A STUDY ON THE APPLICABILITY OF BISMUTH FILM PLATED CARBON PASTE ELECTRODES IN HIGHLY ALKALINE MEDIA

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A silicone oil-based carbon paste electrode plated "in situ" with a bismuth film, BiF(C/SO), has been tested for differential pulse anodic stripping voltammetry of heavy metal ions in highly alkaline media (with $pH \geq 12$). First, the BiF(C/SO) was examined with respect to its polarisability in solutions of either NaOH or KOH with varying concentration. Further, stripping characteristics of selected metals (Zn, Cd, Pb, and Tl) were investigated in order to define analytical performance of the BiF(C/SO) in 0.1 M KOH chosen as optimal medium. The study has revealed some specifics of measurements in solutions with high pH due to complex-forming capabilities of the OH^- ions, contributing thus to the continuing characterisation of bismuth film-based electrodes.

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Introduction

Bismuth film electrodes (BiFEs) represent one of the latest trends in the development of new detection systems for electrochemical stripping analysis (ESA [1]). BiFEs were invented a few years ago [2] in an effort to find an alternative to electrodes based on elementary mercury. Since then, intensive investigations on the applicability of BiFEs have resulted in a series of reports [3–12] offering the first experience with their testing in various electrochemical measurements. Promising results of these pioneering studies have attracted soon other research groups [13–17] and new teams are still appearing at the scene [18,19].

Originally proposed configuration of the BiFE was a bismuth film plated *in situ* onto the glassy carbon electrode (GCE [2]); nevertheless, other types of substrates have also been tested, including carbon pastes [13–15]. Compared to glassy carbon and related compact materials, carbon paste electrodes (CPEs) offer a quick and easy surface renewal [20,21] being required, from time to time, for each support in order to regenerate its surface [22]. In addition, the heterogeneous nature of CPEs allows one to use another way of generating bismuth film *in situ* by direct admixing solid Bi_2O_3 into the paste [13]. This approach — besides the fact that it has served as the initial step in the preparation of Bi_2O_3-modified carbon inks for screen-printed electrodes [14] — may simplify the measurements that do not need any addition of the Bi(III) species into the supporting electrolyte. The usefulness of bismuth film plated carbon paste electrodes, BiF(CPEs), in combination with modern ESA techniques has already been demonstrated on the determination of some heavy metals (Zn, Cd, and Pb) in real samples such as urine or drinking and natural water [14,23]. However, all these practical applications could not be possible without the basic characterisation of the individual types of BiF(CPEs) via suitably chosen testing measurements [13–15,24].

Also, the article presented herein concerns such a topic when falling into the category of special testing studies. Very recently [25], during additional characterisation of a bismuth film plated carbon paste made of silicone oil, BiF(C/SO), the performance of this electrode was examined in highly alkaline solutions of sodium hydroxide. Some observations were quite interesting, inspiring thus our electroanalytical group to carry out a separate study whose results are summarised below.

Experimental

Chemicals and Reagents

All the chemicals used for the preparation of stock and standard solutions were of analytical reagent grade and obtained from Lachema (Brno, Czech Republic) or Merck unless stated otherwise. Stock solutions for preparation of 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 appropriate, the respective solutions were diluted as needed. All the solutions of diluted standards with concentration lower than 0.001 mol l^{-1} were always stabilised by acidifying with an adequate amount of 65 % HNO_3 to yield pH approx. 2.

Water used throughout the experimental work was obtained by distilling deionised water in a laboratory-made glass distillation unit. Water purified in this way was stored in a polyethylene bottle. All solutions to be analysed were deoxygenated by bubbling with argon (purity 99.99 %, Linde Technoplyn, Prague).

Apparatus and Instrumentation

An electrochemical station (Model BAS 100B, Bioanalytical Systems Inc., West Lafayette, IN, USA) connected to a personal computer and controlled by a BAS 100W, version 2 software. The three-electrode cell compartment was an integral part of this assembly (see below) as well as a magnetic stirrer agitating a Teflon®-coated magnetic bar (length 12 mm, diameter 2 mm) and providing the convective transport 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 electrode (model OP-0808P, Radelkis, Budapest) made of special glass resistant in solutions with high pH.

