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**ATTRACTIVE APPLICATIONS OF LESS NOBLE
METAL IONS IN STRIPPING VOLTAMMETRY
AT METAL FILM ELECTRODES**

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An overview is dished up to show how the presence of a less noble metal ion in the samples subjected to electroanalytical measurements may sometimes lead to a positive effect on determinations of some analytes at the trace concentration level. First, an unexpected behaviour of Sb-based electrodes is mentioned allowing one its application also in the anodic potential range. A role of less noble metals is documented on the stripping voltammetric determination of mercury(II) or bismuth(III) at antimony film-coated carbon paste electrodes, where an apparent catalytic effect caused by the presence of cadmium(II) was observed offering a significant improvement of the analytical signal for both the cations. This

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phenomenon was attributed to the formation of intermetallic compounds during the electrolytic accumulation at the electrode surface.

Very recently, a new approach was reported based on the preparation of metal film electrodes that utilize the combination of ex situ and/or in situ plating methods and the use of reversibly deposited mediator. By plating the metal film onto the surface of glassy carbon electrode together with zinc acting as mediator metal, followed by its subsequent oxidation and further deposition of the metal of interest, a higher surface coverage of the electrode with metal particles could be achieved. Application of the newly developed technique was demonstrated on the determination of nickel(II) at a lead film electrode with the aid of adsorptive stripping voltammetry, as well as on the determination of tin(IV) at a bismuth film electrode when using square-wave anodic stripping voltammetry.

Introduction

Undoubtedly, all currently used voltammetric techniques devolved from polarography, invented by Jaroslav Heyrovský at the beginning of the thirties of the last century [1,2]. In this technique – as well known – a dropping mercury electrode (DME) is used as the working electrode, which is useful for its wide cathodic range and renewable surface. Further development of methods derived from polarography led to electrochemical stripping analysis (both voltammetric and chronopotentiometric), in which the hanging mercury drop electrode (HMDE) had initially been used, later replaced by the mercury film electrode (MFE). In fact, mercury electrodes are among the best and exceptional sensors for electroanalytical measurements. First, because of the dropping regime at DME, it imitates behaviour of the ideally polarized electrode. Secondly, thanks to the high hydrogen overvoltage at both DME and HMDE, these electrodes can be applied in a wide range of negative potentials. Regardless of these characteristics, some environmental activists have begun to spread phobia of mercury and started to call for the so-called “green chemistry”, resulting in a search for new electrode materials. As indicated by recent results, HMDEs or MFEs can, in many cases, be substituted with the solid amalgam electrodes (SMEs) [3] being claimed to be non-toxic since the mercury in the amalgam is not readily released [4].

Nevertheless, also other materials were recently applied as new “green” metal and metal film electrodes. First, the bismuth film electrode (BiFE) was reported in 2000 [5]. Whole topic has already achieved a respectable position within the research activities devoted to the development and application of bismuth-based electrodes (see e. g. reviews [6-9]). Similarly, attempts with modification of screen-printed carbon electrodes using either Bi_2O_3 or Sb_2O_3 were realized [10], but first antimony film electrodes (SbFEs) employed in combination with stripping analysis utilizing either the glassy carbon [11] or carbon paste

supports [12] were reported in 2007. Within next five years, gallium [13], lead [14], selenium [15], tantalum [16] and tin film electrodes [17] were also been recommended. It should be mentioned that all the metals mentioned are capable to form alloys comparable to amalgams formed on mercury. Concerning the supports, glassy carbon is usually subjected to *ex situ* or *in situ* modification to achieve the desired metal film, but carbon paste electrodes can be applied as well (see [18-22] and references therein).

As well known, stripping analysis is a combination of separation and electrochemical procedures performed in two main steps [23-26]. The first one involves a pre-concentration of the target metal(s) under controlled conditions; the deposition being performed either by adsorption or by electroplating on the electrode surface. The analyte accumulated is then electrolytically or chemically dissolved – “stripped off”; this stripping step being followed by a voltammetric or chronopotentiometric measurement. In this paper, we would like to show some of the effects associated with the use of selected metal film electrodes and especially, how the presence of less noble metal ions may sometimes improve the stripping voltammetric determination of target analytes.

