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A STUDY ON SIMULTANEOUS DETERMINATION OF INDIUM AND CADMIUM AT MERCURY BASED- AND BISMUTH FILM-PLATED ELECTRODES

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Linear sweep anodic stripping voltammetry (LSASV) and differential pulse anodic stripping voltammetry (DPASV) have been used for the simultaneous determination of In and Cd in hydrochloric acid-based media at the hanging mercury drop electrode (HMDE), mercury-, and bismuth-plated glassy carbon electrode (MF-GCE and BiF-GCE, respectively). The main focus of the study was concentrated on the comparison of the resolution of In- and Cd-signals achieved by means of the three investigated working electrodes. Whereas the LSASV as well as DPASV signals for indium and cadmium almost overlapped when using the HMDE, the corresponding In- and Cd-peaks were well-separated at both MF-

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GCE and BiF-GCE. In addition, at the latter film electrode, a typical resolution as well as the sensitivity of the respective stripping signals were even superior to those evaluated for the MFE. Based on the results obtained, the possibilities and limitations of the individual electrodes are outlined with particular emphasis on the bismuth film-plated electrode substrate.

Introduction

At present, indium and its compounds are used in the production of low-melting alloys and semiconductors. This metal is also occasionally applied in medical research as an internal standard [1] or as labelling element (the indium species are able of binding proteins that can then be detected by immunoassays or some stripping voltammetric methods [2,3]). Since the 1990's, industrial importance of indium is predominantly associated with the boom in computer technologies; namely, with mass production of LCD-monitors. Hand in hand with these trends, the determination of indium is of increasing interest.

Within the spectrum of instrumental techniques applicable to determination of indium, spectrometric and optical measurements are usually preferred; especially, absorption spectrometry with flame and electrothermal atomisation (FAAS, ET-AAS [4-6]) or inductively coupled plasma atomic emission and mass spectrometry (ICP-AES, ICP-MS, [7–9]). The respective methods often offer excellent analytical performances; nevertheless, economical aspects are less favourable due to high purchase expenses, operational costs, and considerable energy consumption. Moreover, the instrumentation needed for such measurements is only scarcely adaptable to field analysis.

The latter factors are not usually the case of electrochemical stripping analysis (ESA [10]), offering also a number of methods elaborated for the determination of indium — either alone [11,12] or along with other metals [13–15]. Predominantly, the hanging mercury drop electrode (HMDE) or mercury film electrode (MFE) are employed, both utilising effective electrolytic preconcentration *via* amalgamation

$$In^{3+} + 3e^- + xHg \rightarrow In(Hg)_x \qquad (1)$$

During the subsequent stripping step, the intermetallic adduct is re-oxidised back to the In^{3+} ions, thus giving rise to high, well-developed anodic peaks, typical of the three-electron transfer. However, because the re-oxidation (dissolution) potential for reaction $In^0 \rightarrow In^{3+}$ is very close to those of some other metals (Cd,

Pb, Tl, and Sn), the determination of indium using ESA and based on the above principles may suffer from lower selectivity [10]. In addition, the proper stripping step may proceed by two reaction pathways [16,17],

$$In \longrightarrow In^{+} + e^{-} \quad (2)$$

$$In \longrightarrow In^{3+} + 3e^{-} \quad (3)$$

including their combination, i.e., *via* a two-step re-oxidation ($In^0 \rightarrow In^+ \rightarrow In^{3+}$). The problems connected with the poorer selectivity due to insufficient resolution of the peaks of interest can be solved using some special procedures. For instance, one may use other modifications of ESA, based on non-electrolytic pre-concentration mechanisms such as adsorptive stripping voltammetry (AdSV [10]). Regarding the determination of indium, this is the case of a method with *Morin* [18], which is a classical analytical reagent binding the In^{3+} ions into a complex with strong affinity to the electrode surface.

Should the electrolytic accumulation be the principle of choice, there are also some possibilities of how to improve the selectivity parameters for the determination of indium; in particular, if cadmium is the main interfering element. In these cases, often overlapped signals of In and Cd can be — partially or completely — resolved (i) by mathematical analysis of experimental curves (deconvolution voltammetry, see e.g. [19] and the Refs therein) or by adding some special reagents such as (ii) complexing agents [20] or (iii) surfactants [14,15]. Furthermore, even (iv) appropriate combination of a detection mode and an electrode can be helpful as demonstrated on stripping potentiometry with a MFE [21].

