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A CONTRIBUTION TO THE CHARACTERISATION OF MERCURY- AND BISMUTH FILM CARBON PASTE ELECTRODES IN STRIPPING VOLTAMMETRY

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The results are summarised on the continuing characterisation of mercury- and bismuth-film-plated carbon paste electrodes for electrochemical stripping analysis in the differential pulse anodic stripping voltammetric (DPASV) mode. Both types of electrodes, denoted as MF(C/SO) and BiF(C/SO), were based on silicone oil-containing carbon paste support with the respective metal film plated "in situ". MF(C/SO) and BiF(C/SO) were first studied with respect to their polarisability in a variety of supporting electrolytes such as diluted mineral acids, some acidic or basic buffers, and highly alkaline media with sodium hydroxide. Stripping characteristics of numerous metals (Mn, Zn, Pb, Cd, Tl, Bi, Sb, In, Sn, and Cu) detectable using DPASV were also investigated. The whole study has provided some additional and supplementing information to the previous investigations on the two types of film plated carbon paste electrodes.

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Introduction

In electroanalysis, mercury film electrode (MFE [1]) is already for several decades used as a successful alternative to the mercury drop electrodes [2]. In combination with modern computer-controlled electrochemical stripping techniques, the MFE is one of the best detecting tools in trace analysis for the determination of heavy metals [3]. As supports for mercury films, commercially available glassy carbon electrodes (GCE) are usually being chosen [4]. Also hand-made carbon pastes may represent occasionally applicable substrates for mercury films [5–7]. As documented in some very recent papers [8,9], mercury-film-plated carbon paste electrodes still attract attention of electroanalysts emphasising a simple and quick surface renewal of carbon pastes in contrast to time consuming polishing procedures typical for GCE supports.

A new competitor to MFE and to mercury-based electrodes in general appeared a few years ago [10]. This type of electrode utilises a thin layer of bismuth — non-toxic and environmentally friendly metal — as the proper electrode material. Very promising results of two main electrochemical groups dealing with the research on bismuth film electrodes (BiFEs) [11–25] have soon inspired some other teams [26,27], contributing also to another popularisation of bismuth-film based electrodes. More recently, a first review paper appeared devoted exclusively to the topic [28].

This paper summarises some new results on the continuing research work on both mercury- and bismuth-film-plated carbon paste electrodes, MF(CPEs) and BiF(CPEs), respectively. Special attention has been paid to their polarisability in a variety of supporting electrolytes over a wide pH-interval as well as to the peak characteristics of almost all metals that can be accumulated and detected in the anodic stripping voltammetric mode at both types of film-plated CPEs. In this respect, this paper apparently represents the most comprehensive study of its kind at present.

Experimental

Chemicals and Reagents

All the chemicals used for the preparation of stock and standard solutions were of analytical reagent grade and purchased from Lachema (Brno, the Czech Republic) or Merck unless stated otherwise. The stock solutions serving to prepare the supporting electrolytes were made 1 mol l^{-1} in concentration, the standards of metal ions were prepared as 0.01 mol l^{-1}. Where needed, the corresponding solutions were diluted appropriately. All the solutions of diluted standards whose concentration was lower than 0.001 mol l^{-1} were always stabilised by acidifying

with a small amount of 65 % HNO_3 to yield pH ca 2. For some interference studies, the standard of Ga(III) was prepared by dissolving the adequate amount of metallic gallium in hot aqua regia.

Water used throughout the experimental work was obtained by passing deionised water through a laboratory-made glass distillation unit. All solutions to be analysed were deoxygenated by purging with argon (purity 99.99 %, Linde Technoplyn).

Apparatus and Instrumentation

A "PPA 02" polarographic analyser (Labio a.s., Prague, the Czech Republic) connected to a personal computer and controlled by a software in DOS operational system. This assembly was coupled with an external electrode stand (Laboratorní přístroje a.s., Prague) adapted for experimental work with a CPE in the three-electrode configuration. Stirring was performed with a Teflon® -coated magnetic bar (length, $l = 12$ mm, diameter, $\varnothing = 2$ mm) immersed in the solution and agitated by electromagnetic stirrer (mechanical workshops, the University of Pardubice) at approx. 300 rpm.

The pH was measured using a portable pH-meter (model "CPH 52", Elteca, Turnov, Czech Republic) equipped with a combined glass pH-sensor (model "OP-0808P", Radelkis, Budapest, Hungary). Ohmic resistance of newly made carbon pastes was checked with a Voltcraft® multimeter (model "VC 404", Conrad Electronics, Germany).

Electrodes

Carbon Paste Electrode. The carbon paste was prepared by intimately homogenising a mixture of 0.5 g spectroscopic graphite powder ("RW-B", Ringsdorff Werke, Germany) + 0.3 ml silicone oil ("Lukoil MV 15500"; Lučební závody Kolín, the Czech Republic) using a pestle and mortar. The ready-made paste was then packed into specially designed electrode holder equipped with a piston [29].

Reference and Auxiliary Electrodes. A self-made Ag/AgCl electrode (containing 3 M KCl as the inner electrolyte) as the reference and a Pt-plate (ca 0.5 cm^2) as the counter electrode completed the cell.

Procedures

Renewal of the Carbon Paste Electrode Surface. The surface of CPE was renewed by extrusion of approx. 0.5 mm carbon paste from the electrode holder, cutting off, and smoothing with a wet filter paper. Typically, such mechanical renewal was made only when starting a new series of experiments (e.g., prior to analysis of each new solution).

