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ANODIC STRIPPING VOLTAMMETRY AT BISMUTH-MODIFIED ELECTRODES IN AMMONIA-BUFFERED MEDIA

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In this contribution, the analytical performance of a bismuth-modified carbon paste electrode (Bi-CPE) in square-wave anodic stripping voltammetry (SWASV) with ammonia buffer-based supporting media (pH 8.6-9.0) has been studied. Possibilities and limitations of such combination used for the determination of various metal ions were explored with the electrode of choice, containing 17 % (w/w) Bi, when analysing model solutions with Mn^{2+}, Zn^{2+}, Cd^{2+}, Pb^{2+}, In^{3+}, and Tl^{+} — added in as either single species or selected mixtures. SWASV of these ions has been investigated focused on the individual peak characteristics, calibration measurements and definition of linear concentration ranges attainable, limits of detections, reproducibility, and interference effects from other ions. The latter was examined in more detail for Zn^{2+} + Cd^{2+} + Pb^{2+} and, particularly, for Tl^{+} + Cd^{2+} + Pb^{2+} mixtures where the formation of intermetallic compounds and low-melting

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alloys with bismuth had significantly affected the SWASV detection of the respective metals, giving rise to overlapped and additional signals. As shown, these phenomena would represent one of the key-factors which have to be considered when elaborating procedures for practical determinations.

Introduction

Since the pioneering study [1], bismuth film electrodes (BiFEs) and related bismuth-based electrodes (BiEs) have already achieved a respectable position in modern electroanalysis [2-4] despite a relatively short period of their existence. This is because of the fact that electrodes and sensors made of environmentally less-harmful bismuth represent one of the most successful attempts ever made to replace problematic mercury electrodes. And since both BiFEs and BiEs may offer a variety of attractive applications in electrochemical stripping analysis, there is still growing publication activity within the field, comprising now 75 original papers published by more than 20 research teams over the whole world [5].

One of the typical features of electroanalysis with bismuth-modified electrodes is the dominant use of acetate buffer (AcB) in the supporting electrolytes. As confirmed in many original studies (see [2-4] and refs. therein), solutions with equimolar mixtures of $CH_3COOH + CH_3COONa$ at concentrations from 0.01 to 0.5 mol l^{-1} offer optimal pH, adequate ionic strength, minimal complex-forming capabilities, and a favourable background over the whole potential range of interest. Nevertheless, reliable measurements with both BiFEs and BiEs can also be carried out in other supporting media such as diluted mineral acids (used to decompose weak organic complexes in real sample matrices [6-9]) or ammonia buffer (AmB), representing the proper medium for some chelate-forming reactions and methods arranged in the adsorptive/catalytic stripping voltammetric mode (Ad/CtSV [10-20]).

Regarding the AmB-based media and the application of a bismuth-based electrode, the detection systems of choice may incorporate either (i) externally pre-plated BiFEs [10-20] or (ii) bismuth bulk electrodes (BiBEs) made of the compact metal [21] or, alternatively, (iii) from carbonaceous substrates containing finely dispersed bismuth powder [22-24]. In contrast to these configurations, the use of the AmB cannot be combined with a BiFE operated *in situ*, which is undoubtedly the most popular variant of bismuth electrodes [2-4], requiring no special pre-plating step or pre-treatment and regeneration of the surface. For *in-situ* preparation of BiFEs, however, it is necessary to ensure the presence of single Bi^{3+} ions (or Bi^{III} species) in the supporting electrolyte as a source for the formation of the film during electrolytic deposition. This is not the case of ammonia buffer and its mild alkalinity of about pH 9-11 where bismuth(III) salts undergo a rapid and spontaneous hydrolysis, giving rise to insoluble and electrolytically inactive

products such as bismuthyl salts, BiO^+X^-, oxid-hydroxide, BiO(OH), or tri-hydroxide, $Bi(OH)_3$, which cause the failure of each thin bismuth film-based electrode prepared and operated under such conditions [25].