Unexpected Behaviour of Antimony-Based Electrodes

Replacement of mercury electrodes with other metal-based ones resulted in partial limitation of their application in the cathodic range because of the hydrogen evolution occurring at less negative potentials. Nevertheless, they can successfully be applied in the determinations of trace amounts of heavy metal ions, such as lead(II), cadmium(II), etc. On the side of positive potentials, we are usually limited by anodic dissolution of the respective metal.

In connection with that, an interesting phenomenon was noticed in the stripping voltammetric determination of copper(II). Regarding this metal ion, bismuth-coated glassy carbon [27] or carbon paste electrodes [28] have been shown applicable despite its more positive stripping potential versus bismuth. Anyway, when one looks at the records obtained, it appears that there is a competition in deposition and/or re-dissolution of both metals; with increasing concentration of Cu(II), the peak of Bi(III) decreases (see Fig. 1). However, when an antimony-based electrode is applied in similar measurements, there is nothing like this (see Fig. 2). How to explain this phenomenon? Most likely, this is due to other oxidation reaction taking place at antimony film and proceeding in solid state. In a medium acidified by hydrochloric acid, an oxidation product may be either antimony oxide, Sb_2O_3 , or more probably antimonyl chloride, SbOCl ; both the compounds being practically insoluble in HCl. Thus, where there is no diffusion, there is no current response. As a result, the electrode can also be applied at more anodic potentials, although in this region it cannot be classified as the SbFE.

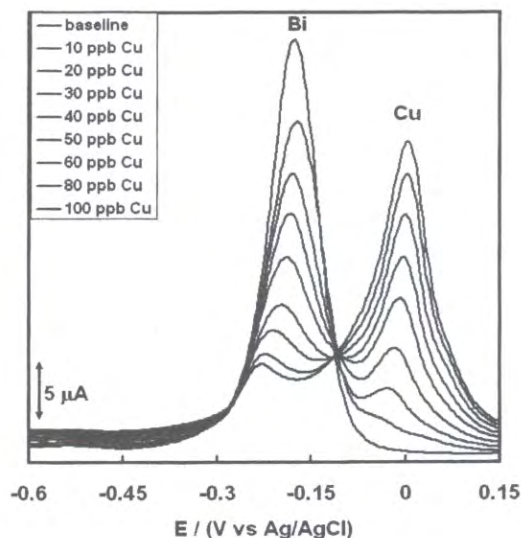


Fig. 1 Anodic stripping voltammograms of copper calibration obtained at a CPE. Carbon paste contained silicone oil and was operated *in situ*. Experimental conditions: Square-wave anodic stripping voltammetry (SWASV); 0.2 M acetate pH 4.5 buffer spiked with 1 ppm Bi(III); deposition potential, -1.3 V; final potential, $+0.2$ V (both vs. Ag/AgCl/KCl); deposition time, 60 s; equilibrium period, 15 s; square-wave frequency, 25 Hz; pulse height, 50 mV; step increment, 4 mV. According to Ref. [28]

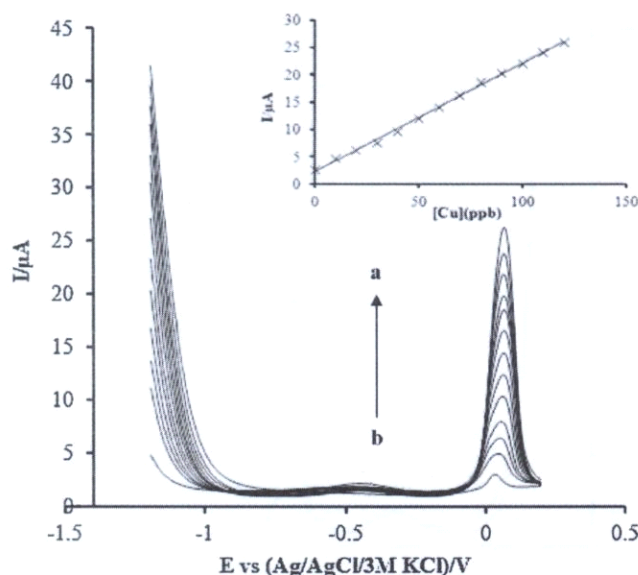


Fig. 2 Construction of the calibration plot for determination of copper(II) in the concentration range of 0-120 ppb. Measured in 0.01 M HCl; Sb(III) concentration, 600 ppb; accumulation potential, -1.2 V; accumulation time, 120 s; equilibrium period, 15 s; square-wave frequency, 25 Hz; pulse amplitude, 25 mV; step increment, 4 mV. Reproduced from Ref. [29] with permission