Preparation of Mercury Film-Plated Carbon Paste Electrode. Onto the CPE support, either mercury or bismuth film was deposited *in situ* when adding 0.01 M solution of the respective ion (made of nitrates: $Hg(NO_3)_2$ and $Bi(NO_3)_3$, respectively) into the supporting electrolyte. Its total concentration in the solution was chosen to be approx. one order higher than that of metal ions to be analysed [1,6]; typical concentration being 5×10^{-5} M Hg(II) or Bi(III) for determinations of metals at the micromolar level. The potential chosen for depositing of the film then corresponded to that used in the DPASV procedure.

Differential Pulse Anodic Stripping Voltammetry (DPASV). After preparation of the solution to be analysed and its deaeration with inert gas, the accumulation step ("preconcentration") was performed under stirring at selected accumulation potential, E_{ACC}, for a given period, t_{ACC}. After the equilibrium period, t_{EQ}, in quiet solution (usually for 15 s), the voltammetric measurement in the differential pulse mode was performed by anodic scanning from the E_{ACC} to a final potential, E_{FIN}. The individual stripping parameters are specified directly in Discussion. Regarding other conditions, typical scan rate was 20 mV s^{-1}, the pulse height, ΔE, –50 mV and 5 data s^{-1} as the sampling rate.

Data Processing and Evaluation

When using the PPA 02 software, the analytical signals were evaluated as the peak heights (via current intensities in μA) or as peak potentials (vs Ag/AgCl in volts) by manually fitting a tangent to the base of the peak.

Results and Discussion

Polarisability of MF(C/SO) and BiF(C/SO) in Various Supporting Electrolytes

In principle, polarisation capabilities of each working electrode in a supporting electrolyte are defined by its useful operational potential range ("potential window") where the analytical signal is significantly higher than that of the background [3,6]. The polarisability of any electrode is determined by the chemical composition and pH of the supporting medium together with the physico-

chemical character of the electrode material used. Another important aspect is the electrode configuration, which is the particular case of film-plated sensors. Regarding this type of electrodes, also the way of film plating is very important.

The definition of polarisability of both MF(CPEs) and BiF(CPEs) is still more complicated. Unique nature of carbon pastes, their laboratory preparation as well as possibilities to choose various compositions of carbon paste mixtures represent, in a sum, other factors that can be reflected in the resultant behaviour of a MF(CPE) or a BiF(CPE). Thus, their polarisation characteristics have to be defined *extra* via suitable testing measurements prior to use in practical electroanalysis [30].

Table I Potential limits and potential ranges in various supporting electrolytes. Characterisation of MF(CPE) and BiF(CPE)

Medium (supporting electrolyte)	pH (exp.)	MF(CPE)				BiF(CPE)				Notes
		E_1, V	E_2, V	ΔE, V	I_{BG}, μA	E_1, V	E_2, V	ΔE, V	I_{BG}, μA	1–3
0.1 M HCl	0.96	–1.15	+0.10	1.25	0.3	–1.05	–0.15	0.90	< 0.1	
0.1 M H_2SO_4	1.22	–1.20	+0.30	1.50	0.3	–1.20	–0.15	1.05	0.1	
0.1 M $HClO_4$	1.00	–1.00	+0.35	1.35	0.2	–1.05	–0.05	1.10	0.2	
0.1 M HNO_3	0.98	–1.10	+0.35	1.45	> 0.5	–1.05	–0.10	1.15	0.2	4
0.2 M acetate buffer	4.24	–1.30	+0.25	1.55	0.2	–1.25	–0.25	1.00	0.3	
0.2 M tartaric buffer	6.22	–1.35	+0.05	1.40	> 0.5	–1.30	–0.35	0.95	0.4	
0.2 M KCl	6.49	–1.60	+0.05	1.65	0.5	–1.45	–0.20	1.25	0.2	5
0.2 M phosphate buffer	7.03	–1.25	+0.20	1.45	.0.5	--	--	--	--	6
0.2 M borate buffer	8.60	–1.55	+0.15	1.70	0.1	--	--	--	--	6
0.2 M ammonia buffer	9.35	–1.55	–0.05	1.60	0.3	--	--	--	--	6
0.1 M NaOH	12.17	–1.50	-0.10	1.40	> 0.5	-1.55	-0.55	1.00	0.2	7

Experimental conditions: DPASV; initial potential, E_{INIT}, from –1.2 to –1.7 V; final potential, E_{FIN}, 0 - +0.5 V; accumulation time, t_{ACC} = 30 s, equilibrium period, t_{EQ} = 10 s, scan rate: 20 mV s^{-1}, pulse height: –50 mV.

Notes: 1) potential limit E_1 given by the background currents exceeding an arbitrary value of 1 μA (according to [30]); 2) limit E_2 determined by the position of Hg-peak or Bi-signal (evaluated as potential at the foot of the starting peak); 3) background currents estimated as the average within an interval $\Delta E \in (E_1, E_2)$; 4) at MF(CPE), another peak: E_P = –1.22 V; 5) at BiF(CPE), other two peaks: E_{P1} = –1.25 V, E_{P2} = +0.15 V; 6) bismuth film not formed (base-line without Bi-peak); 7) at BiF(CPE), very broad Bi-peak

In this work, the polarisabilities of both MF(CPEs) and BiF(CPEs) have been studied with carbon paste made of highly viscous silicone oil (C/SO) and plated *in situ* with the respective film, which is a combination used successfully in some previous investigations [5,6,20–22]. In order to evaluate the polarisation characteristics as generally as possible, a wide spectrum of supporting electrolytes was prepared. They covered practically the entire pH-interval ranging from highly acidic solutions of mineral acids to alkaline media of sodium hydroxide. The results of polarisation studies with both MF(C/SO) and BiF(C/SO) in eleven different supporting media are summarised in Table I.