It seems that a general awareness of these hydrolytic processes as well as influential experience from widespread use of the *in-situ* regime are both due to the fact that ammonia buffers have been selected mainly for Ad/CtSV measurements with pre-plated BiFEs, whereas potentially attractive applications in anodic stripping voltammetry with pre-concentration and the subsequent re-oxidation at highly negative potentials [26] were almost omitted. Possible adaptability of bismuth-based electrodes for such a combination has been demonstrated first by our group in association with the discovery and initial characterisation of bismuth-powder modified carbon paste electrode (Bi-CPE [22,23]), which is a configuration that can be operated in mild alkaline solutions [2,4].

In this report, some continuing investigations on the analytical performance of Bi-CPEs for the determination of selected metal ions and their mixtures in ammonia buffer-based media are presented and — if useful — even compared with experiments carried out with the bare (unmodified) carbon paste electrode (CPE [27]).

Experimental

Chemicals and Reagents

All chemicals used for the preparation of both stock and standard solutions were of analytical reagent grade and purchased from Lachema (Brno, Czech Rep.), Sigma-Aldrich or Merck. Bismuth powder used for preparation of the modified carbon paste was obtained from Sigma-Aldrich (99.99+ %, 100 mesh, product "00914HQ"). Stock solutions of either ammonia buffer or acetate buffer (for some comparative measurements), were made as mixtures of 1 M NH_3 + 1 M NH_4Cl and of 1 M CH_3COOH + 1 M CH_3COONa, respectively. As a complex-forming reagent, a solution of 0.1 M EDTA was also prepared. Stock standard solutions of Mn^{2+}, Zn^{2+}, Cd^{2+}, Pb^{2+}, In^{3+}, and Tl^+ were then made containing 1000 mg l^{-1} of the respective ion.

All the solutions prepared from doubly distilled water were diluted as required and the metal ion standards with concentrations lower than 0.001 mol l^{-1} stabilised by acidifying with HNO_3 to pH 2. The water used throughout the experimental work was obtained by passing deionised water through a laboratory-made distillation unit.

Apparatus and Instrumentation

A modular electrochemical system AUTOLAB equipped with PGSTAT-12 and ECD modules (Eco Chemie, Utrecht, Holland) was used in combination with GPES software (Eco Chemie). This assembly was connected to an external electrode stand incorporating the three-electrode cell with the working bismuth-based electrode (see below), Ag | AgCl | 3 M KCl reference, and Pt-plate (approx. 0.5 cm^2) auxiliary electrodes. Stirring was devised with a magnetic bar (12 × 2 mm) rotated at 900 rpm by using a PC-controlled compact tap-disk (model "IKA®-White"; *IKA*, Staufen, Germany).

The pH was measured using a portable pH-meter (model "CPH 52", Elteca, Turnov, Czech Republic) and a combined glass pH-sensor (OP-0808P, Radelkis, Budapest, Hungary). Ohmic resistance of newly made carbon paste was checked with a Voltcraft® multimeter (VC 404, Conrad Electronics, Germany). All the solutions used for voltammetric measurements were introduced to cell using a set of automatic transfer-pipettes with adjustable volumes from 10 µl to 10 ml (Finnpipettes; Labsystems, Finland).

Working Electrode

Bismuth-Modified Carbon Paste. The bare (unmodified) carbon paste mixture was prepared by intimately hand-mixing 0.5 g spectroscopic graphite powder (RW-B, Ringsdorff, Germany) with 0.3 ml highly viscous silicone oil (LUKOIL MV 15500; Lučební závody Kolín, Czech Republic). Both components were homogenised by using a recommended procedure [28] to obtain the resultant mixture. Afterwards, into a 0.5 g portion of the bare carbon paste, the appropriate amount of powdered bismuth was added to form a mixture with 17 % Bi (w/w). Additional homogenisation then yielded the resultant modified carbon paste (denoted below as "$Bi_{17\%}$-CPE").

Preparation of the Electrode for Measurements. Modified carbon paste was packed into a piston-driven carbon paste holder designed in our laboratory [29] and such freshly prepared carbon paste electrode was checked with respect to ohmic resistance; a value of *ca.* 10 Ω indicating a sufficient homogeneity [27-29].