Effect of Cadmium(II) on the Stripping Voltammetric Determination of Mercury(II) and Bismuth(III) at Antimony Film-Plated Carbon Paste Electrodes

As mentioned in the previous paragraph, thanks to the unexpected behaviour of the antimony-based electrode — namely, its relative resistance in a highly acidic medium — determination of both mercury(II) and bismuth(III) could be realized although the deposition potential of both cations is near to that of antimony(III). Moreover, as observed during experiments, the presence of a less noble metal ion, in this case cadmium(II), had an apparent catalytic effect on the determination of both the above-mentioned heavy metal ions giving rise to a significant improvement of the measured analytical signal. As reported a long time ago, intermetallic compounds CdSb and unstable Cd_3Sb_2 are formed in the cadmium-antimony system [30]; revised data from available databases (e.g. [31]) then indicating a formation of the CdSb alloy in the presence of excess of antimony.

In determination of mercury(II) [32], the presence of Cd(II) has a positive effect upon the shape of stripping voltammograms. As shown in Fig. 3, cadmium gives a peak at -0.8 V. Then, two separated oxidation peaks are observed — a very small one for antimony at -0.2 V and a perspicuous one for mercury at 0.0 V. This phenomenon can hardly be attributed to the above-mentioned alloy formation but, anyway, it can be considered as the catalytic effect of cadmium. Maybe, amalgam-forming capabilities of mercury influence such behaviour as well. In this way, the SbFE proved itself more competent than analogous bismuth-based electrodes.

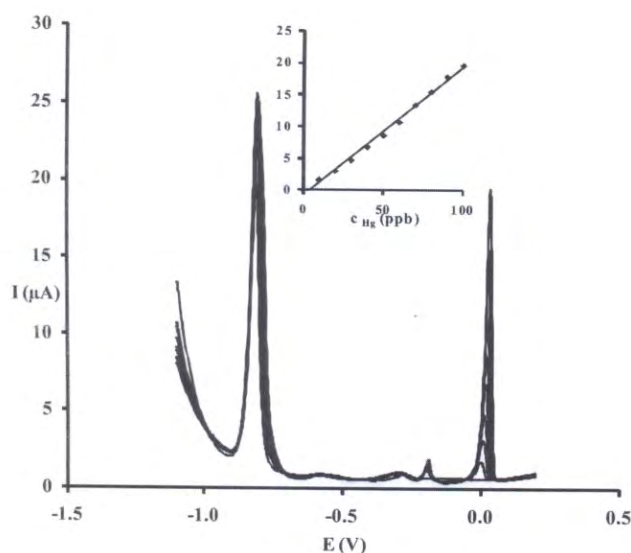


Fig. 3 Square-wave stripping voltammograms for increasing concentration of mercury(II) under optimized conditions in the presence of 1 ppm Sb(III), 150 ppb Cd(II) and successive additions of Hg(II) in 10 ppb steps realized in 0.01 M HCl. Recorded at accumulation potential, -1.1 V; accumulation time, 150 s; SW scan frequency, 25 Hz; pulse amplitude, 25 mV; step height, 4 mV. Calibration graph (inset) for 0-100 ppb Hg(II). Reproduced from [32] with permission

Similarly in the determination of bismuth(III), the use of SbFE in the presence of Cd(II) produced superior results when compared to measurements in the absence of these ions. The most probable reason is that the above-mentioned intermetallic alloys are formed when Sb film is deposited together with Cd(II). This was also documented by microstructural analysis; the morphology of the deposit in the presence of Cd(II) was completely different from that obtained from pure Sb(III) solution [33]. A formation of the intermetallic alloy was confirmed also by voltammograms of the “background” stripping curve obtained from pure Sb(III) plating solution and that obtained in the presence of Cd(II); the small Sb peak occurring at -0.1 V was even smaller and shifted to more negative potentials in the presence of Cd(II). Thus, it seems that, in this case, no pure antimony film but a new intermetallic film is formed having its own characteristic behaviour toward Bi(III). Under optimized conditions, calibration dependence was studied and the corresponding graph constructed (see Fig. 4).