Individual interpretations of experimental observations and the respective data given in the table can be formulated as follows:

(i) The most negative potentials (slightly beyond –1.5 V vs Ag/AgCl) attainable at MF(C/SO) were obtained in neutral or weakly basic media. At the same time, however, measurements in these media exhibited the highest background currents. When using BiF(C/SO), similar potential windows were achieved in a majority of the electrolytes tested. The most significant differences in behaviour of both electrodes under test were noticed in some "aggressive" electrolytes such as 0.1 M HNO_3 or 0.1 M NaOH. Whereas the MF(C/SO) could not be operated satisfactorily due to very high backgrounds, the BiF(C/SO) exhibited acceptable base-line. Potential applicability of the latter electrode in highly alkaline media was found to be rather attractive and inspired us to carry out a special study whose results are discussed in elsewhere [31].

(ii) Both film plated CPEs could be best anodised in perchloric and nitric acids. Due to lesser nobleness of metallic bismuth compared to mercury, the BiF(C/SO) exhibited considerably lower anodic limit compared to that of the MF(C/SO). As can be seen in Table I, the electrolytic dissolution of bismuth film in all supporting media selected have taken place still within the negative potential range.

(iii) The widest potential window of mercury film plated carbon paste was obtained in 0.2 M borate buffer reaching nearly 1.75 V vs Ag/AgCl. In the case of bismuth film counterpart, however, basic media like borate were inapplicable due to a hydrolysis of bismuth film (see Notes). Thus, with the BiF(C/SO), the widest polarisability of about 1.25 V was ascertained in neutral solution such as 0.2 M KCl.

With respect to residual currents within the potential range of interest, bismuth deposited onto carbon paste appeared to be somewhat better than a mercury film on the same substrate. The BiF(C/SO) exhibited base-line with background typically down to 200 nA and, in 0.1 M HCl, its absolute level was even below 100 nA. This value represented the lowest background observed for both types of film plated carbon pastes.