As mentioned above, the Bi-CPE type did not require any pre-plating of the film or special surface regeneration. Solely, if needed, the carbon paste surface was mechanically renewed by extruding *ca.* 0.5 mm of carbon paste out of the holder with subsequently smoothing against a wet filter paper. Typically, this simple operation was performed before starting a new set of experiments (*e.g.*, prior to analysis of each sample).

Square-Wave Anodic Stripping Voltammetry (SWASV). All the measurements were carried out in the anodic stripping voltammetric mode (ASV) with the square-wave modulation ramp (SW). Voltammetric experiments consisted of three conventional steps: time-controlled electrolytic accumulation (preconcentration), the rest period, and the voltammetric stripping scan run under conditions chosen. The individual conditions and parameters used are specified below – either in the text or in the legend of the respective figure.

Analytical signals measured as the peak currents were evaluated by manual base-line setting controlled by the software. Where applicable, the results were processed by conventional statistical methods for small sets of data [30].

Results and Discussion

The following sections summarise the results and observations obtained by analysing a sextet of ions (Mn^{2+}, Zn^{2+}, Cd^{2+}, Pb^{2+}, In^{3+}, and Tl^{+}), involving a majority of heavy metals which can be determined in the ASV mode. As shown in our investigations, Sb^{3+} and Sn^{2+} could also be analysed by anodic voltammetry when using either Bi-CPE or BiFE [5,31]; however, in this case, highly acidic media had to be selected in order to prevent a transformation of both ions into insoluble hydrolytic and oxidised products (SbOCl, SbO(OH), and $Sb(OH)_3$ or $Sn(OH)_2$, $SnO(OH)_2$, and SnO_2 . n H_2O, respectively [32]). Regarding copper, which is nobler than bismuth itself, its re-oxidation cannot be detected within the operational potential range of bismuth-based electrodes [4]. Nevertheless, possible ASV determination of Cu^{2+} at carbon-based electrode plated *in situ* with a bismuth film — *i.e.*, in the presence of Bi^{3+} ions — has also been studied in detail and some interesting results are discussed elsewhere [33,34].

Determination of Mn^{2+}. Except mercury-based electrodes, classical arrangements of ASV in aqueous solutions normally do not allow one to reduce bivalent manganese which requires extremely high negative potentials to be applied during the preconcentration step. At solid electrodes, such a reduction is already accompanied by spontaneous evolution of H_2 whose large wave overlaps the response for the reoxidation $Mn^0 \rightarrow Mn^{II}$. In ammonia buffers — i.e., under conditions of higher pH – and in combination with a suitable electrode, undesirable reduction of H^+ ions can be effectively suppressed and the ASV peak of Mn obtained [26].

Bi-CPEs were shown to be the electrode of choice enabling such an experiment. This is illustrated in Fig. 1 where, despite still rather high background

due to hydrogen evolution, the response for manganese can be clearly identified (together with the respective signals for Cd and Pb being also added to this model solution).

