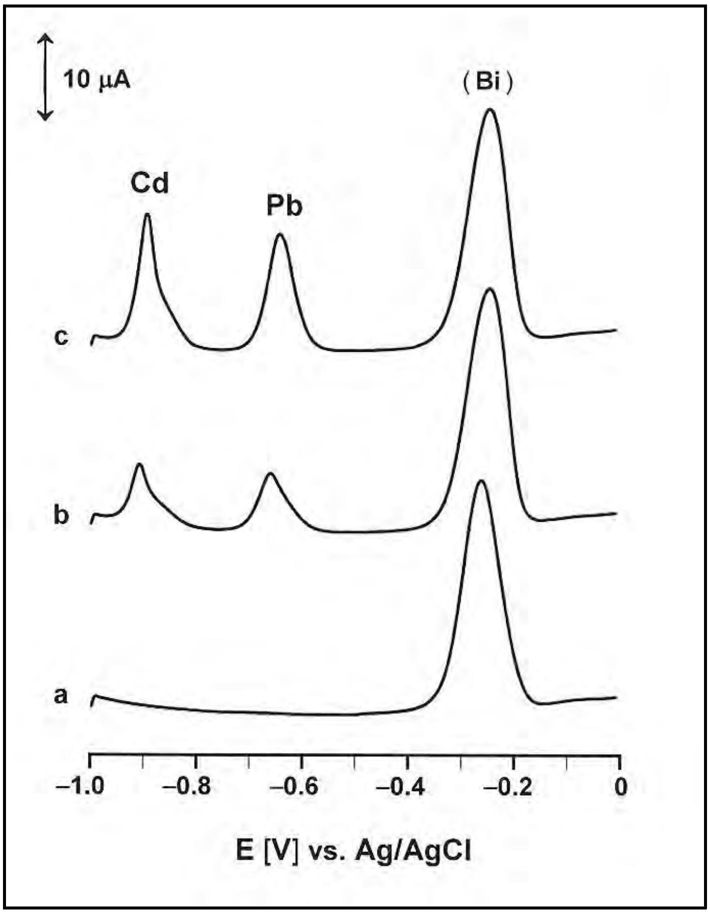

Fig. 6 Square-wave anodic stripping voltammetry of Cd^{II} and Pb^{II} at the BiF-CPE in the presence of bromide traces. Legend: a-c) see Fig. 3. Experimental conditions: s.e.: 0.1 M AcB + 1×10^{-5} M NaBr; for other parameters, see Fig. 1

Bi-peak (with no gradual increase that is so typical for re-oxidations of mercury films [12,15,52-53]).

Iodide, I$^-$: At both BiFEs and SbFEs, highly reactive iodide species, I$^-$ or I_3^- respectively, have hitherto been of interest in a microscopic study focused on the formation of the Bi-films in halide-based and complex-forming media [42], and in other two investigations concerning the simultaneous determination of heavy metals in various mixed media, including a solution of 0.2 M AcB + 0.1 M KI [26] or extraction of such metals with iodide prior to the subsequent detection at a BiFE [54]. And, in association with the Bi^{III} and Sb^{III} and their interactions with I$^-$ at a CPE, yet another report should be quoted [55], describing the voltammetric beha-