Electrodes

Carbon Paste Electrode. The carbon paste was prepared by intimately hand-mixing of 0.5 g spectroscopic graphite powder (RW-B, Ringsdorff Werke, Germany) with 0.3 ml silicone oil (LUKOIL MV 15500; Lučební závody Kolín, Czech Republic) using a pestle and mortar. The ready-made paste mixture was then packed into specially designed electrode holder [26] equipped with a piston for pulling out the used paste and its subsequent renewal.

Reference and Auxiliary Electrodes. A self-made Ag/AgCl electrode (containing

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3 M KCl as the inner electrolyte) as the reference and a Pt-plate (with the area of ca 0.5 cm^2) as the counter electrode completed the cell.

Procedures

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

Preparation of Bismuth Film-Plated Carbon Paste Electrode, BiF(C/SO). Bismuth film was deposited onto the CPE support *in situ* after adding the appropriate amount of 0.01 M Bi(NO$_3$)$_3$ standard into the supporting electrolyte. The total Bi(III) content in the solution was chosen to be approx. one order higher than that of metal ions to be analysed [13,25], typical concentration being 2×10^{-5} M Bi(III) for the determination of metals at the micromolar level. The potential chosen for depositing of the film then corresponded to that used in the stripping voltammetric 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 time period, t_{ACC}. After the equilibration period (t_{EQ}) in quiet solution for 10 s, the measurement in DPV mode was performed by anodic scanning from the E_{ACC} to a final potential, E_{FIN}. The individual stripping parameters are specified in Discussion. Regarding other conditions, typical scan rate was 50 mV s^{-1}, pulse height −50 mV, pulse width 20 ms, pulse period 200 ms, and sample width 10 ms.

Data Processing and Evaluation

Using the BAS 100W-2 software, the analytical signals were evaluated as the peak heights (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

Bismuth Film Electrodes and pH Dependence of Their Function

When using anodic stripping voltammetry with BiFEs prepared *in situ*, the choice of acidic solutions spiked with the Bi(III) species ensures that cathodic preconcetration produces a bismuth film formed from the free Bi(III) ions according to the scheme

$$Bi^{3+} + 3e^- \rightarrow Bi^0 \qquad (1)$$

Any other metal ion present in this sample solution is then co-deposited onto the support together with bismuth. In the stripping step of ESA, the bismuth deposit — i.e., reduced metal at bismuth layer — can then be re-oxidated ("stripped off") by imposition of anodic scan. If the scanning potential permits also re-oxidation of the bismuth layer itself, it is dissolved in a process reverse to the above reaction

$$Bi^0 \rightarrow Bi^{3+} + 3e^- \qquad (2)$$

In the case of acidic solutions, both redox pathways ((1) and (2)) are analogous to that known for measurements with mercury film electrodes (MFEs [27]). However, when comparing the chemistry of mercury and bismuth, the different situation occurs in the electrolytes with higher pH. In such media, considerable inclination of Bi(III) salts to hydrolysis gives rise to insoluble and electrolytically non-reducible products

$$Bi^{3+} + H_2O \rightarrow BiO^+ + 2H^+ \qquad (3)$$

or

$$Bi^{3+} + 3H_2O \rightarrow Bi(OH)_3 + 3H^+ \qquad (4)$$
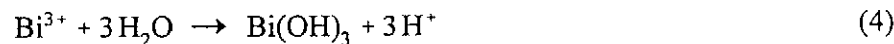
Thus, when using solutions such as phosphate, ammonia or borate buffer (with pH ca 8 – 10), the formation of such precipitates — being visible with the naked eye as an opalescence [28] — does not permit the proper formation of bismuth film and the respective DPASV measurements may fail.

Similar behaviour was expected also during experiments in alkaline solutions since even the MF(C/SO) started to exhibit tendencies to fail when being polarised in 0.1 M NaOH [25,28]. It should be mentioned that the dissolution peak of mercury was already very low and substantially distorted compared to that from measurements in solutions with pH 1 – 10. This suggested that MF(CPE) could also suffer from disintegration of the film due to the formation of hydrated mercury oxides, $HgO \cdot xH_2O$, in highly alkaline media [25]. However, at the BiF(C/SO), no hydrolysis was noticed in the same solution of NaOH and under identical experimental conditions. The corresponding voltammograms comprised all the peaks of metals contained in model samples and also the signals of bismuth were well developed.