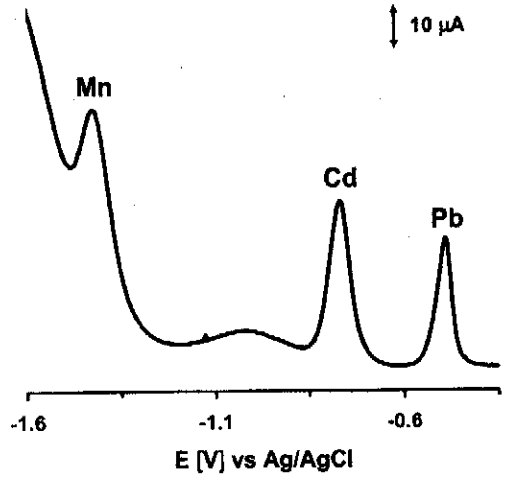


Fig. 1 Anodic stripping voltammetry of Mn(II), Cd(II), and Pb(II) at the Bi-CPE. Experimental conditions: square-wave anodic stripping voltammetry (SWASV); carbon paste modified with 17 % (w/w) of bismuth powder ($Bi_{17\%}$-CPE) supporting electrolyte: 0.1 M NH_3 + NH_4Cl (pH 8.80); c(Mn) = 1000 μg l^{-1}, c(Cd,Pb) = 250 μg l^{-1}; accumulation time, t_{ACC} = 120 s; the rest period, t_R = 10 s; accumulation potential, E_{ACC} = –1.8 V vs. ref.; initial potential, E_{INIT} = –1.6 V; final potential, E_{FIN} = –0.4 V; square-wave frequency, f_{SW} = 25 Hz; pulse height, ΔE = 50 mV; step increment, *s.i.* = 4 mV. *Note:* A value specifying the arrow size is the peak currect, I_p, and its actual range (intensity)

In contrast to the initial study with Mn^{2+} ions [23] which has solely reported on poor sensitivity for ASV detection without any further specification, the experiments carried out within this study offer some details on possible determination. Namely, it was ascertained that carbon paste modified with 17% (w/w) bismuth powder ("$Bi_{17\%}$-CPE") could be used to quantify manganese at concentrations of 500-3000 mg^{-1} Mn^{2+} with the RSD = ±10 % and a limit of detection (LOD, 3σ) of about 300 ppb Mn^{2+}. Although these data have only little promise for practical analysis, even such results can be considered as a rare and successful attempt on how to determine manganese *via* ASV and a non-mercury electrode.

Determination of Zn^{2+}. Applicability of Bi-CPEs to the ASV determination of zinc in ammonia buffers was also initially tested in the above-referred study [23], but first good experience from the choice of NH_3 + NH_4Cl mixtures to analyse samples with Zn^{2+} ions at a metallic film electrode had already been made a decade earlier [26].

Less pronounced hydrogen evolution in ammonia buffers is also beneficial to Zn^{2+} and its electrolytic reduction at potentials beyond −1.0 V vs. Ag/AgCl. SWASV of Zn^{2+} ions in AmB can be seen in Fig. 2, comprising responses obtained in four ammonia buffers, a mixture with 0.1 M NH_3 + 0.1 M NH_4Cl being found optimal and chosen for all further investigations.

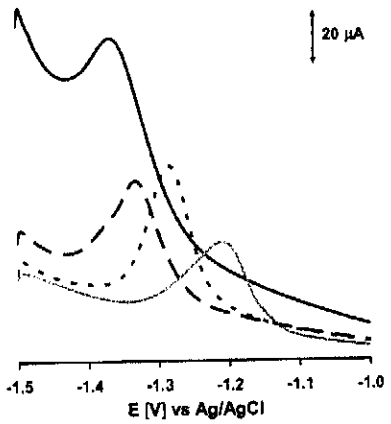


Fig. 2 Anodic stripping voltammetry of Zn(II) in ammonia buffer at varied concetrations: Legend: ——— ... 0.01 M AmB (pH 8.56); - - - - ... 0.1 M AmB (pH 8.79), – – – ... 0.5 M AmB (pH 8.88), ——— ... 1 M AmB (8.94). Experimental conditions: SWASV; $Bi_{17\%}$-CPE; $c(Zn) = 100\ \mu g\ l^{-1}$; $t_{ACC} = 60$ s; $t_R = 10$ s; $E_{ACC} = -1.5$ V vs. ref.; $E_{INIT} = -1.4$ V. For other conditions, see legend in Fig. 1

Some additional experiments involved a series of calibrations over a concentration interval of 20-100 µg l^{-1} Zn^{2+}, resulting in linear regression equation: $I_P(Zn) = 0.879c(Zn) - 1.609$ (where $I_P(Zn)$ is the peak current [µA] and $c(Zn)$ is the concentration [µgl^{-1}]), with $R^2 = 0.998$, the signal reproducibility (for $n = 6$) with the RSD of ± 8.8 %, and a LOD (3σ) of about 15 µg l^{-1} Zn^{2+} (estimated for three replicates in a model sample with 25 µg l^{-1} Zn^{2+} and preconcentration for 120 s)

A quite important finding was made with mixtures of Zn^{2+}, Cd^{2+} and Pb^{2+} where the response for zinc had always been found higher than that obtained in solutions with Zn^{2+} ions alone. This enhancement (caused by both Cd^{2+} and Pb^{2+}) is illustrated in Fig. 3, making comparison between the Zn-peaks before and after addition of Cd^{2+} + Pb^{2+} ions.