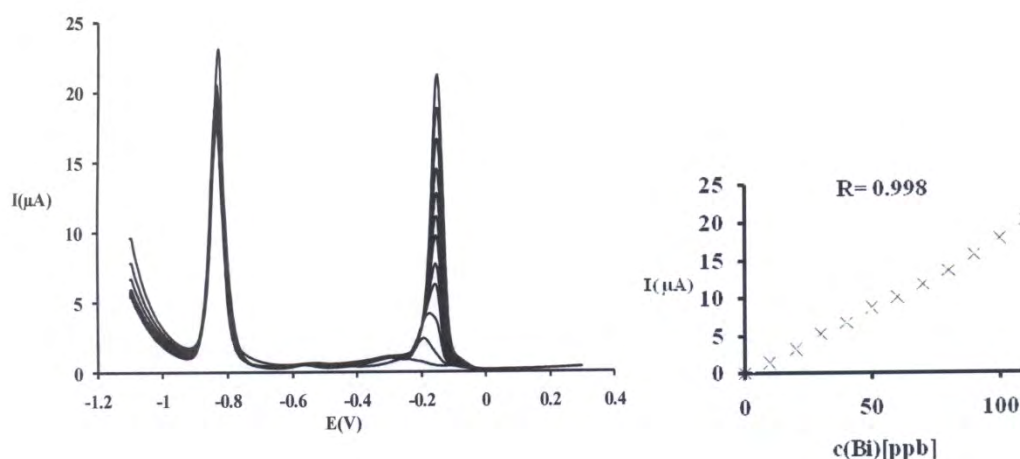


Fig. 4 Square-wave stripping voltammograms for increasing concentration of Bi(III) under optimized conditions in the presence of 1 ppm Sb(III), 50 ppb Cd(II) and successive additions of Bi(III) in 10 ppb steps realized in 0.01 M HCl. Accumulation potential, -1.1 V; accumulation time, 160 s; SW scan frequency, 25 Hz; pulse amplitude, 25 mV; step height, 5 mV (left). Calibration graph (right) for 0-100 ppb Bi(III). Reproduced from [33] with permission

Adsorptive Stripping Voltammetry of Nickel(II) at a Lead Film Electrode Prepared with the Use of a Reversibly Deposited Mediator

Recently, a new technique for preparation of the lead film electrode (PbFE) utilizing the combination of *ex situ* and *in situ* plating methods and the use of reversibly deposited mediator was presented [34]. A necessary feature of the mediator is that it must be less noble than the metal of interest (Pb). Initially, Zn(II) was used as mediator for the preparation of such a “hybrid” PbFE prepared using an electrochemical defect-mediated thin-film growth method [35-37]. Using

this way of plating, lead is first co-deposited with zinc. Subsequently, zinc is oxidized with the ongoing deposition of lead at less negative potentials (for more detailed experimental conditions, see legend in Fig. 5). The use of such mediator in the lead film pre-plating step caused about two-fold increase of voltammetric nickel(II) signal, obtained in the presence of nioxime as a complexing agent. Moreover, the corresponding detection limit was lower than those obtained using unmodified electrodes or electrodes plated with other metal films (MFE, BiFE, SbFE). These favourable properties of the “hybrid” PbFE prepared with the use of the mediator zinc made it suitable for measurements of nickel(II) at the trace level by adsorptive stripping voltammetry. As observed in studies of potentially interfering ions added into the solution with 5×10^{-9} M nickel(II), neither 1000-fold excess of zinc(II), iron(III), copper(II), manganese(II), molybdenum(VI) nor 100-fold excess of vanadium(V) and cobalt(II) affected the nickel(II) stripping voltammetric determination [34].