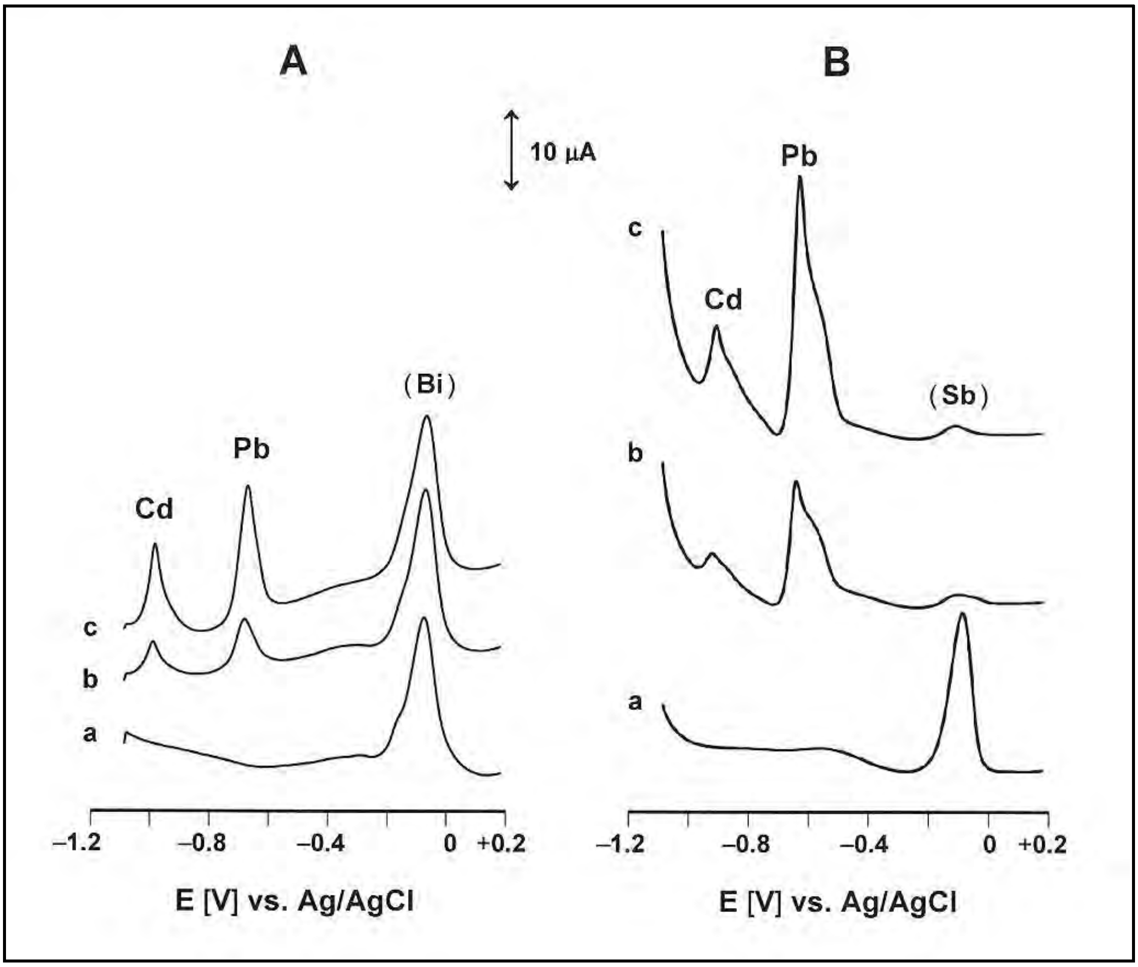

Fig. 7 Square-wave anodic stripping voltammetry of Cd^{II} and Pb^{II} at two non-mercury metal film electrodes in the presence of iodide. Legend: A) BiF-CPE, B) SbF-CPE; a-c) see Fig. 3. Experimental conditions: s.e.: 0.05 M NaCl + 0.05 M NaI (in both cases); for other parameters, see Figs 1 and 2

viour of the $[BiI_4]^-$ and $[SbI_4]^-$ complexes and their possible utilisation for differentiating of bismuth and antimony as electrochemically very similar metals.

Within this study, iodide has been undoubtedly one of the most efficient complex-forming species, which is also demonstrated in Fig. 7. In accordance with the effect of the remaining halides upon the sensitivity of both BiF-CPE and SbF-CPE towards Cd and Pb, iodide further amplified the signal of the latter, which is particularly evident in set “B”. This record is also notable for feasibility to employ the SbFE in nearly neutral solutions; i.e., at pH, when this electrode configuration cannot be normally operated [9,10].

Thus, by completing the observations with all the halides, it can be seen that the sensitivity of both film electrodes towards Cd and Pb mutually changes from a higher sensitivity for the first in favour of the second accordingly to an order of $F^- < Cl^- < Br^- < I^-$, resulting in the final stage, when the corresponding responses are comparably sensitive, or even better developed for lead. This undoubtedly reflects quite different stability of Cd^{II}- and Pb^{II}- complexes (or precipitates, respectively) formed with the individual halides — see data in Table II, as well as the discussion in Conclusion.