Lastly, a better peak resolution after electrolytic accumulation can be achieved with the aid of (v) the working electrode alone.

As shown recently, the last eventuality applies to bismuth film electrodes, BiFEs [22] that have been introduced some years ago [23] as an environmentally friendly alternative to MFEs and mercury-based electrodes in general. In initial studies, glassy carbon electrodes (GCEs) coated with bismuth films have been found to exhibit relatively favourable stripping characteristics for indium [24]. And, as ascertained in a very recent study making a direct comparison in performance of both BiFE and MFE [25], the bismuth film-plated substrates have shown markedly better resolution of In-peaks with respect to other signals of

potentially interfering heavy metals, including cadmium. Thus, it seems that especially the use of BiFEs offers new and elegant approaches in electrochemical stripping analysis of indium.

The same topic is of main interest in this report focused exclusively on ESA of model mixtures of In^{3+} + Cd^{2+} ions when confronting directly the performance of the HMDE, MFE, and BiFE. Possibilities and limitations of the three electrodes are then discussed with respect to the resolution and other distinct stripping characteristics of both In- and Cd-signals obtained in two different anodic voltammetric modes. The observations and results obtained are summarised below.

Experimental

Chemicals and Reagents

Hydrochloric acid (Suprapur® grade, *Merck*), In^{3+}, and Cd^{2+} standard stock solutions (1.000 ± 0.001 g l^{-1} In^{3+} and Cd^{2+}, respectively) were used when diluted as required prior to use. A solution for plating with bismuth film *in situ* containing 0.04 M Bi^{3+} was prepared by dissolving the appropriate amount of recrystallised $Bi(NO_3)_3$ in 100 ml water. For experiments with the MFE, a solution containing 0.04 M Hg^{2+} was prepared from $Hg(NO_3)_2$ (p.a. grade; *Polskie Odczynniky Chemiczne*, Gliwice, Poland).

All the solutions were prepared using deionised water produced in an ion-exchange purification system (*Cobrabid-Aqua*, Warsaw, Poland). Argon (99,99%) was used to remove dissolved oxygen from solutions before the analysis.

Apparatus and Instrumentation

All the voltammetric measurements were carried out with a multipurpose electrochemical analyzer (model "EA9"; *MTM* Krakow, Poland) connected to a personal computer and controlled by EAGRAPH software, version 5.0. The measurements were performed with the three-electrode configuration (see below). Magnetic Teflon®-coated bar was used for stirring of the solution during the accumulation period when agitated at approx. 300 rpm by an electric motor integrated into the electrode stand.

Electrodes

Working Electrodes. As the electrode substrate for plating with either bismuth or mercury film, a glassy carbon electrode (GCE, disc configuration, ⌀ = 3 mm;

BAS, USA) was employed. The third working electrode used was a hanging mercury drop electrode ("Control Growth Mercury Drop Electrode", *MTM*, Krakow, Poland) set throughout the work to operate with the drop surface area of 1.17 mm^2.

Reference and Auxiliary Electrodes. A self-made Ag/AgCl electrode with 3 M KCl as inner electrolyte and a Pt-plate (2×3 mm) completed the electrode cell.

Procedures

Polishing of the Glassy Carbon Electrode Surface. The surface of the GCE was cleaned mechanically by polishing with two subsequent portions of an alumina slurry (0.3 or 0.05 μm; Buehler, USA) on a polishing pad to obtain a mirror-like appearance. Before each measurement, the electrochemical pre-cleaning (regeneration) was used as well.

Preparing of Bismuth Film Glassy Carbon Electrode, BiF-GCE. The bismuth film was deposited *in situ* onto the GCE surface. If not stated otherwise, the total concentration in solutions containing 0.1 M HCl was 1×10^{-5} M Bi^{3+}. In the case of using MF-GCE, the plating regime was the same, inclusive of the concentration of the Hg^{2+} ions.