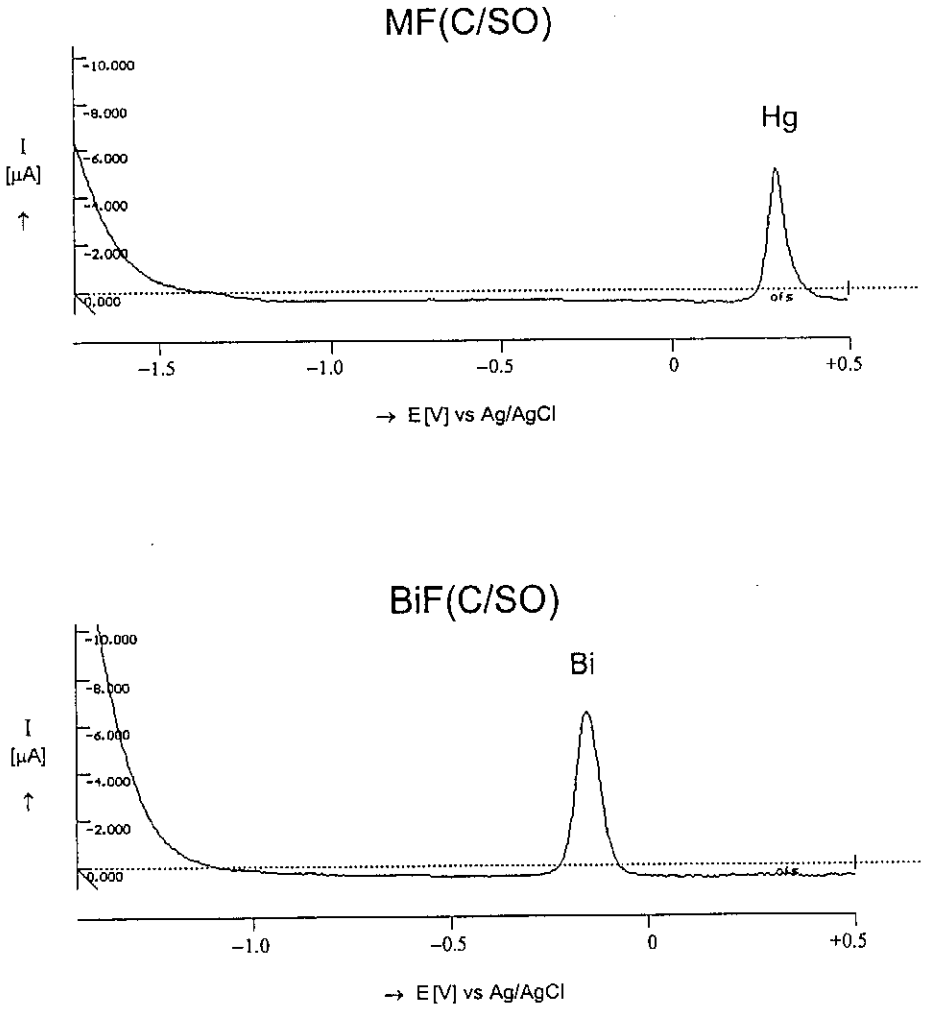

Fig. 1 Anodic stripping voltammograms at MF(C/SO) and BiF(C/SO). Base-lines in acetate buffer. Experimental conditions: differential pulse anodic stripping voltammetry (DPASV); supporting electrolyte, 0.2 M CH_3COOH + 0.2 M CH_3COONa (pH = 4.24); c(Hg, Bi) = 5×10^{-5} mol l^{-1}; accumulation (preconcentration) time, t_{ACC} = 30 s; equilibration time, t_{EQ} = 10 s; initial potential, E_{INIT} = –1.8 V for MF(C/SO), –1.5 V for BiF(C/SO); final potential, E_{FIN} = +0.5 V; scan rate, v = 20 mV s^{-1}; pulse height, ΔE = –50 mV

Figure 1 illustrates typical polarisation curves obtained at MF(C/SO) and BiF(C/SO) in an acetate buffer. By the way, regarding the bismuth film electrode, the same type of supporting medium has already been repeatedly recommended as the medium of choice for practical electronalytical determinations using DPASV

and stripping potentiometry in the CCSA and PSA modes [10,12–15,19–24].

Table II Peak characteristics of various metal ions in selected supporting media. Characterisation of MF(S/SO)

	0.1 M HCl pH = 0.96			0.2 M acetate buffer pH = 4.24			0.2 M ammonia buffer pH = 9.35		
	E_P, V	I_P, μA	Notes	E_P, V	I_P, μA	Notes	E_P, V	I_P, μA	Notes
Mn^{II}	--	--	1	–1.58	0.5	4	–1.52	5.4	
Zn^{II}	–1.14	1.4		–1.14	2.4		–1.30	6.6	
Cd^{II}	–0.75	1.8		–0.75	2.3		–0.85	3.3	
Tl^{I}	–0.71	1.5		–0.86	3.2		–0.78	0.9	8
Pb^{II}	–0.53	3.0		–0.54	2.3		–0.59	2.9	
In^{III}	–0.66	0.7		–0.71	2.8		--	--	1
Sn^{II}	–0.57	2.0		–0.31	0.3	5,6	--	--	9
Sb^{III}	–0.19	8.0	2	–0.21	0.8	6,7	--	--	9
Bi^{III}	–0.11	5.4		–0.29	10.9		--	--	9
Cu^{II}	–0.19	1.5		–0.17	4.4	7	–0.49	1.3	
Hg^{II}	+0.05	--	3	+0.31	--	3	–0.01	--	3

Experimental conditions: $c(Me^{II}) = 5\times10^{-6}$ mol l^{-1}; for further conditions, see Table I.
Notes: 1) not obtained; 2) another peak; E_P = –1.15 V, I_P = 0.5 μA; 3) I_P not evaluated; 4) peak deformed by high background of H_2 evolution; 5) another peak; E_P = +0.25 V, I_P = 2.5 μA; 6) causes deformation of base-line; 7) if present as a mixture, causes the decrease in other signals; 8) very broad peak; 9) not studied

Anodic Stripping Voltammetry of Various Metal Ions with MF(C/SO) and BiF(C/SO) in Selected Supporting Media

Methods combining ASV technique and either mercury- or bismuth-film electrodes were developed and applied predominantly to the detection and quantification of three heavy metal ions: Zn(II), Cd(II), and Pb(II) [1–3,12–15,19,21–23]. The Cu(II) species representing one of the most common metal ions are determined relatively rarely with detection systems based on thin film electrode configurations [14]. The reason is that the corresponding procedures suffer from problems due to serious interference effects [2,3]. Occasionally, also Tl(I) [32,33], In(III) [14,34], Sb(III) [35,36], Sn(II) [37], and Mn(II) [38] were of interest when using MFEs. The aim of investigations discussed in the following text was to particularly ascer-

Table III Peak characteristics of various metal ions in selected supporting media. Characterisation of BiF(C/SO)

	0.1 M HCl pH = 0.96			0.2 M acetate buffer pH = 4.24			0.1 M NaOH pH = 12.17		
	E_P, V	I_P, μA	Notes	E_P, V	I_P, μA	Notes	E_P, V	I_P, μA	Notes
Mn^{II}	--	--	1	−1.55	0.5	4,6	--	--	1
Zn^{II}	--	--	1	−1.15	5.1		−1.37	0.9	
Cd^{II}	−0.81	0.6		−0.82	3.4		−0.94	1.0	
Tl^{I}	−0.76	0.5		−0.71	3.2		−0.68	1.5	
Pb^{II}	−0.53	0.8		−0.55	3.7		−0.79	3.5	
In^{III}	−0.70	0.4	4	−0.67	1.9		--	--	1
Sn^{II}	−0.56	0.5		--	--	1,6	--	--	9
Sb^{III}	−0.21	0.1	4,6	−0.21	0.8	4,6,7	--	--	9
Bi^{III}	−0.11	--	3	−0.18	--	3	−0.49	--	3,8

For experimental condition and Notes, see Table II

tain which metals could be detected and, as the case may be, determined at mercury- and bismuth-film-plated carbon pastes. To date, MF(CPEs) and BiF(CPEs) have been tested mainly for the determination of a triad of Zn, Cd and Pb, including their mixtures [5,7,21–23].