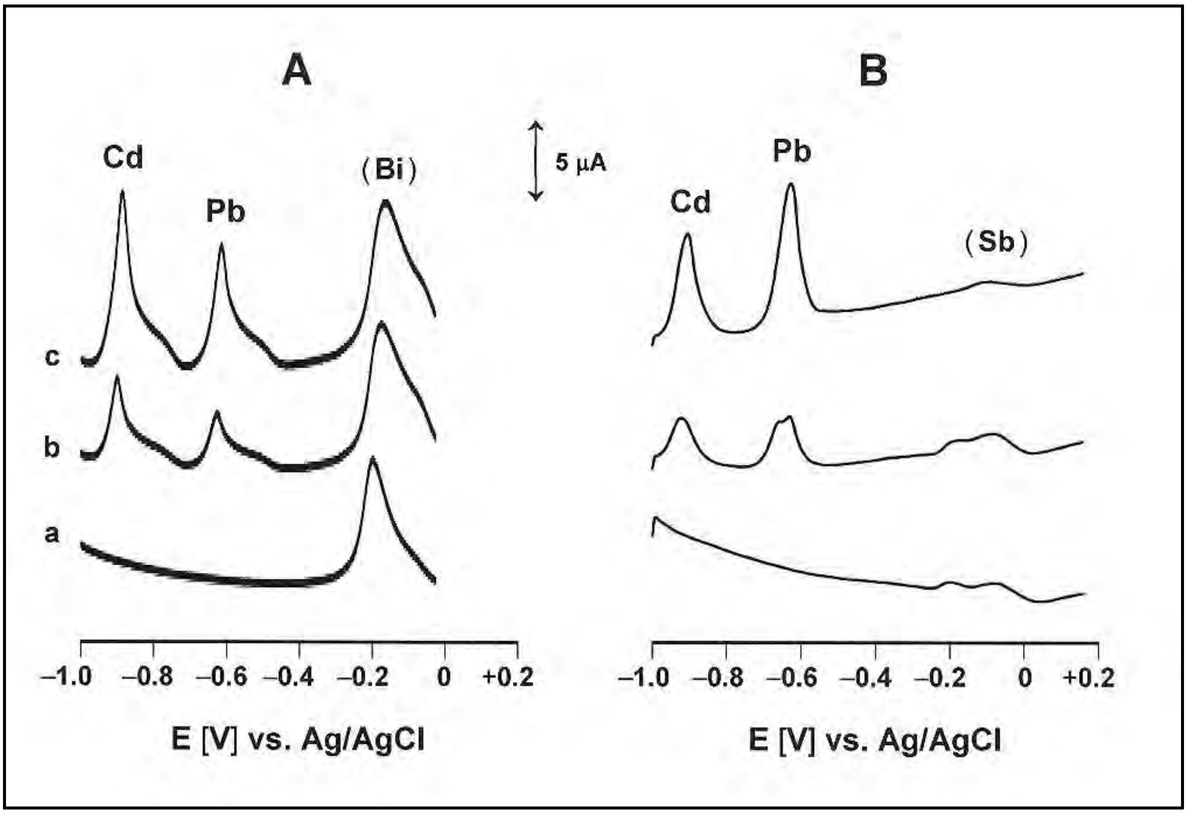

Fig. 8 Square-wave anodic stripping voltammetry of Cd^{II} and Pb^{II} at two metal film electrodes in the presence of thiocyanate. Legend: A) BiF-CPE, B) SbF-CPE; a-c) see Fig. 3. Experimental conditions: 0.05 M NaCl + 0.05 M NaSCN; for other parameters, see Figs 1 and 2

Effect of the Pseudohalides

Thiocyanate, SCN^-: Complexing capabilities of this anion are widely known and used for decades in both qualitative and quantitative analysis, but in electroanalysis with BiFEs and SbFEs they have been tested only seldom [26,31].

Figure 8 compares the performance of BiF-CPE (a set on the left) and its antimony analogue (right) showing an interesting difference between the sensitivity of both electrodes towards the two model heavy metals. In this case, this phenomenon can be explained by a different stability of two related complex structures, $[BiI_4]^-$ and $[SbI_4]^-$ [38-40,55], whose formation codetermines the quality of the respective films and, subsequently, the pathway of both deposition and stripping processes.

Concerning the dissolution of Bi and Sb, the effect of the SCN^- ion upon their peaks is quite specific — in both cases, the corresponding responses are stable and not changing size such extent as in the presence of genuine halides.

Last but not least, yet another benefit of SCN^- should be mentioned here although it cannot be seen in the figure. According to a recent observation [31], the presence of thiocyanate has only minor effect upon the signals for Cd and Pb, but amplifies profoundly the re-oxidation peak of zinc whose response at comparable concentrations is much smaller and badly developed. In this case, the reason might be the specific behaviour of the $[Zn(SCN)_4]^{2-}$ species compared to similar structures with Cd^{II} and Pb^{II} atoms; namely, the strong affinity of zinc(II)-thiocyanate complex towards the electrode surface and its enhanced accumulation under the experimental conditions used.

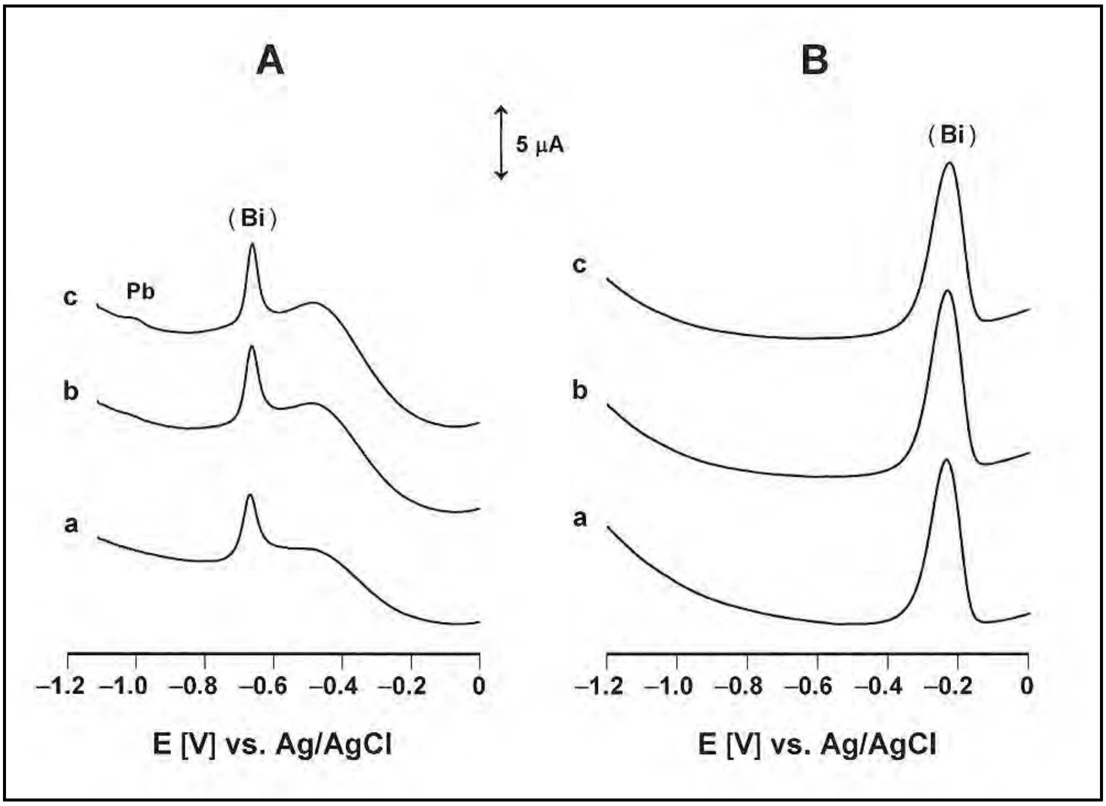

Fig. 9 Square-wave anodic stripping voltammetry of Cd^{II} and Pb^{II} at BiF-CPE in solutions with particularly strong complexants. Legend: A) with cyanide, using 0.1 M NaOH + 0.01 M NaCN (pH 12.45); B) with a chelating agent, 0.1 M AcB + 0.001 M EDTA (pH 4.20); a-c) see Fig. 3. Experimental conditions: see Figs 1 and 2