Stripping Voltammetry. After preparation of solutions and their deaeration with inert gas, typical measurement was performed as follows. First, pre-cleaning step was made by applying a potential of +200 mV vs Ag/AgCl when using BiF-GCE and +300 mV in the case of MFE; both lasting for 30 s. Then, the deposition (accumulation) was performed at a potential of –1000 mV for 90 s when using MF-GCE and 60 s for BiF-GCE; both in stirred solution. For the HMDE, the deposition was also 60 s. Stripping curves were recorded anodically in the linear sweep voltammetric (LSV) or differential pulse voltammetric (DPV) mode. The scan (run at 200 mV s^{-1} for LSV and 25 mV s^{-1} for DPV) was terminated at a potential according to the electrode used (BiF-GCE: +200 mV, MF-GCE: +300 mV, HDME –250 mV).

Data Processing and Evaluation

Analytical signals were measured as the peak heights (i.e., current intensities [μA]) or as peak potentials (vs. Ag/AgCl, [mV]). The individual peaks were then evaluated by manual base-line setting controlled by the EAGRAPH software.

Results and Discussion

The peak characteristics of the In- and Cd-signals obtained using both linear sweep anodic stripping voltammetry (LSASV) and differential pulse anodic stripping voltammetry (DPASV) at the HMDE, MF-GCE, and BiF-GCE are listed in Table I, parts A and B. The final resolutions, representing the primary criterion in this study, are then given *extra* in part C. Representative sets of voltammograms obtained with all three electrodes are then illustrated in Figs 1, 2, and 3.

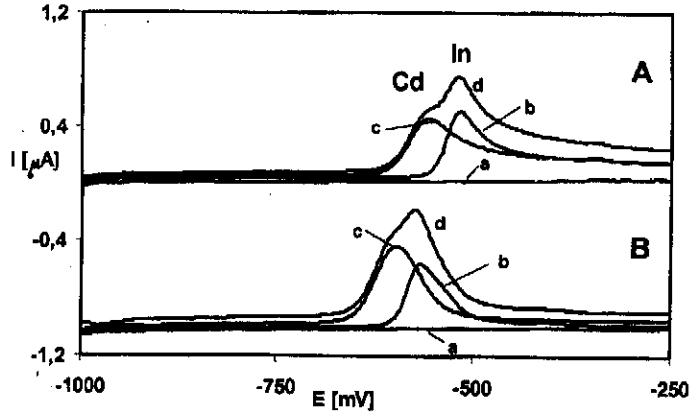

Fig. 1 Anodic stripping voltammograms obtained by analysing the In^{3+} and Cd^{2+} ions separately and as an $In^{3+} + Cd^{2+}$ mixture at the HDME using linear sweep anodic stripping voltammetry, LSASV (A), and differential pulse anodic stripping voltammetry, DPASV (B). Legend: a) base-line, supporting electrolyte: 0.1 M HCl (pH ca. 1), b) + 350 $\mu g\, l^{-1}$ In^{3+}, c) + 350 $\mu g\, l^{-1}$ Cd^{2+}, d) + 350 $\mu g\, l^{-1}$ In^{3+} and 350 $\mu g\, l^{-1}$ Cd^{2+}. Experimental conditions: mercury drop surface, 1.17 mm^2; deposition time, t_{DEP} = 60 s; deposition (initial) potential, E_{DEP} = -1000 mV; final potential, E_{FIN} = -250 mV; LSV mode: scan rate, v = 200 $mV\, s^{-1}$, DPV mode: v = 25 $mV\, s^{-1}$, pulse height (amplitude), ΔE = -50 mV

All the experiments were carried out in 0.1 M HCl selected as the supporting electrolyte of choice in order to demonstrate, in a straightforward way, analytical performance of the individual types of electrodes. As can be seen from the data in Table I as well as from the respective voltammograms, the HMDE was almost inapplicable to separate the peaks of interest, whereas both MF-GCE and BiF-GCE offered relatively satisfactory results. In order to evaluate the resolution of both In- and Cd-signals as reliably as possible, the concentrations of both In^{3+} and Cd^{2+} ions had been selected at levels yielding approx. the same magnitude of the peaks intended for evaluation. Such a choice had also respected rather different