The results of a study presented herein are surveyed in Tables II and III. The individual data have been obtained by evaluating the voltammetric curves obtained at both MF(C/SO) and BiF(C/SO) by analysing the single metals or their selected mixtures. In this article, some selected experiments are shown in Figs 2–5; complete sets of voltammograms can be found elsewhere [39,40].

If not stated otherwise, the concentration of metal elements at the micromolar level was chosen to be equal in order to compare also the relative ratio among the respective stripping signals (measured and given in the table as current intensities).

Figure 2 illustrates a pair of interesting voltammograms obtained by analysing mixtures of bivalent heavy metals that could be accumulated and detected simultaneously. Measurement in 0.2 M acetate buffer has provided a "stripping spectrum" which included — along with the dissolution signal of mercury — a quintet of well-separated peaks.

In order to obtain such a nice constellation of peaks, it was necessary to analyse a solution containing the Cu(II) ions at substantially lower concentration

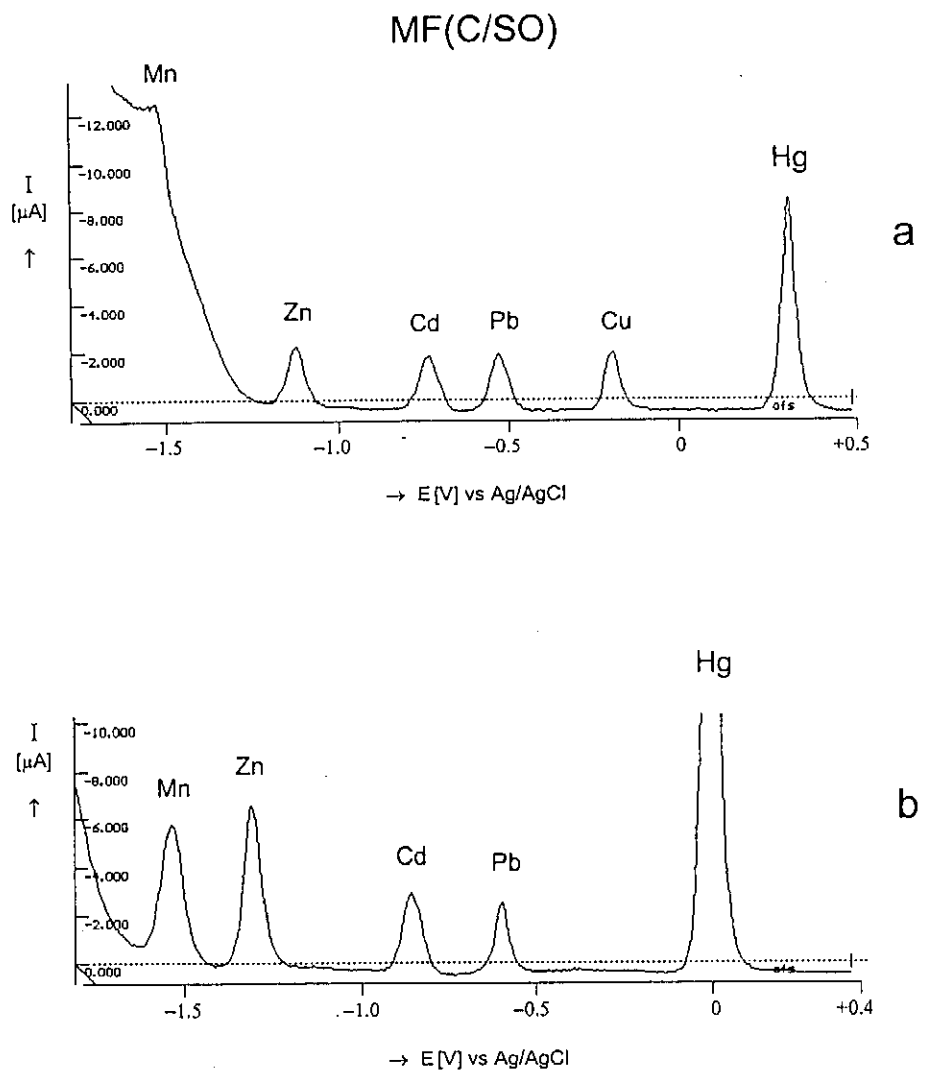

Fig. 2 Anodic stripping voltammetry of metal ion mixtures at MF(C/SO) in acetate (a) and ammonia buffer (b). Experimental conditions: 0.2 M CH_3COOH + 0.2 M CH_3COONa (pH = 4.24); 0.2 M NH_4Cl + 0.2 M NH_3 (pH = 9.35); c(Hg) = 5×10^{-5} mol l^{-1}; c(Mn, Zn, Cd, Pb) = 5×10^{-6} mol l^{-1}, c(Cu) = 1×10^{-6} mol l^{-1}; E_{INIT} = −1.8 V; E_{FIN} = +0.5 V (or +0.4 V); for other conditions, see Fig. 1

than that of the remaining heavy metal ions. When using a ratio of Cu : Me = 1 : 5 chosen accordingly to the previous experience [5], undesirable interference due to the formation of Cu-Me intermetallic compounds (causing the "erase" of other stripping peaks) could be minimised. The voltammogram recorded in acetate buffer also comprises a small response of manganese superimposed upon the background of the starting hydrogen evolution. Poorly developed and considerably