Cyanate, CNO^- and Cyanide, CN^-: The applicability of these two anions in analytical chemistry is of rather special character. In particular, this is the case of cyanide whose capabilities to form very stable complexes are well known and utilised for the total masking of various interfering ions (Cu^{2+}, Fe^{3+}, Al^{3+}, Ca^{2+}, *etc.* [37]). Nonetheless, electroanalysis with BiFEs and SbFEs practically did not offer any attempt of this kind; except a lone assay with CNO^- as a constituent of mixed AcB-based media [26], exhibiting no notable effect.

Nearly the same statement can also be made for the experiments carried out within this study: there have been only insignificant nuances in amplifying the signal(s) of interest and changes in sensitivity or suppressing the dissolution peaks of Bi and Sb with the surrounding background. Regarding CN^-, it could be effective for Cd and Pb, as seen in Fig. 9A on a marked shift and practical disappearance of both peaks within the operational potentials.

Herein, however, one can hardly distinguish between the effect of CN^- and of the OH^- ions, the latter being present in model solutions at a large concentration excess (to keep the cyanide in the ionic form) and having itself sufficiently strong complex-forming capabilities [14-16], which can also be illustrated by the respective data in Table II. Also, a notable shift in the dissolution signal of Bi (from ca. –0.3 V to –0.7 V vs. ref.) speaks in favour of hydroxo complex; especially, if one compares voltammograms in Fig. 9A with those obtained in pure 0.1 M NaOH (shown in Ref. [30] and exhibiting comparably deformed, parabolic base-line). Moreover, an anticipated reaction of NaCN with trivalent bismuth in alkaline media is unlikely due to the immediate hydrolysis of Bi^{III} to $Bi(OH)_3$ — or related products like $BiO(OH)$ and $Bi_2O_3 \times n\ H_2O$ [37,38] — with tendency to be readily converted into the $Bi(OH)_4^-$ as well as some polynuclear structures of the $[Bi_n(OH)_m]^{(m-n)+}$ type (see Table II and [14,16,38]).

In any case, within all stripping voltammetric experiments performed, each complexed form of Cd^{II} and Pb^{II} on one side and Bi^{III} on the other is reduced and re-oxidised less willingly than the single (non-complexed) ions and the above-mentioned shift is then a way of visualisation for such difference, fulfilling the relation that the more stable complex, the more pronounced shift towards the negative potentials [12]. Finally, it should be stated that the whole assay in Fig. 9A could be performed solely with BiF-CPE which — in contrast to SbF-CPE — might be operated in solutions of diluted hydroxides via the $Bi(OH)_3 \rightleftharpoons Bi(OH)_4^-$ equilibrium and a fair solubility of the latter complex in aqueous solutions.

Note: *Azide,* N_3^-, and *Isocyanate, OCN⁻*, complete the group of classic pseudohalides [38,56] and the corresponding assays were also considered. However, the experimentation with both N_3^- and OCN^- anions was abandoned for safety reasons — due to possible precipitation of highly explosive $Pb(N_3)_2$ ([57] and Table II) or even $Pb(ONC)_2$ (similarly dangerous *fulminate* [58] formed by intramolecular conversion of lead isocyanate) during the preparation and manipulation of model solutions with the respective ions.

Effect of EDTA and Selected Organic Anions

EDTA, $C_{10}H_{14}N_2O_8^{2-}$: One of the most efficient complex-forming reagents [37,38] was tested more or less to complete the study and to check the functioning of the systems studied. As expected, the effect of EDTA was almost absolute for both

Cd^{2+} and Pb^{2+} ions, forming highly stable and electroinactive complexes under the conditions chosen (see also Table II), when none of the voltammograms exhibited any responses of these metals (Fig. 9B). Large and almost constant peaks of bismuth can then be attributed to the response of non-complexed Bi^{III} as there is no evident shift towards less positive potentials (compare Figs. 9A, 9B, and any other one depicted above and showing measurements with BiF-CPE).

The reason for such assumption is that, in the model media of 0.1 M AcB + 0.001 M EDTA with 5×10^{-5} M Bi^{3+} (for *in-situ* deposition), the bismuth(III) species were present at a rather high concentration and hence, they might not be fully chelated; see [38] and equilibria diagrams inside, as well as an earlier report [59] with related considerations and calculations.

Tartrate, $C_4H_4O_6^{2-}$*, and citrate,* $C_6H_5O_7^{3-}$: In contrast to nearly non-complexing acetate [35] which represents an essential constituent for supporting electrolytes used in combination with BiFEs [1-7], the title anions of other two weak organic acids may provide interesting results if being mixed with suitable components and at appropriate pH [26,29,37].