Table I Anodic stripping voltammetric analysis of the In^{3+} and Cd^{2+} ions separately and in mixtures; A survey of peak characteristics and parameters (peak currents correlated to the concentration and deposition time used, $I_{REL}(Me) = I_p(Me)/c(Me) \times t_{DEP}$ [$\mu A\, l\, \mu g^{-1}\, s^{-1}$]; the peak potential, E_p; and the half-width, $W_{1/2}$, evaluated for measurements at three different working electrodes. Data for: A) indium, B) cadmium, and C) the final resolutions, ΔE_p. Experimental conditions: 0.1 M HCl (pH = 1); $c(In)$ = 350 $\mu g\, l^{-1}$ for MF-GCE and BiF-GCE, 1000 $\mu g\, l^{-1}$ for HMDE; $c(Cd)$ = 50 $\mu g\, l^{-1}$ for MF-GCE, 100 $\mu g\, l^{-1}$ for BiF-GCE, and 350 $\mu g\, l^{-1}$ for HMDE; deposition time, t_{DEP} = 60 s for HMDE and BiF-GCE, 90 s for MF-GCE; deposition (initial) potential, E_{DEP} = −1000 mV; final potential, E_{FIN} = −250 mV for HMDE, +200 mV for BiF-GCE, +300 mV for MF-GCE; scan rate, ν = 200 mVs^{-1} for LSV mode, 25 mVs^{-1} and the pulse height (amplitude), ΔE = −50 mV for DPV mode. Note: Numbers in parentheses represent approximate values

Part A: In, In + Cd		Stripping signals for In (analysed alone)			Stripping signals for In in the presence of Cd		
Electrode used	Stripping Technique	$I_{REL}(In)$ $\times 10^{-5}$	$E_p(In)$ mV	$W_{1/2}(In)$ mV	$I_{REL}(In)$ $\times 10^{-5}$	$E_p(In)$ mV	$W_{1/2}(In)$ mV
HMDE	LSASV	2.19	-516	-55	3.14	-520	—
	PASV	2.09	-566	-55	3.52	-572	—
MF–GCE	LSASV	9.51	-565	27	6.08	-553	27
	DPASV	2.31	-616	26	1.68	-610	24
BiF–GCE	LSASV	30.01	-634	36	32.28	-637	39
	DPASV	6.28	-696	40	6.67	-700	44

Part B: Cd, Cd + In		Stripping signals for Cd (analysed alone)			Stripping signals for Cd in the presence of In		
Electrode used	Stripping technique	$I_{REL}(Cd)$ $\times 10^{-5}$	$E_p(Cd)$ mV	$W_{1/2}(Cd)$ mV	$I_{REL}(Cd)$ $\times 10^{-5}$	$E_p(Cd)$ mV	$W_{1/2}(Cd)$ mV
HMDE	LSASV	1.9	-556	80	2.14	-552	—
	DPASV	2.52	-598	64	2.76	-600	—
MF-GCE	LSASV	69.33	-675	39	87.11	-672	42
	DPASV	38.34	-726	42	51.33	-721	42
BiF-GCE	LSASV	80.33	-778	48	104.3	-778	30
	DPASV	52.33	-828	54	61.01	-828	36

Part C: $\Delta E_p = E_p(Cd) - E_p(In)$ Resolution, mV			
Electrode used	Stripping technique	ΔE_{SNG} mV	ΔE_{MIX} mV
HMDE	LSASV	40	32
	DPASV	32	28
MF-GCE	LSASV	110	119
	DPASV	110	111
BiF-GCE	LSASV	144	141
	DPASV	132	128

Legend: (Parts A–C): -- ... not evaluated; ΔE_{SNG} ... the peak potential difference calculated from single signals (In^{3+} and Cd^{2+} analysed separately); ΔE_{MIX} ... the difference calculated from paired signals (In^{3+} and Cd^{2+} analysed in mixtures).