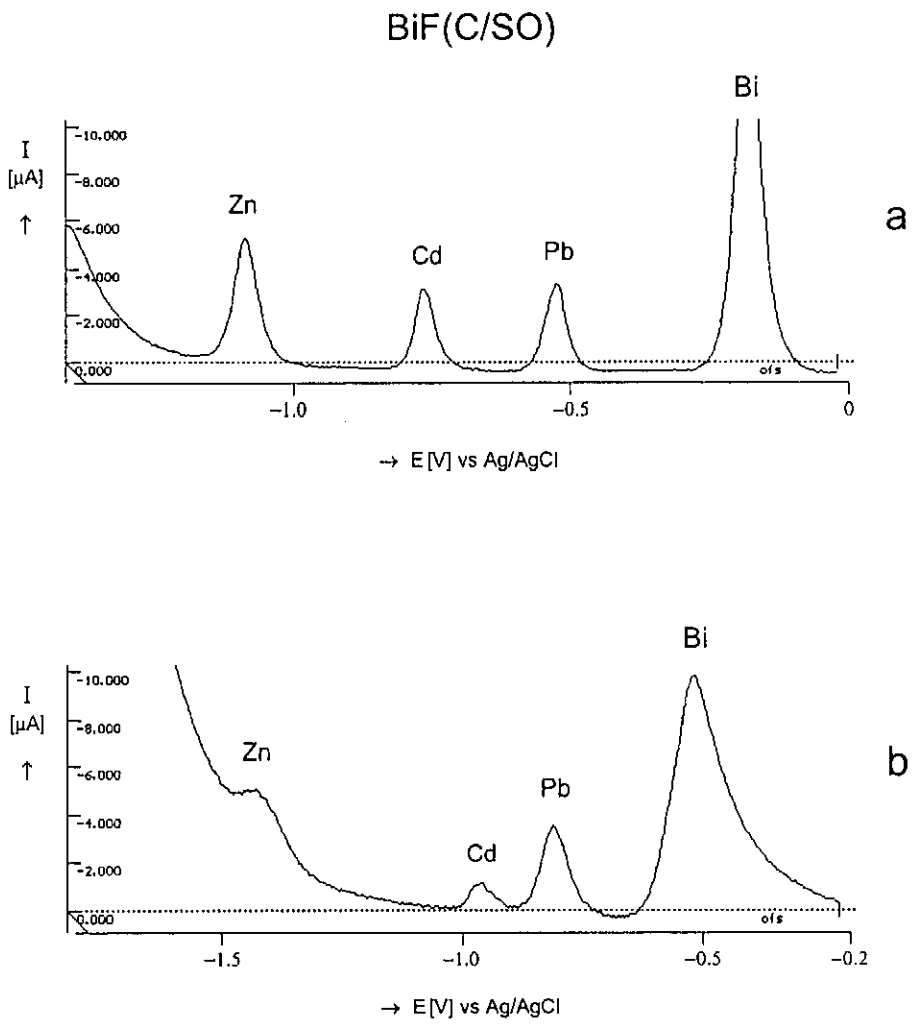

Fig. 3 Anodic stripping voltammetry of metal ions mixtures at BiF(C/SO) in acetate buffer (a) and sodium hydroxide (b). Experimental conditions: 0.2 M CH_3COOH + 0.2 M CH_3COONa (pH = 4.24); 0.1 M NaOH (pH = 12.17); c(Bi) = 5×10^{-5} mol l^{-1}; c(Zn, Cd, Pb) = 5×10^{-6} mol l^{-1}; E_{INIT} = −1.8 V; E_{FIN} = 0 V (or −0.2 V); for other conditions, see Fig. 1

deformed peak is not very promising for analytical applications; nevertheless, it manifests that the re-oxidation Mn(0) ⟶ Mn(II) at extremely negative potentials can also be recorded when using a MF(CPE) in combination with an acidic medium. Up until now, it has been believed that the determination of manganese at a mercury film-plated carbon pastes in the DPASV mode can be performed solely in basic electrolytes such as ammonia buffer [5,6].

The suitability of ammonia buffer as supporting medium for the detection of Mn is documented in Fig. 2 on the second voltammogram. Simultaneous determination of Zn, Cd, and Pb was also possible; however, in this case, the solution did not contain Cu(II) ions.

Figure 3 reveals possibilities of simultaneous determination of selected metals at the bismuth film-plated carbon paste. A result of measurement in 0.2 M acetate buffer is shown first. All three peaks of Zn, Cd, and Pb are again well shaped and separated sufficiently from each other. If one compares this curve with analogous experiment at the MF(C/SO) (Fig. 2a), the resolution of the individual peaks at the BiF(C/SO) is even better. For instance, whereas the separation of signals for Cd and Pb at the MF(CPE) was about 0.2 V, the respective value evaluated for the BiF(CPE) was nearly 0.3 V (see also Tables II and III).

Figure 3b illustrates a voltammogram obtained by analysing a mixture of Zn(II), Cd(II), and Pb(II) in a solution of sodium hydroxide. Compared to the polarisability ascertained in the supporting electrolyte alone (see Table I), cathodic potential limit of the BiF(C/SO) in the presence of depolarising metals was somewhat lowered, which was similar to the behaviour known for mercury or gold films [1,5,6]. Nevertheless, capability of BiF(C/SO) to be operated in such highly alkaline medium (pH > 12) was remarkable in itself. In the same electrolyte, related MF(C/SO) had exhibited tendencies to malfunction. (A large dissolution peak of mercury, indicating normally its re-oxidation during the anodic scanning, was very low and substantially distorted, which indicated some disintegration effects; perhaps, due to the formation of hydrated mercury oxides at the electrode surface.) As already mentioned above, atypical phenomena associated with measurements with BiF(C/SO) in highly alkaline media resulted in a separate study presented elsewhere [31].