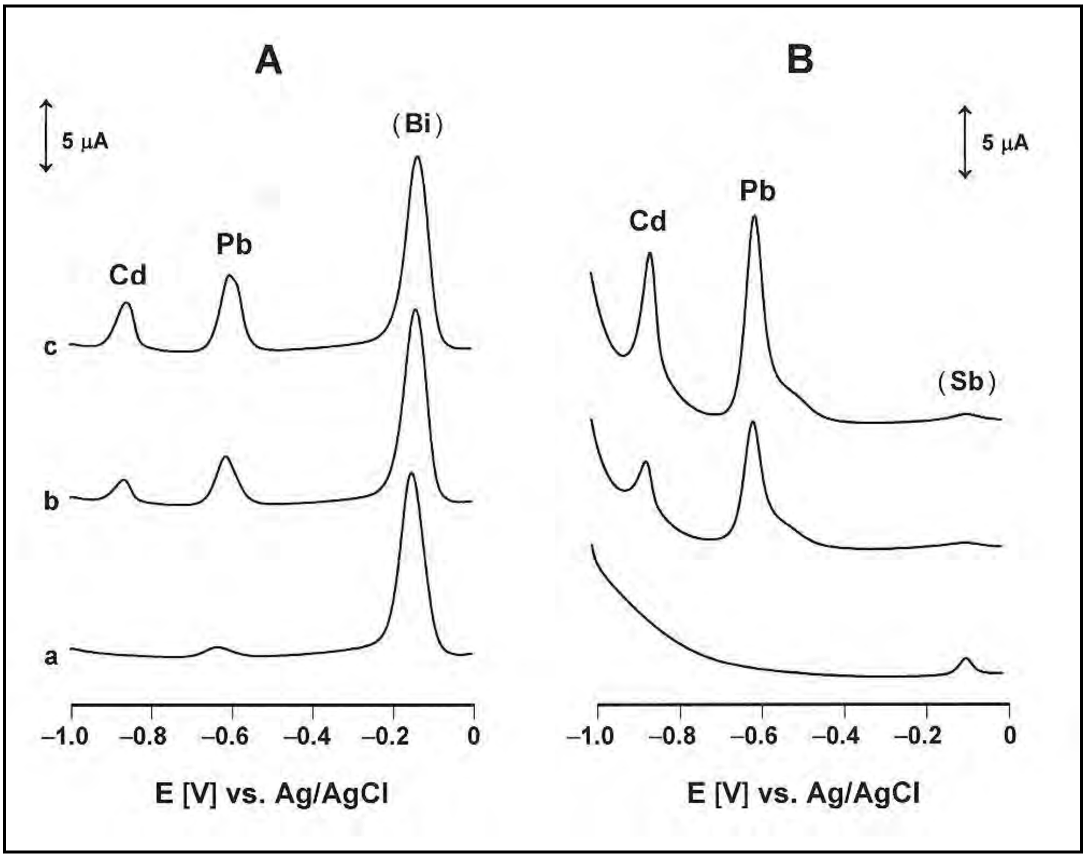

Fig. 10 Square-wave anodic stripping voltammetry of Cd^{II} and Pb^{II} at two metal film electrodes in acidic media with dihydrogen citrate. Legend: A) BiF-CPE, B) SbF-CPE; a-c) see Fig. 3. Experimental conditions: 0.05 M $HClO_4$ + 0.001 M $NaH_2C_6H_5O_7$ (pH 1.03); for other parameters, see Figs 1 and 2

In this study, possible benefits of adding tatrate or citrate into the model solutions have resulted in a triple effect, which is illustrated by Fig. 10 in both sets “A” and “B”. Namely, in acidic media with dihydrogen citrate, one can highlight: (i) a very good separation of both signals of interest — see the mutual position of Cd- and Pb-peaks and compare their peak potentials, E_P(Me), with those obtained in the presence of common halides (Figs. 3-7); (ii) the overall shape and mutual size of all stripping signals; (iii) particularly smooth base-line for both BiF-CPE and SbF-CPE, when the choice of the same supporting electrolyte enabled to attain somewhat lower cathodic limit for the latter (see curvature of the base-line in set “B”). Similar observations were also made with analogous media with tartrate, except for the base-lines at BiF-CPE and SbF-CPE, showing minor deformations (not shown).

Although the individual effects described under points (i-iii) were not so pronounced like those for halides or thiocyanate, their fine constellation has made the citrate moiety quite attractive for further studies, expanding the hitherto very basic knowledge [28,29].

Conclusion

In this article, a new study based on the results of a recent diploma thesis [28] and arranged as continuation of our previous investigations [14-16,26,31] is presented, concerning the possibilities and limitations of some complex-forming reagents in stripping voltammetry with BiFEs and SbFEs, contributing thus to the further characterisation of these at present very popular non-mercury and metal-based electrodes.

As shown above, the experimentation with both BiF-CPE and SbF-CPE in a variety of solutions with halides and pseudohalides, as well as some organic anions, has shared a number of similarities, allowing us to postulate some relations, trends, and typical features that characterise the employment of such solutions as the supporting media of choice. The individual observations and results can be summarized in the following points:

(I) Apparently, the most notable phenomenon during testing the complex-forming agents was their effect on the *sensitivity* of the two metallic film electrodes with respect to both model ions tested; in other words; upon the *mutual size* of Cd- and Pb-peaks. This was most evident for mixed solutions with iodide, to a lesser extent for bromide, chloride, and thiocyanate; usually, being more pronounced for the SbF-CPE. When looking for the proper interpretation, there are two possible processes and their relevance for the particular constellation; both have theoretical background in chemical equilibria expressed by the respective constants in Table II.

Firstly, it is a highly complexing capacity of iodide being in favour of lead, which would give rise to a corresponding shift of its peak towards more negative potentials. As seen, this effect is negligible, compared to, e.g., cyanide, hydroxide, or EDTA. Secondly, it is a completely different solubility of the two iodides, $\mathrm{CdI_2}$ and $\mathrm{PbI_2}$, whose formation and existence in model solutions can be assumed.