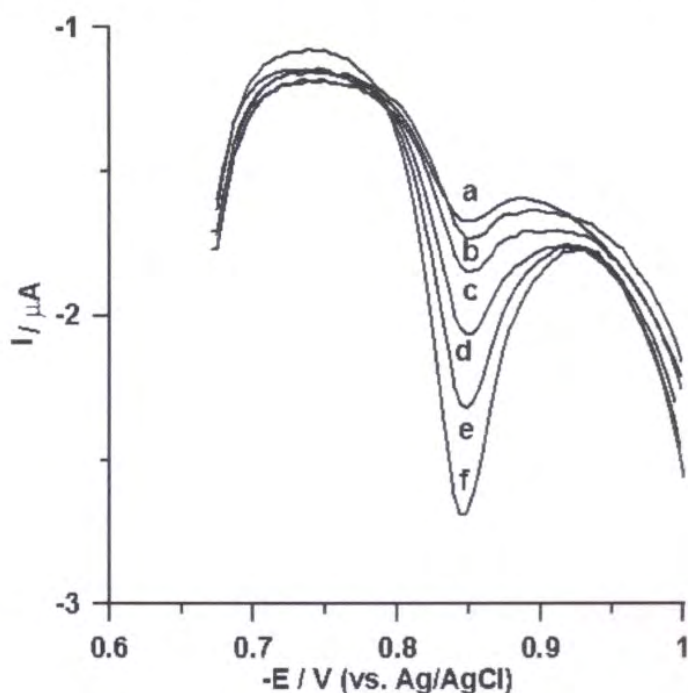


Fig. 5 Square wave voltammograms obtained at the “hybrid” PbFE prepared with the use of the mediator zinc in the course of increasing Ni(II) concentration changing in the range from 0 to 2×10^{-9} mol l⁻¹. The *ex situ* plating of Pb was performed at -1.4 V for 45 s and then at -0.75 V for 30 s in solution containing 0.1 M pH 5.6 acetate buffer, 7.5×10^{-5} M Pb(II) and 5×10^{-6} M Zn(II). The *in situ* plating of Pb and the accumulation of Ni(II) were performed in solution containing also 0.2 M ammonia pH 9.0 buffer, 2×10^{-5} M nioxime and 0.25 M NaNO₂. Scan frequency, 200 Hz; pulse amplitude, 50 mV; step height, 4 mV. Reproduced from [34] with permission

Enhanced Sensitivity of Sn(IV) on Bismuth Film Electrodes with the Use of a Mediator

Similarly as mentioned in the previous paragraph, the ability of the mediator to improve the electrochemical performance of an *in situ* plated bismuth film electrode was investigated [38]. For this purpose, zinc as a less noble metal (compared to bismuth) was applied again to serve as a reversibly deposited mediator. Changes in the surface morphology of bismuth deposit under different conditions of *in situ* electroplating were noticed after atomic force microscopy (AMF) observations (Fig. 6). Resulting tin(IV) stripping responses exhibited at least two-fold increase when the mediator had been added to the sample solution