Such behaviour might be explained by formation of intermetallic compounds of the Zn_aMe_b type, which is typical for the ASV of zinc at metal-film plated electrodes and related sensors (see Refs in [26]). In the presence of Cd^{2+} + Pb^{2+}, the response for zinc could also be calibrated with a LOD lowered down to

5 μg l^{-1} Zn^{2+}; however, with respect to practical determinations, the whole phenomenon would require additional studies yet in order to ensure a satisfactory reproducibility for quantitative determinations.

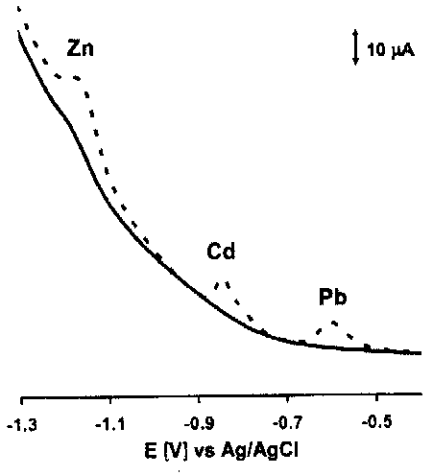


Fig. 3 The effect of Cd^{2+} + Pb^{2+} ions on the anodic stripping voltammetric response for zinc: Legend: —— ... 50 μg l^{-1} Zn^{2+}, – – – ... 25 μg l^{-1} Cd^{2+} + 50 μg l^{-1} Pb^{2+}. Experimental conditions: 0.1 M AmB. For other conditions, see Fig. 2

Determination of In^{3+}. For this metal ion, measurements with ammonia-buffered solutions were totally unsuccessful, exhibiting no response for indium over the entire concentration range examined (50-3000 μg l^{-1} In^{3+}). As experimentally confirmed, the reason for such a behaviour was the precipitation of oxo / hydroxo compounds, InO(OH) and $In(OH)_3$ .n H_2O, formed at pH > 7 (see [32]).

Determination of Cd^{2+} + Pb^{2+}. SWASV of these two metal ions, representing nearly "essential" model pair for testing new methods with BiFEs and BiEs [2-4], resulted in well-developed signals. As can be seen in Fig. 4, both Cd and Pb peaks are slightly shifted towards more negative potentials compared to the respective signals in acetate buffer (dotted line), which corresponds to a capability of NH_3 + NH_4Cl mixtures to form weak ammin-complexes, e.g. $[Me^{II}(NH_3)_4]^{2+}$, with both cations (see [35] and the corresponding equilibrium constants given).

Simultaneous analysis of Cd^{2+} and Pb^{2+} in ammonia buffers has also revealed that the Bi-CPE could detect cadmium with a twice higher sensitivity than that for lead. This — also evident in Fig. 3 when the concentrations of both ions and the resultant peak currents are compared — is a specific feature of bismuth-based electrodes and being opposite to a relation known for traditional mercury electrodes [2-4].

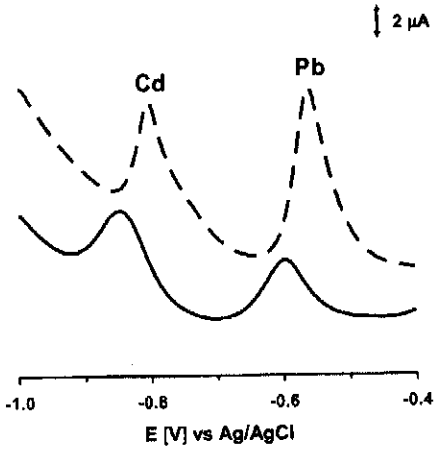


Fig. 4 Anodic stripping voltammetry for a mixture of Cd(II) and Zn(II) in ammonia buffer (——) and acetate buffer (– – –). Experimental conditions: 0.1 M NH_3 + NH_4Cl (pH 8.80); 0.1 M CH_3COOH + CH_3COONa (pH 4.45); c(Cd) = 25 μg l^{-1}, c(Pb) = 50 μg l^{-1}; E_{ACC} = –1.1 V, E_{INIT} = –1.0 V. For other conditions, see Fig. 2