The latter is insoluble (with $K_S(\mathrm{PbI_2}) = 7.1\times10^{-9}$) and hence, it is possible that this precipitate is accumulated at the electrode surface more effectively than the single Cd^{2+} ions

$$\mathrm{Pb}^{2+} + 2\mathrm{I}^- \rightarrow \mathrm{PbI}_2\downarrow \qquad x\mathrm{PbI}_2 + 2e^- + y\mathrm{Me} \rightarrow \mathrm{Pb}_x\mathrm{Me}_y + 2\mathrm{I}^- \qquad (1a, b)$$

$$(\mathrm{Cd}^{2+} + 2\mathrm{I}^-) \qquad x\mathrm{Cd}^{2+} + 2e^- + y\mathrm{Me} \rightarrow \mathrm{Cd}_x\mathrm{Me}_y \qquad (2a, b)$$

where "Me" is Bi or Sb, and "$\mathrm{Pb}_x\mathrm{Me}_y$" is the respective fused alloy [4-6,60]. The resultant effect is a proportionally larger response for Pb compared to Cd (see Figs 7 A, B). Herein, it should be stated that such hypothesis is not new and similarly improved accumulation was, e.g., the case of electrolytic deposition of silver in the presence of anionic surfactant enhancing the transport of the Ag^+ ions *via* the respective ion-pairs [61].

Otherwise, the changes in the overall sensitivity of either BiF-CPE or SbF-CPE towards cadmium and lead seem to have some promise for controlling the selectivity at both electrodes in practical measurements. However, similar approaches will have a limited use only due to the considerable chemical reactivity of most of halides and pseudohalides.

(II) Surprisingly, another output that was to come from the assays with various supporting media — the effect of some constituents upon the overall resolution of the signals of interest [4-6,12]; i.e., the respective $E_P(\mathrm{Cd})$, $E_P(\mathrm{Pb})$ and the resultant ΔE_P — has been mostly negligible, except the use of solutions with hydroxide. In such media, the marked difference in stability between the corresponding complexes (see Table II and values $\beta\ \mathrm{Cd(OH)}_4^{2-} = 4.9\times10^8$ *vs.* $\beta\ \mathrm{Pb(OH)}_4^{2-} = 1.2\times10^{32}$) is reflected in substantial shift of Pb-peak and in the reversed order for re-oxidation of both metals during anodic scanning. This phenomenon (pictured on fine voltammograms in [14] and [28]) can be expressed by simple relation "$E_P(\mathrm{Pb}) < E_P(\mathrm{Cd})$" and corresponds to quite curious situation, when electrochemically nobler lead is stripped off earlier than cadmium [6,16].

For the halides and pseudohalides tested in this study, the overall resolution was nearly the same, with $\Delta E_P = |\mathrm{E_P}(\mathrm{Cd})| - |E_P(\mathrm{Pb})|$ varying within 25-30 mV. Slightly better resolution could then be evaluated for measurements in the presence of tartrate and citrate, the respective values of ΔE_P reaching even above 30 mV (for both anions).

(III) Another benefit from the use of some complex-forming reagents in the supporting media is a *suppression of the large dissolution (stripping) peak of bismuth* in measurements with a BiFE. (In the case of its antimony counterparts, this effect is irrelevant as the stripping voltammograms obtained with SbFEs comprise only very small re-oxidation responses.) The suppression of Bi-peak was most effective with fluoride at a concentration level of about 0.05 M F^-. With respect to the chemistry behind, it can be deemed that a probable transformation into insoluble bismuth fluoride, BiF_3, could be a rational explanation

$$Bi^{3+} + 3F^- \rightarrow BiF_3\downarrow \qquad (BiF_3 + F^- \rightarrow BiF_4^-) \qquad (3a, b)$$

because the subsequent complexation (3b) into water-soluble and re-oxidisable BiF_4^- is improbable due to a very low stability of this complex species (see again Table II). The suppression of large dissolution peak attainable by F^- is significant mainly with respect to "smoothing" the base-line around the anodic potential limit, which may, e.g., be crucial for the successful determination of Cd^{2+}, Pb^{2+} together with Cu^{2+} [29,62-66]; the latter representing maybe the most frequent heavy metal in real samples [12,52,53].

Herein, it can be stated that practical applicability of media with F^- appears to be quite attractive; especially, when electroanalysis with BiFEs and SbFEs is still an unexplored area [1,4-7]. For example, in samples of natural waters and soils, the presence of fluoride could be advantageous for masking Fe^{III}, Co^{II}, and Ni^{II}; however, after having controlled undesirable precipitation of CaF_2 in water with higher hardness or some calcite-based samples.

(IV) Besides halides and pseudohalides, the study included also EDTA and two organic anions. Whereas the former has confirmed to be an unrivalled chelating agent, useful, e.g., for the determination of Tl^+ in the presence of other heavy metal ions [29,66-68], both tartrate and citrate have been shown to provide fair supporting media with the most favourable signal-to-noise characteristics with particularly smooth base-line over the whole potential range of interest. For either BiFEs or SbFEs, these features can be of principal importance in practical measurements, if one takes into account the actual current intensities for extremely low concentrations, dropping down to the nA level or even below.

(V) Last but not least, the experiments highlighted and commented in previous paragraphs have also some value from an inspiration point of view, showing that the classical chemical reactions can suitably be combined with the latest achievements in instrumental analysis, among which *electroanalysis with BiFEs and SbFEs* occupies at present a highly respectable position [1,69-70].