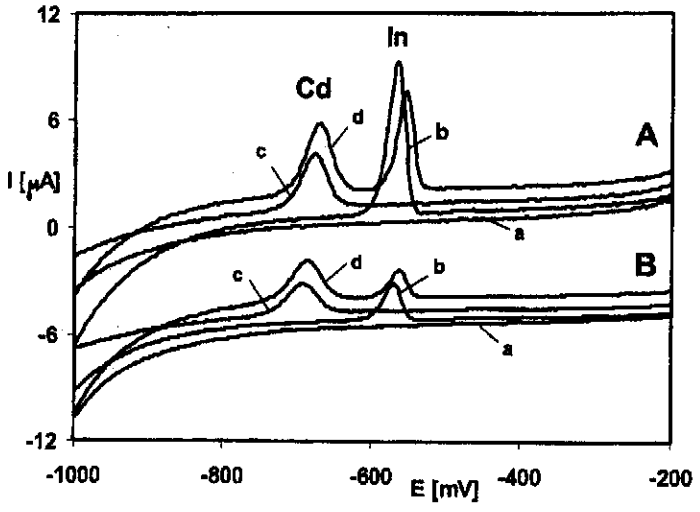

Fig. 2 Anodic stripping voltammograms obtained by analysing the In^{3+} and Cd^{2+} ions separately and as an In^{3+} + Cd^{2+} mixture at MF-GCE using LSASV (A) and DPASV (B). Legend: a) base-line, 0.1 M HCl + 2 mg l^{-1} Hg^{2+}, b) + 1000 μg l^{-1} In^{3+}, c) + 50 μg l^{-1} Cd^{2+}, d) +1000 μg l^{-1} In^{3+} and 50 μg l^{-1} Cd^{2+}. Experimental conditions: t_{DEP} = 90 s; E_{FIN} = +300 mV. For other conditions, see legend in Fig. 1

sensitivities of the three sensors (see the concentrations analysed and the respective current intensities in figures). This variability in experimental conditions had to be reflected in the tabled data, where the peak heights are given as quotients, I_{REL}(Me), correlating the different concentrations and deposition periods (see table headlines). The original current intensities, I_p(Me), can then be imaged from the voltammograms in Figs 1 – 3.

In the case of the HMDE and LSASV mode (Fig. 1A), both In- and Cd-peaks can still be identified, but they are merged together and the response for cadmium is seen solely as a small shoulder superposed upon the left side of the In-peak (curve d). The difference in the respective peak potentials, $\Delta E_p = E_p(Cd) - E_p(In)$, was found to be below 40 mV for both situations studied regardless whether one had differentiated the signals obtained in separate solutions or from model mixtures of In^{3+} + Cd^{2+} (see again Table, sections A-C). Almost identical voltammograms were registered when combining HMDE with DPASV, the resultant resolution being even worse (Fig. 1B). Badly developed signals at the HMDE, giving rise to a tailing of peaks, also explain why the corresponding $W_{1/2}$

parameter could not been evaluated properly (see Note in table headlines). It can be stated that experiments with the HMDE have confirmed that the application of a mercury drop electrode in ESA of indium requires an additional intervention; i.e., some of special steps pointed out in the Introduction.

When similar assays were carried out with the MF-GCE, the resolutions in the stripping peak potentials were significantly better, extending up to ΔE_p = 120 mV as illustrated in Table and Fig. 2. The sets of voltammograms obtained with MF-GCE revealed also some phenomena behind the stripping process as well as some interesting relations. First, when comparing the overall shape of both peaks (and the corresponding $W_{1/2}$ values), it is apparent that the re-oxidation of indium has involved three electrons according to the above-given chemical equation — see Introduction, Eq. (3).