Regarding the choice of ammonia buffer and a Bi-CPE to determine Cd^{2+} and Pb^{2+}, SWASV responses for both ions were found proportional to concentrations of 10-200 μg l^{-1} with LODs reaching down to the low microgram level. In fact, even such values could not compete with the results attainable in acetate buffers, in which one can achieve a wider signal-to-concentration proportionality and the LODs far below 1 μg l^{-1} [22,23]. This also applies to other heavy metal ions [2-4] and thus, acetate buffer-based solutions seem to stay the most appropriate supporting solutions for both BiFEs and BiEs with respect to their overall analytical performance in the ASV mode.

Determination of Tl^+. In the schedule of experimental work with the Bi-CPE in ammonia buffer, ASV of univalent thallium was surprisingly the most interesting topic, exposing some atypical phenomena and unexpected behaviour. First, as found, SWASV of model solutions with c(Tl) > 100 μg l^{-1} gave rise to a couple of peaks featured in Fig. 5, which was unusual observation compared to the ASV behaviour of Tl(I) at BiFEs in acetate buffers [1,25].

When considering minimal complexing capabilities of Tl(I) [35], the appearance of the second peak with E_P = of –0.7 V vs. Ag/AgCl can likely be explained by (i) the formation of an intermetallic compound or a low-melting alloy with bismuth itself [2–4], dispersed at very high concentration in the electrode surface layer. Other interpretations for the occurrence of two peaks could be (ii) a consecutive reoxidation $Tl^{I} \rightarrow Tl^{III}$ in complex species formed at a higher pH

[32,35] and reducible at more negative potentials or (ii) due to the electrode heterogeneity exhibiting a different activity (energy) for two distinct surface regions [27].

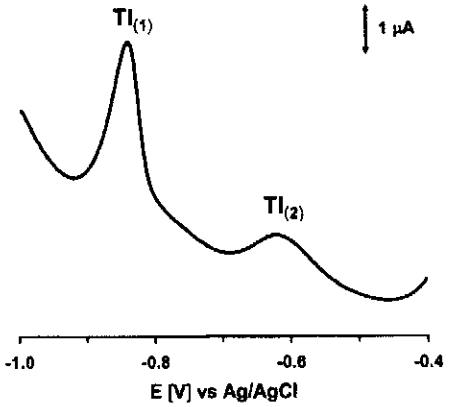


Fig. 5 Anodic stripping voltammetry of Tl^+ ions at a higher concentration in 0.1 M ammonia buffer. Experimental conditions: $c(Tl) = 250\ \mu g\ l^{-1}$. For other conditions, see Figs 2 and 4

Both peaks, denoted as $Tl_{(1)}$ and $Tl_{(2)}$, were found to be proportional to the additions of Tl^+ ions within a concentration range of 100-500 $\mu g\ l^{-1}$. They could be characterised by a pair of regression equations: $I_P[Tl_{(1)}] = 0.073\ c[Tl_{(1)}] - 0.484$ with $R^2 = 0.997$, and $I_P[Tl_{(2)}] = 0.006\ c[Tl_{(2)}] - 0.048$ with $R^2 = 0.974$, respectively (where I_P is again the peak current in μA and c is the concentration in $\mu g\ l^{-1}$). Otherwise, SWASV analysis of model solutions with lower concentrations (20-100 $\mu g\ l^{-1}$ Tl^+) resulted in single peaks with $E_P = -0.9$ V reproducible with the RSD ($n = 6$) of ± 4.6 % and detectable down to a LOD (3σ) of about 12 $\mu g\ l^{-1}$ Tl^+.