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References

[1] Švancara I., Prior C., Hočevar S.B., Wang J.: Electroanalysis **22**, 1405 (2010).

[2] Wang J., Lu J.-M., Hočevar, S.B., Farias, P.A.M., Ogorevc B.: Anal. Chem. **72**, 3218, (2000).

[3] Królicka A., Pauliukaitë R., Švancara I., Metelka R., Norkus E., Bobrowski A., Kalcher K., Vytřas K.: Electrochem. Commun. **4**, 193, (2002).

[4] Wang J.: Electroanalysis **17**, 1341 (2005).

[5] Economou A.: TrAC – Trends Anal. Chem. **24**, 334 (2005).

[6] Švancara I., Vytřas K: Chem. Listy **100**, 90 (2006).

[7] Kokkinos C., Economou A.: Curr. Anal. Chem. **4**, 183 (2008).

[8] http://thomsonreuters.com/products_services/science/science_products/a-z/web_of_science/; dowloaded on Aug. 30 (2011).

[9] Hočevar S. B., Švancara I., Ogorevc B., Vytřas K.: Anal. Chem. **79**, 8639 (2007).

[10] Švancara I., Hočevar S. B., Baldrianová L., Tesařová E., Vytřas K.: Sci. Pap. Univ. Pardubice, Ser. A **13**, 5 (2007).

[11] Heyrovský J., Kůta J.: *Principles of Polarography*, Academic Press, New York, 1966.

[12] Wang J.: *Stripping Analysis: Principles, Instrumentation, and Applications*, VCH Publ., Deerfield Beach, 1985.

[13] Barek J., Fogg A.G., Muck A., Zima J.: Crit. Rev. Anal. Chem. **31**, 291 (2001).

[14] Elsuccary S.A.A., Švancara I., Metelka R., Baldrianová L., Hassouna M.E.M., Vytřas K.: Sci. Pap. Univ. Pardubice, Ser. A **9**, 5 (2003).

[15] Švancara I., Fairouz M., Ismail Kh., Metelka R., Vytřas K.: Sci. Pap. Univ. Pardubice, Ser. A **9**, 31 (2003).

[16] Švancara I., Baldrianová L., Tesařová E., Hočevar S.B., Elsuccary S.A.A., Economou A., Sotiropoulos S., Ogorevc B., Vytřas K.: Electroanalysis **18**, 177 (2006).

[17] Wang J., Lu J.-M.: Electrochem. Commun. **2**, 390 (2000).

[18] Hutton E.A., Hočevar S.B., Ogorevc B., Smyth M.R.: Electrochem. Commun. **5**, 765 (2003).

[19] Švancara I., Baldrianová L., Tesařová E., Mikysek T., Vytřas K.: Sci. Pap. Univ. Pardubice, Ser. A **12**, 5 (2006).

[20] Lee G.-J., Lee H.-M., Uhm Y.-R., Lee M.-K., Rhee C.-K.: Electrochem. Commun. **10**, 1920, (2008).

[21] Vytřas K., Švancara I., Metelka R.: Electroanalysis **14**, 1359 (2002).

[22] Prior C., Walker G.S.: Electroanalysis **18**, 823 (2006).

[23] Królicka A., Bobrowski A., Kalcher K., Mocák J., Švancara I., Vytřas K.: Electroanalysis **15**, 1859 (2003).

[24] Guzsvány V., Kádár M., Gaál F., Bjelica L., Tóth K.: Electroanalysis **18**,

1363 (2006).

[25] Grincienė G., Selskienė A., Verbicka R., Norkus E., Pauliukaitė R.: Electroanalysis **21**, 1743 (2009).

[26] Tesařová E., Baldrianová L., Królicka A., Švancara I., Bobrowski A., Vytřas K.; in: *Sensing in Electroanalysis* (Vytřas K., Kalcher K., Eds.), pp. 75-87. Univ. Pardubice Press, Pardubice, 2005.

[27] Tesařová E., Vytřas K.: Electroanalysis **21**, 1075 (2009).

[28] Bartoš K.: *Deposition of the Bismuth and Antimony Films from Atypical Solutions with Possible Applicability in Electroanalysis*, Diploma Thesis (MSc), The University of Pardubice Press, Pardubice, 2010.

[29] Putek M., Bobrowski , Zarebski J.; in: *YISAC '11: 18th Young Investigators' Seminar on Analytical Chemistry,* Book of Abstracts, p.14. University of Novi Sad, 2011.

[30] Guzsvány V., Nakajima H., Soh N., Nakano K., Imato T.: Anal. Chim. Acta **658**, 12 (2010).

[31] Guzsvány V., Nakajima H., Soh N., Nakano K., Švancara I., Imato T.: Sci. Pap. Univ. Pardubice, Ser. A **16**, 19 (2010).

[32] Guzsvány V., Nakajima H., Soh N., Nakano K., Švancara I., Vytřas K., Bjelica L., Imato T.: Electroanalysis **23**, 1593 (2011).

[33] Švancara I., Schachl K.: Chem. Listy **93**, 490 (1999).

[34] Švancara I., Metelka R., Vytřas K.; in: *Sensing in Electroanalysis* (Vytřas K., Kalcher K., Eds.), pp. 7-18. University of Pardubice, Pardubice, 2005.

[35] Kalcher K., Švancara I., Metelka R., Vytřas K., Walcarius A.; in: *Encyclopedia of Sensors,* Vol. 4 (Grimes C.A., Dickey E.C., Pishko M.V., Eds.), pp. 283-430. ASP - American Scientific Publishers, Stevenson Ranch, 2006.