This rather surprising observation has led us to the following interpretation. In contrast to bivalent mercury, the Bi(III) species present in diluted sodium hydroxide are capable of forming the hydroxo-complexes soluble in aqueous solutions and can therefore be reduced at the electrode. For example, one has

$$Bi^{3+} + OH^- \longrightarrow Bi(OH)^{2+} \tag{5}$$

$$Bi(OH)^{2+} + 3e^- \longrightarrow Bi^0 + OH^- \tag{6}$$

The results presented here confirm that bismuth film prepared in this way can be used for conventional measurements in the DPASV mode; nevertheless, with some specifics given by the nature of highly alkaline solutions.

Choice of Hydroxide-Containing Supporting Medium

Table I surveys the basic stripping characteristics of the BiF(C/SO) evaluated from measurements in hydroxides of two most common alkali metals with varying concentration. The data document some trends that correspond well to the theoretical considerations. First, experiments confirmed that the more concentrated

hydroxide, the more pronounced is the shift of the dissolution signal of bismuth towards more negative potentials. Secondly, it can be seen that the higher pH, the larger peak of bismuth is registered (except for a slightly lower peak in 0.5 M NaOH). Finally, both relations between the peak shift and peak height and the concentration of either NaOH or KOH are nearly proportional. This has implied that the increased pH of solutions gives rise to the complexes with higher stability, which can be explained by the formation of hydroxo-complexes such as $Bi(OH)^{2+}$ ($\log\beta$ = 12.9, $Bi(OH)_2^+$ (24.0), $Bi(OH)_3^0$ (33.1), and $Bi(OH)_4^-$ (34.2) or even some polynuclear structures like $Bi_6(OH)_{12}^{6+}$ or $Bi_9(OH)_{20}^{7+}$ (see e.g. [29]).

Table I Potential limits, potential ranges, residual currents, and peak characteristics [1–3] of the dissolution signal of bismuth in solutions of alkali metal hydroxides

Alkaline medium (supporting electrolyte)	pH exp.	Polarisation and peak characteristics					
		E_C, V	E_A, V	ΔE, V	I_R, µA	E_{Bi}, E_C	I_{Bi}, µA
0.01 M NaOH	11.98	> −1.50	−0.50	> 1.00	< 0.2	− 0.45	8.5
0.05 M NaOH	12.32	−1.50	−0.55	0.95	0.3	−0.50	22.5
0.10 M NaOH	12.44	−1.50	−0.60	0.90	0.4	−0.53	25.5
0.20 M NaOH	12.82	−1.45	−0.63	0.82	0.7	−0.55	37.5
0.50 M NaOH	13.06	−1.30	−0.65	0.65	> 1.0	−0.57	35.0
0.01 M KOH	12.41	> −1.50	−0.50	>1.00	0.3	−0.45	7.5
0.10 M KOH	12.97	> −1.50	−0.60	> 1.00	0.5	−0.54	23.0
0.50 M KOH	13.68	−1.50	−0.63	0.87	> 0.5	−0.58	38.0

Experimental conditions: DPASV; initial potential, E_{INIT}, −1.5 V; final potential, E_{FIN}, 0 V; accumulation time, t_{ACC} = 20 s; equilibrium period, t_{EQ} = 10 s; scan rate: 50 mV s^{-1}.
Notes: 1) cathodic potential limit, E_C, given by the residual (background) currents that exceeded an arbitrary value of 1 µA (according to [24]); 2) anodic limit, E_A, determined by the position of bismuth signal (evaluated as a potential at the foot of its starting peak); 3) residual currents estimated as the average within an interval $\Delta E \in (E_C, E_A)$

Regarding the importance of the above-discussed results for analytical purposes, optimisation studies with both hydroxides have shown that a solution of 0.1 M KOH would be optimal with respect to the bismuth film formation (indicated via the respective dissolution signal) as well as due to acceptably low residual currents.