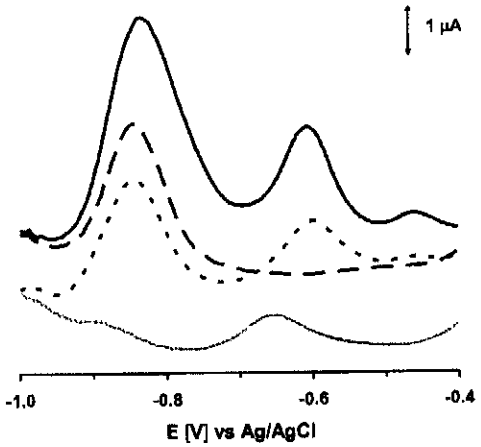
Last but not least, the most valuable experience throughout the study was connected with mixtures of $Tl^+ + Cd^{2+} + Pb^{2+}$ ions. All the relevant results are depicted as four sets of voltammograms, gathered in Fig. 6 A–D.

As can be seen from the corresponding legends, the crucial factor for the behaviour of each metal present in these mixtures was also the order in which the respective ion had been introduced to the solution. The individual observations can then be described as follows:

(A) When Cd^{2+} and Pb^{2+} ions were added first, a couple of well-defined signals for both metals could be obtained with $E_P(Cd) = -0.85$ V and $E_P(Pb) = -0.60$ V vs. Ag/AgCl.

The introduction of Tl^+ into this mixture resulted in a marked enhancement of the Cd-peak, giving rise to a large signal — the overlapped response "Cd +

A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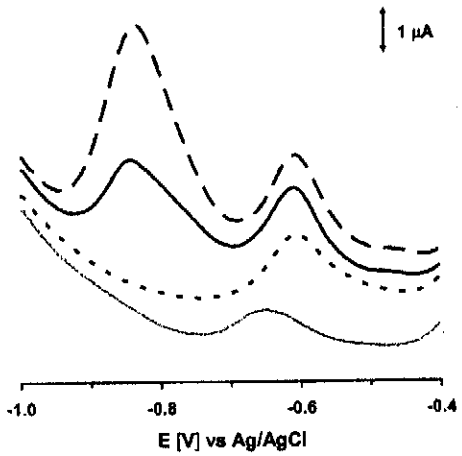
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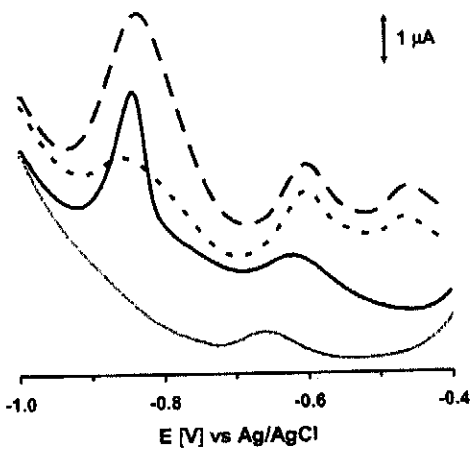
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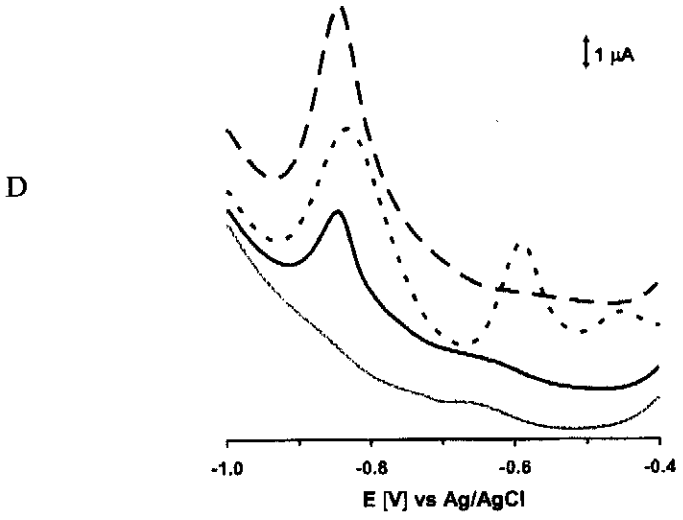