[36] Mikysek T., Švancara I., Bartoš M., Kalcher K., Vytřas K., Ludvík J.: Anal. Chem. **81**, 6327 (2009).

[37] Svehla Gy: *Vogel's Qualitative Inorganic Analysis*, 7th Rev. & Exp. Ed. Longman, Singapore, 1996.

[38] Kotrlý S., Šůcha L.: *Handbook of Chemical Equilibria in Analytical Chemistry*: *Tables and Diagrams*. Ellis Horwood, Chichester, 1985.

[39] Lide D.R. (Ed.): *CRC Handbook of Chemistry and Physics*, 85th Ed. (2004/2005), CRC Press, Boca Raton, 2004.

[40] http://www.csudh.edu/oliver/chemdata/data-ksp.htm; accessed: Sept 15 (2011).

[41] Lever M.: Anal. Biochem. **81**, 21 (1977).

[42] Sadler P.J., Guo Z-J.: Pure Appl. Chem. **70**, 863 (1998).

[43] Afkhami A., Zarei A.R.: Anal. Sci. (Japan) **19**, 917 (2003).

[44] Mostafa G.A.E.: Talanta **71**, 1449 (2007).

[45] Verplaetse H., Kiekens P., Temmerman E., Verbeek F.: Talanta **28**, 431 (1981).

[46] Sun H.-Z., Yan S.-C., Cheng W.-S.: Eur. J. Biochem. **267**, 5450 (2000).

[47] Sopha H., Baldrianová L., Tesařová E., Grincienė G., Weidlich T., Švancara I., Hočevar S.B.: Electroanalysis **22**, 1489 (2010).

[48] Stočes M., Švancara I.; in: *YISAC '11: 18th Young Investigators' Seminar on Analytical Chemistry*, Book of Abstracts, p. 9. Univ. Novi Sad Press, 2011.

[49] Stočes M., Švancara I., Vytřas K.; in: *Sensing in Electroanalysis*, Vol. 6 (Vytřas K., Kalcher K., Švancara I.; Eds.), pp. 205-218, University of Pardubice Press, Pardubice, 2011.

[50] Švancara I., Baldrianová L., Vlček M., Metelka R., Vytřas K.: Electroanalysis **17**, 120 (2005).

[51] Hočevar S. B., Daniele S., Bragato C., Ogorevc B.: Electrochim. Acta **53**, 555 (2007).

[52] Švancara, I. Kalcher K., Vytřas K.: Sci. Pap. Univ. Pardubice, Ser. A **3**, 207 (1997).

[53] Economou E., Fielden P.R.: Analyst (U.K.) **128**, 205 (2003).

[54] Kamio A., Nagaosa Y.: Anal. Sci. (Japan) **24**, 1363 (2008).

[55] Švancara I., Vytřas K.: Anal. Chim. Acta **273**, 195 (1993).

[56] Holub A.M., Kohler H., Skopenko V.V. (Eds.): *The Chemistry of Pseudohalides (Topics in Inorganic and General Chemistry)*, Elsevier Sci., New York, 2000.

[57] Akhavan J.: *The Chemistry of Explosives*, 2nd Ed. RSC Paperbacks, Cambridge, 2001.

[58] Mishra B., Raraz A.G., Olson D.L., Averill W.A.: J. Hazard. Mater. **56**, 107 (1997).

[59] Švancara I., Ostapczuk P., Arunachalam J., Emons H.,Vytřas K.: Electroanalysis **9**, 26 (1997).

[60] Krueger J., Winkler P., Luederitz E., Lueck M.; in: *Ullman's Encyclopedia of Industrial Technology*, Vol. A 4 (W. Gerhartz, Ed.), pp. 171-189. VCH, Weinheim, 1985.

[61] Švancara I., Kalcher K., Diewald K., Vytřas K.: Electroanalysis **8**, 336 (1996).

[62] Vytřas K., Baldrianová L., Tesařová E., Bobrowski A., Švancara I.; in: *Sensing in Electroanalysis* (Vytřas K., Kalcher K.; Eds.), pp. 49-58. The University of Pardubice, Pardubice, 2005.

[63] Prior C., Lenehan C.E., Walker G.S.: Electroanalysis B, 2486 (2006).

[64] De Carvalho L.M., do Nascimento P.C., Koschinsky A., Bau M., Stefanello R.F., Spengler C., Bohrer D., Jost C.: Electroanalysis **19**, 1719 (2007).

[65] Pacheco W.F., Miguel E.M., Ramos G.V., Cardoso C.E., Farias P.A.M., Aucélio R.Q.: Anal. Chim. Acta **625**, 22 (2008).

[66] Slavec M., Hočevar S.B., Baldrianová L., Tesařová E., Švancara I., Ogorevc B., Vytřas K.: Electroanalysis **22**, 1617 (2010).

[67] Lee G.-J., Lee H.-M., Uhm Y.-R., Lee M.-K., Rhee C.-K.: Electrochem.

Commun. **10**, 1920 (2008).
[68] Kokkinos C., Raptis I., Economou A., Speliotis T.: Electroanalysis **22**, 2359 (2010).
[69] Arduini F., Quintana Calvo J., Amine A., Palleschi G., Moscone D.: TrAC – Trends Anal. Chem. **29**, 1295 (2010).
[70] Hočevar S.B., Švancara I.: Electroanalysis **22**, 1399 (2010).