Regarding other metals and mixtures to be investigated using either MF(C/SO) or BiF(C/SO), the following variants were of interest: Tl(I) + Cd(II) + Pb(II); Bi(III); Tl(I) + Bi(III); In(III); Tl(I) + Bi(III) + In(III); Sb(III); Bi(III) + Sb(III); Sn(II); Sb(III) + Sn(II).

Studies with a mixture of Cd(II) + Pb(II) + Tl(I) have shown that neither MF(C/SO) nor BiF(C/SO) can determine the three metals with a sufficient separation of their peaks. Especially the peaks of Cd and of Tl were partly overlapped in all the electrolytes (except for measurements with BiF(C/SO) in 0.1 M NaOH). Such observations were in contrast with some previous results obtained with BiF(GCE) reporting on a very good separation of both peaks in acetate-based media [10,14].

Tests with Tl(I) ions performed at the MF(C/SO) have also provided an insight into the electrode pathways taking place during electrolytic reduction and the consecutive re-oxidation in each DPASV experiment. For example, when comparing the response for Tl with that for Bi obtained during one run, we could see that the character of both peaks depended on the different number of electrons

involved in the of electrode process. Whereas one-electron transfer Tl(0) → Tl(I) gave rise to typically broad peaks of Tl, three-electron process Bi(0) → Bi(III) resulted in a sharp and very high peak. Incidentally, the peak of Bi obtained in 0.2 M acetate buffer was absolutely the highest stripping signal recorded at the MF(CPE), which is also documented by the corresponding data in Tables II and III.

Studies with indium(III) were performed with selected electrolytes containing either the single element or its mixtures with Tl(I) and Bi(III). In all the cases, small and poorly developed responses were obtained positioned very close to the peak of Tl. At the BiF(C/SO), stripping signals for Tl and In were partially or even completely overlapped. When comparing the absolute magnitude and the shape of response for indium with the respective characteristics of the peak of bismuth, it seemed that the process preceding the re-oxidation of indium was a reduction In(III) → In(I) rather than an alternative mechanism involving the three-electron transfer In(III) → In(0). This deduction was in accordance with the data published in handbooks of electrochemical data (see e.g. [41]), although some sources even admit the latter eventuality [42]. Regarding the electrochemistry of indium as such, it is worth mentioning that the assays described in this paragraph represent so far the only study employing a carbon paste-based electrode for the detection of In(III) ions [43].

Experiments with Sb(III) and Sn(II) were almost irreproducible due to problems with hydrolysis of both ions. Tendencies to hydrolysis were observed in most supporting electrolytes tested, including diluted mineral acids. Moreover, mixtures of Sb(III) + Sn(II) exhibited also other additional effects revealing some mutual interactions. For instance, addition of Sb(III) into the solution with Sn(II) species resulted in disappearance of the original response of Sn followed by formation of a new peak of unknown origin. Antimony itself gave rise to two signals: the first one at approx. –0.2 V vs Ag/AgCl was a sharp and large response corresponding to the re-oxidation Sb(0) → Sb(III), whereas the second one — a plateau-like low response around –1.0 V vs Ag/AgCl, could again originate again from mutual interference with bivalent tin.

The last study presented herein was devoted to the effect of Cu(II) ions on the determination of other heavy metal ions, particularly of Zn(II), when using film electrode configuration. The approach for suppressing such interference based on the addition of gallium(III) to the sample (see e.g. [14] and refs. therein) has already been tested with MF(CPEs) [44] as well as with BiF(CPEs) [7]; but, using different experimental conditions and not in direct confrontation between both film plated CPEs.

The mechanism behind the trick with the Ga(III) ions is the concurrent formation of a Cu_aGa_b intermetallic compound that, due to a higher stability, is able of liberating zinc from the related Cu_aZn_b adduct [14]. As a result, originally suppressed or completely eliminated peak of zinc can be recorded again. Figures