Fig. 6 Studies on the anodic stripping voltammetric behaviour of $Tl^+ + Cd^{2+} + Pb^{2+}$ ions as mixtures in 0.1 M ammonia buffer and the effect of EDTA. Legend: A) order of addition: Cd, Pb, Tl, EDTA; B) Pb, Tl, Cd, EDTA; C) Tl, Pb, Cd, EDTA; D) Tl, Cd, Pb, EDTA; —— ... mixture with Tl (actually present), – – – ... with Cd, - - - - - ... with Pb, —— ... with EDTA. Experimental conditions: $Bi_{17\%}$-CPE; c(Tl) = 100 μg l^{-1}, c(Cd) = 25 μg l^{-1}, c(Pb) = 50 μg l^{-1}; c(EDTA) = 10 mg l^{-1}. Other conditions were as those in Figs 2 and 4

Tl". Meanwhile, a small peak with $E_P = -0.45$ V appeared close to the anodic dissolution of Bi. After adding EDTA, all these peaks had disappeared while a new one was formed at $E_P = -0.65$ V, the origin of this peak being still rather unclear.

(B) Similar observations could also be made after introducing the three ions in the sequence $Pb^{2+} \rightarrow Tl^+ \rightarrow Cd^{2+}$, except that small response at the foot of Bi-dissolution is less developed.

(C) By adding Tl^+ ions as first in the series, the above-emphasised pair of peaks for Tl was obtained as a sharp peak with $E_P(Tl_{(1)}) = -0.85$ V and a flat response at $E_P(Tl_{(2)}) = -0.63$ V vs. Ag/AgCl. After introducing Pb^{2+} ions, the $Tl_{(1)}$ signal significantly decreased, accompanied by the appearance of a fused response "Pb+$Tl_{(2)}$" and a third peak with $E_P = -0.45$ V. The latter remained almost unchanged when adding Cd^{2+} ions, but disappeared in the presence of EDTA and left again not fully identified signal.

(D) Finally, whereas ASV with Tl^+ and Cd^{2+} mixture practically did not revealed the $Tl_{(2)}$-peak, the adding of Pb^{2+} ions and the introduction of EDTA to the solution caused nearly the same changes in the respective peaks noticed in all three preceding experiments.

The individual observations and findings described in the previous paragraphs (A–D) can be summarised as follows: the preconcentration and detection of thallium(I) is accompanied by various interactions, involving the formation of alloy-like adducts with bismuth, the appearance intermetallic compounds with lead or even "extra" redox transformation of thallium under particular conditions of ammonia-buffered media; all these effects giving rise to specific ASV signals.

Conclusion

It can be stated that the above-discussed investigations have provided a useful supplementary material to the already existing studies on the characterisation of bismuth-modified electrodes in solutions of mineral acids [6-8,25], acetate buffers or similar weakly acidic media ([1-4,33]), and alkaline hydroxides [23,25]. As demonstrated herein, ASV with both BiFEs and BiEs can also be accomplished in media of ammonia buffers, additionally offering some specific features for practical measurements.

This is especially true of the determination of thallium where some interesting phenomena observed at the Bi-CPE would require further clarification. For instance, it is inevitable to define the actual concentration relations between Tl(I), Pb(II), Cd(II) and the content of elemental bismuth in the carbon paste mixture. Or, there is still a need to explore mutual redox transformations between Tl^{I} and Tl^{III} oxidation states under different conditions, including the effect of complex-forming supporting media compared to indifferent solutions. In fact, such advanced studies are still missing [2-4] and could, therefore, represent a first report devoted exclusively to the electrochemistry of thallium at bismuth-based electrodes. Also, they could for the first time offer a hitherto unknown procedure for the determination of thallium in real samples — typically, in the presence of other heavy metal ions that may occur at considerably higher concentrations than that of the Tl^{+} ions themselves [36].

Acknowledgements

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