Figure 1 shows a voltammogram obtained by analysing model mixture of four heavy metal ions at the BiF(C/SO) in the selected medium. The DPASV curve illustrates good separation of the individual peaks, which is particularly remarkable for a triad of Tl, Pb, and Cd.
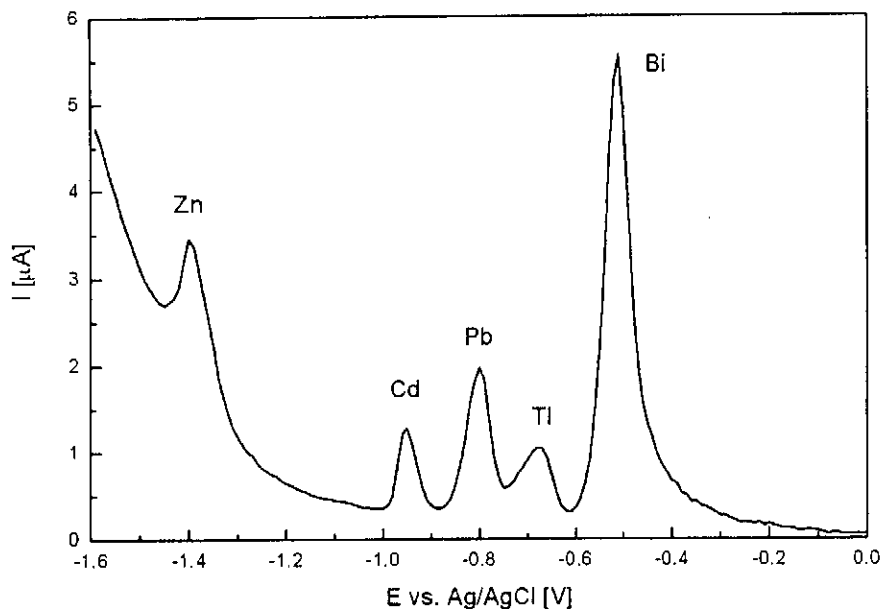

Fig. 1 Anodic stripping voltammogram of Zn, Cd, Pb, and Tl at BiF(C/SO) in 0.1 M KOH. Experimental conditions: differential pulse anodic stripping voltammetry (DPASV); supporting electrolyte, 0.1 M KOH + 20 μM Bi(NO$_3$)$_3$ [pH = 12.97]; c(Zn) = 5 μM, c(Cd, Pb, Tl) = 1 μM; accumulation time, t_{ACC} = 4 min.; equilibration time, t_{EQ} = 10 s; initial potential, E_{INIT} = –1.6 V vs Ag/AgCl, final potential, E_{FIN} = 0 V; scan rate: 50 mV s^{-1}; pulse height: –50 mV

Moreover, compared to similar experiments in acidic media [25], the signals for Tl and Pb are positioned conversely; i.e., thallium is re-oxidised at less negative potentials than lead is. Satisfactory resolution of the Tl-signal from the remaining ones for Pb and Cd was also noticed when using BiF(GCE) in acetate buffer [2]; nevertheless, their peak potentials were in an usual order of "E_P(Cd) < E_P(Tl) < E_P(Pb)" known also for measurements with MFEs [30]. The conversion of the peak potentials into a ranking "E_P(Cd) < E_P(Pb) < E_P(Tl)" can be explained again by complexing capabilities of the OH$^-$ species, which is indicated by the respective stability constants [29]

$$\log\beta(PbOH^+) = 6.5; \quad \log\beta(Pb(OH)_2^0) = 10.9; \quad \log\beta(Pb(OH)_3^-) = 13.9 \quad (7)$$

$$\log\beta(CdOH^+) = 3.9; \quad \log\beta(Cd(OH)_2^0) = 7.9; \quad \log\beta(Cd(OH)_3^-) = 8.7 \quad (8)$$

whereas univalent thallium practically does not undergo any complex formation [29,30]

$$\log\beta(TlOH^0) = 0.8; \quad \log\beta(Tl(OH)_2^-) = -0.8 \quad (9)$$

and the position of its stripping peak upon the potential axis remains nearly the same like that in acidic or neutral media [25].