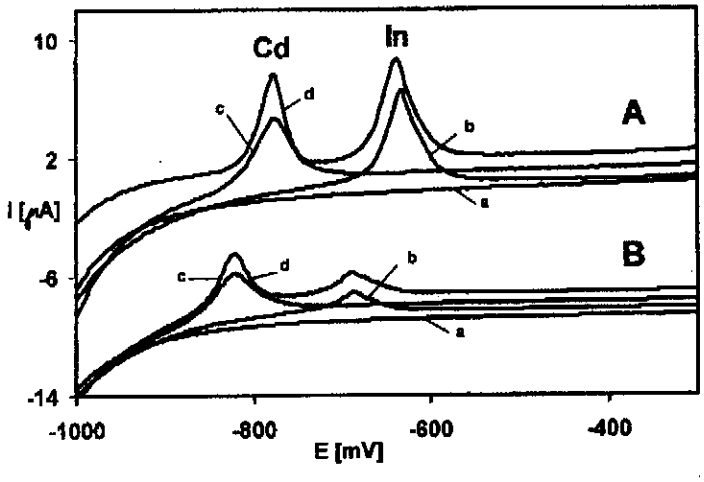

Fig. 3 Anodic stripping voltammograms obtained by analysing the In^{3+} and Cd^{2+} ions separately and as an In^{3+} + Cd^{2+} mixture at BiF-GCE using LSASV (A) and DPASV (B). Legend: a) base-line, 0.1 M HCl + 2 mg l^{-1} Bi^{3+}; b) + 350 μg l^{-1} In^{3+}, c) + 100 μg l^{-1} Cd^{2+}, d) + 350 μg l^{-1} In^{3+} and 100 μg l^{-1} Cd^{2+}. Experimental conditions: t_{DEP} = 60 s; E_{FIN} = +200 mV. For other conditions, see legend in Fig. 1

Secondly, the MF-GCE exhibited quite poor sensitivity towards indium, which required an addition of In^{3+} ions in a 20-fold excess in concentration over Cd^{2+}, which was not very promising with respect to the analytical performance of the MFE. Moreover, it was observed that the addition of Cd^{2+} ions into the solution containing the In^{3+} species had caused an increase of the Cd-signal and contrarily, the In-peak had decreased with the increasing content of cadmium compared to an experiment performed in its absence. This — together with slight changes in the peak positions (see nuances in ΔE_{SNG} and ΔE_{MIX} values) — indicated some mutual interference, probably due to the formation of intermetallic

compounds [10,17].

Similarly as with the MF-GCE, measurements at the bismuth film have also revealed a certain trend in the increase of Cd-response during repetitive scanning. Finally, a mention should be made about the relative sizes of peaks recorded in two different voltammetric modes (compare sets of curves in Figs 2A and B). Normally, at comparable scan rates, DPASV gives much more sensitive responses than LSASV and, in both techniques, the overall magnitude of the signals increases with higher scan rates [10]. If the difference in polarisation ramp is significant, LSASV may give rise to larger signals than DPASV. This is the case of the study discussed herein because preliminary optimisation measurements with the LS voltammetry had favoured sweeps of 200 $mV\ s^{-1}$ with respect to the overall signal-to-noise characteristics. As seen in figure captions, such scans are nearly 10× faster than that applied in the DPASV and, therefore, higher LSASV peaks are obvious.

Regarding the comparison in operability of both metal film electrodes, it can be noticed — besides the peak shape character implying again the three-electron transformation — that the BiF-GCE has offered the most satisfactory resolution of In- and Cd-peaks in the concentration range studied, reaching nearly 150 mV. Similar values seem to be already sufficient to think about elaborating a method for simultaneous determination of indium and cadmium at a BiFE.

Also, such attempts may utilise a markedly higher sensitivity of the bismuth film compared to mercury (see again concentrations of In^{3+} and the corresponding peak heights for all three types of electrodes). For more conclusive statements, however, additional information material is yet necessary. Among others, it is inevitable to gather the data for wider concentration limits of both In^{3+} and Cd^{2+} ions in order to define the detection capabilities of a BiFE, including its combination with other detection modes such as square-wave voltammetry [25]. Also, when using again some comparative experiments with MFE and HMDE, it appears more convenient to choose the same concentrations and deposition periods for both In^{3+} and Cd^{2+} despite different sensitivities of the individual electrodes. Last but not least, investigations on the signal reproducibility and systematic interference studies with selected metal ions should not be omitted either.

Conclusion

One of the main goals of this article was to document the usefulness of bismuth film-plated electrodes that still represent a relatively new type of sensors [22,23] needing another popularisation. As demonstrated by analysing model mixtures of In^{3+} and Cd^{2+} in highly acidic solutions, BiF-GCE may offer the performance superior to traditional mercury electrodes; mainly, with respect to a better resolution of the adjacent stripping signals and considerably higher sensitivity

towards indium. These features are in good accordance with the previous results of a preliminary report [25].

The authors of this report do hope that even not very abundant results presented within this study will be somewhat inspiring for the continuing investigations on applicability of BiFEs to the determination of indium as well as other less-common metals.

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