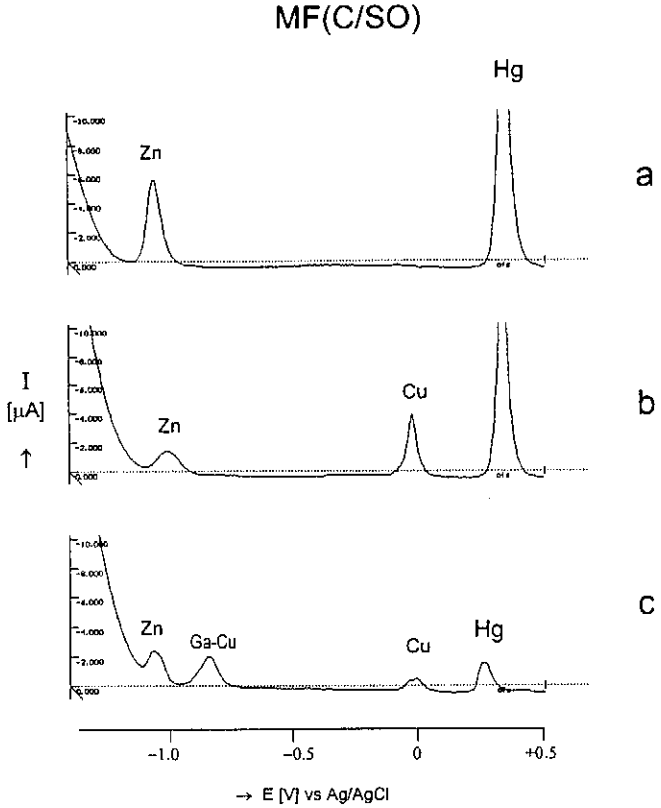

Fig. 4 Anodic stripping voltammetry of Zn(II) and Cu(II) at MF(C/SO) in the presence of Ga(III).Notes: a) Zn(II) [E_P(Zn) = −1.14 V, I_P(Zn) = 5.7 μA]; b) Zn(II) + Cu(II) [E_P(Zn) = −1.11 V, I_P(Zn) = 1.3 μA; E_P(Cu) = −0.06 V, I_P(Cu) = 4.2 μA]; c) Zn(II) + Cu(II) + Ga(III) [E_P(Zn) = −1.14 V, I_P(Zn) = 1.5 μA; E_P(Ga−Cu) = −0.91 V, I_P(Ga−Cu) = 2.1 μA; E_P(Cu) = −0.03 V, I_P(Cu) = 0.8 μA]. Experimental conditions: 0.2 M CH_3COOH + 0.2 M CH_3COONa (pH = 4.24); c(Hg) = 1×10^{-5} mol l^{-1}; c(Zn, Cu) = 1×10^{-6} mol l^{-1}; c(Ga) = 1×10^{-5} mol l^{-1}; E_{INIT} = −1.5 V; E_{FIN} = +0.5 V; for other conditions, see Fig. 1

4 and 5 document the whole process when using either MF(C/SO) or BiF(C/SO). In both cases, due to the presence of Cu(II) ions, the original response for Zn proportionally decreases (compare a vs b); however, the addition of Ga(III) again enlarges the peak of Zn (c).

As found out, the suppression of interference from copper was effective only in mild acidic medium of acetate buffer; model experiments with MF(C/SO) in ammonia buffer or with BiF(C/SO) in neutral solution of 0.2 M KCl have failed [39,40]. When confronting the performance of both MF(C/SO) and BiF(C/SO), it can be seen that measurement with bismuth film is superior to that carried out with

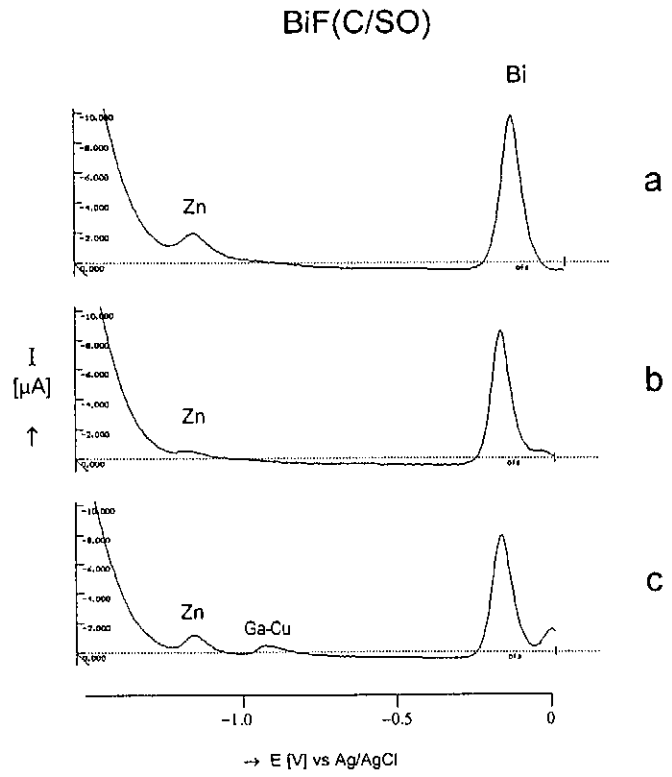

Fig. 5 Anodic stripping voltammetry of Zn(II) and Cu(II) at BiF(CPE) in the presence of Ga(III). Notes: a) Zn(II) [E_P(Zn) = −1.14 V, I_P(Zn) = 1.1 μA]; b) Zn(II) + Cu(II) [E_P(Zn) = −1.12 V, I_P(Zn) = 0.3 μA]; c) Zn(II) + Cu(II) + Ga(III) [E_P(Zn) = −1.14 V, I_P(Zn) = 0.9 μA; E_P(Ga-Cu) = −0.92 V, I_P(Ga-Cu) = 0.6 μA]. Experimental conditions: 0.2 M CH_3COOH + 0.2 M CH_3COONa (pH = 4.24); c(Bi) = 1×10^{-5} mol l^{-1}; c(Zn, Cu) = 1×10^{-6} mol l^{-1}; c(Ga) = 1×10^{-5} mol l^{-1}; E_{INIT} = −1.5 V; E_{FIN} = 0 V ; for other conditions, see Fig. 1

the mercury counterpart where the "renewed" peak of Zn did not reach its original size (see Fig. 4a,c). Since similar relation has already been commented on previously [7], it seems that the BiF(C/SO) would be more suitable to analyse mixtures of Zn(II) + Cu(II) by means of the gallium(III) approach. Nevertheless, in order to evaluate the effectiveness of this masking properly, it will be necessary to test the entire procedure on measurements with real samples [45].

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