Specific stripping characteristics of thallium in hydroxide-based media
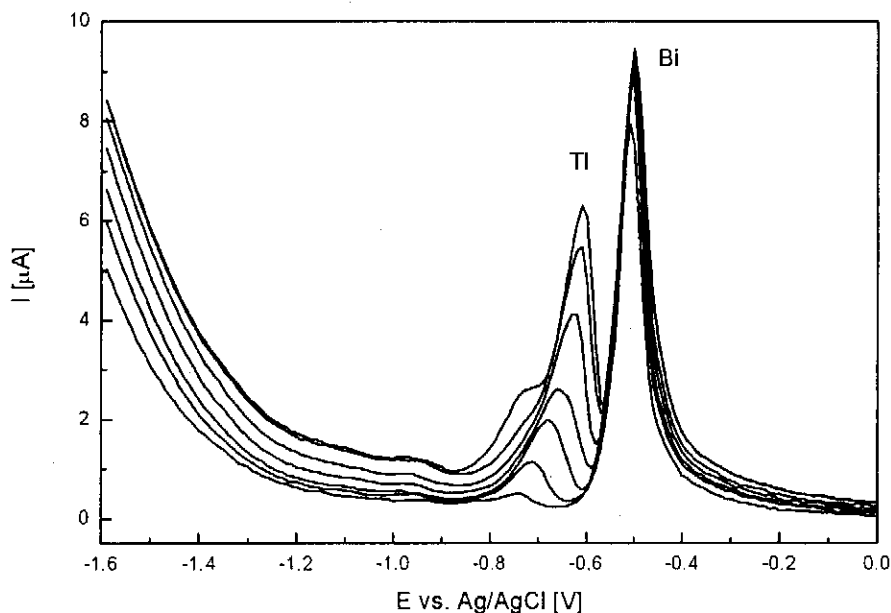
Fig. 2 Voltammograms of thallium(I) at the BiF(C/SO) in 0.1 M KOH. Legend (curves from bottom): 1, 5, 10, 20, 30, 40, and 50 μM Tl(I). Experimental conditions: DPASV; 0.1 M KOH + 200 μM Bi(NO$_3$)$_3$; t_{ACC} = 30 s; for other conditions, see Fig. 1

appeared to be promising for analytical purposes; however, the experiments showed somewhat low sensitivity of detection (see Fig. 1 and the concentration level versus accumulation time used). Then, despite a good linearity ascertained during the calibration measurements in a concentration range of 1 – 50 µM Tl(I) (see Fig. 2), practical applications to the determination of thallium in real samples would be very limited [30]. Similar conclusions can be made when having evaluated the respective calibration voltammograms of Pb(II), Cd(II), and Zn(II) illustrated in Figs 3 – 5.

Unsatisfactory analytical performance of the BiF(C/SO) for DPASV of heavy metals in hydroxide-based media requires some additional studies. For instance, there is a possibility to optimise the concentration of Bi(III) in the solution and, eventually, some other parameters of the plating regime. On the other hand, the results of this study are potentially exploitable for hitherto untested applications of BiF(CPEs) such as electrode reductions of some organic compounds undergoing specific reaction pathways at high pH [21].
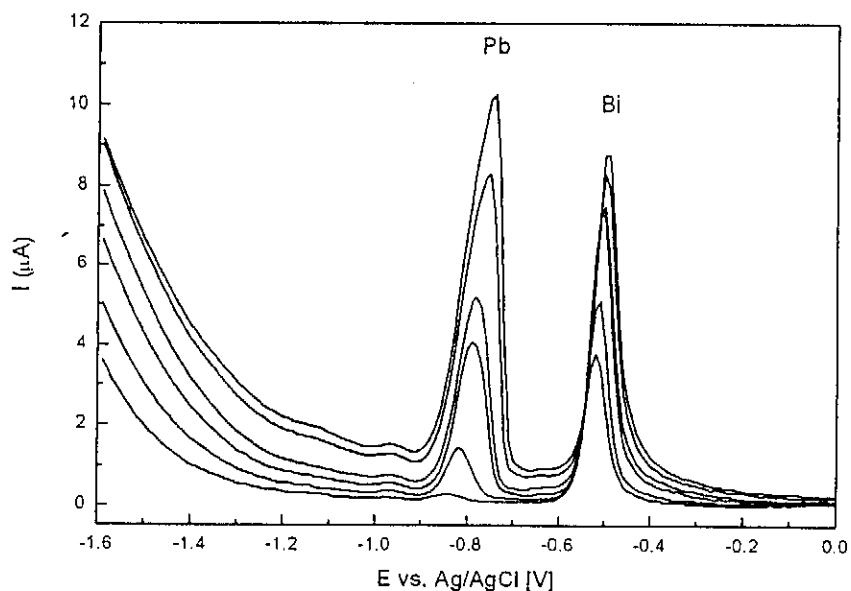

Fig. 3 Voltammograms of lead(II) at the BiF(C/SO) in 0.1 M KOH. Notes: 1, 5, 10, 20, 40, and 50 µM Pb(II). Experimental conditions: 0.1 M KOH + 200 µM $Bi(NO_3)_3$; for other conditions, see Fig. 1
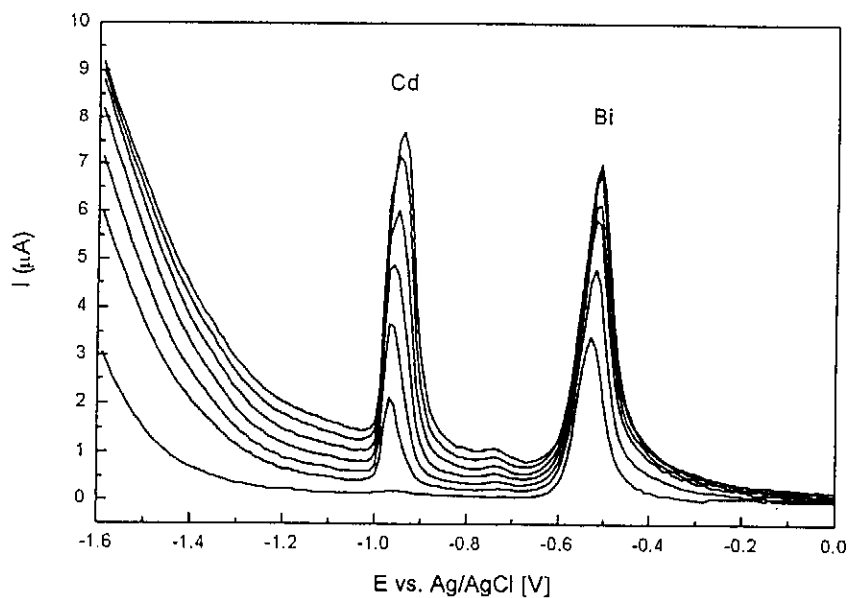
Fig. 4 Voltammograms of cadmium(II) at the BiF(C/SO) in 0.1 M KOH. Notes: 1, 10, 20, 30, 40, 50, and 60 μM Cd(II). Experimental conditions: 0.1 M KOH + 200 μM Bi(NO$_3$)$_3$; for other conditions, see Fig. 1.
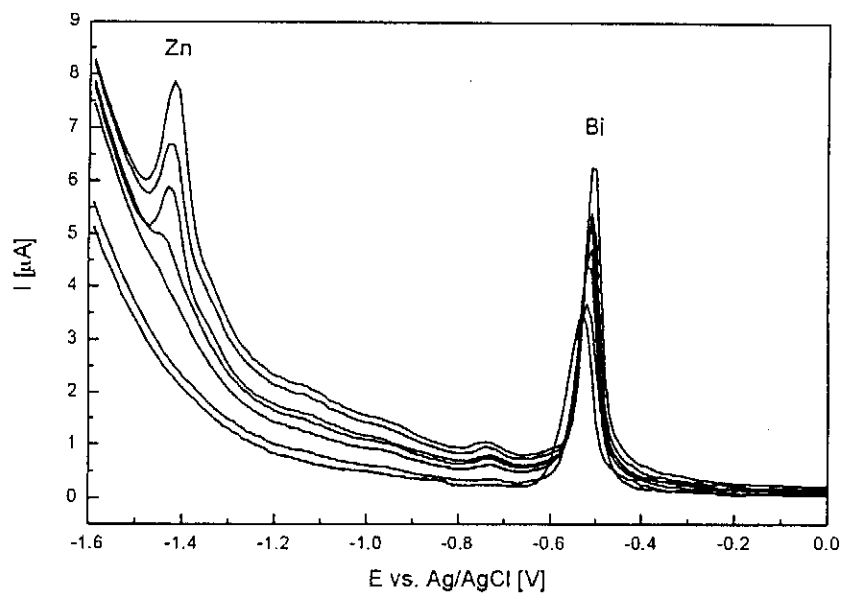

Fig. 5 Voltammograms of zinc(II) at the BiF(C/SO) in 0.1 M KOH. Notes: 0, 1, 5, 10, 30, 40, and 50 μM Zn(II). Experimental conditions: 0.1 M KOH + 200 μM Bi(NO$_3$)$_3$; for other conditions, see Fig. 1.

Acknowledgements

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