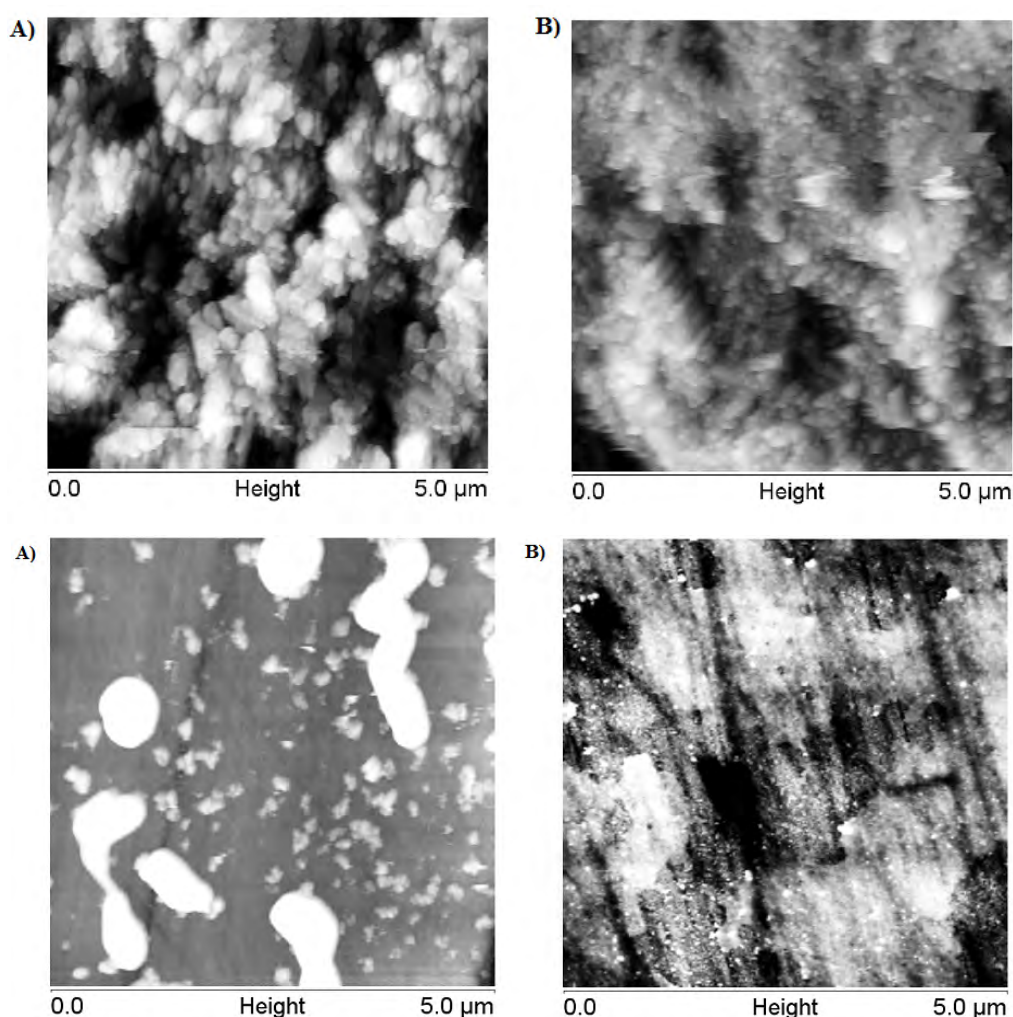


Fig. 6 AFM images of the BiFE surface prepared without (A) and with (B) the use of the reversibly deposited zinc mediator. Above, the bismuth film was deposited from the solution containing 0.1 M acetate pH 4.5 buffer, 0.4 mM Bi(III) (A) or plus 0.04 mM Zn(II) and 1.73 mM caffeic acid (B). In the bottom, the film was deposited from the solution containing 2.39 μM Bi(III), 75 mM oxalic acid and 75 mM CTAB (A) or moreover 7.65 μM Zn(II) (B). Reproduced from [38] with permission

leading to an enhanced electrochemical detection of tin at the micromolar concentration level (Fig. 7). Being initiated by the voltammetric determination of tin(IV) in biodiesel samples [39], two new procedures have been developed. In both, bismuth, zinc, and tin were simultaneously deposited on the glassy carbon substrate, first in the presence of caffeic acid, secondly together with oxalic acid and a cationic surfactant, represented by hexadecyltrimethylammonium bromide (CTAB; for details, see [38]).

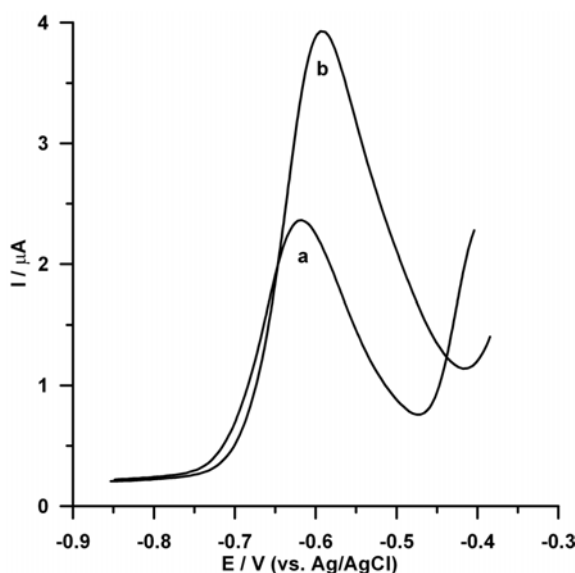


Fig. 7 The comparison of the square-wave anodic stripping voltammograms obtained at the BiFE prepared without (a) and with (b) the use of the mediator in the solution containing 0.1 M acetate pH 4.5 buffer, 0.4 mM Bi(III) (a) or moreover 0.04 mM Zn(II) (b), 1.73 mM caffeic acid and 5×10^{-6} M Sn(IV). The bismuth, zinc and tin were deposited simultaneously at the potential -1.5 V for 90 and then at the potential of -0.85 V for 45 s Zn atoms were stripped from the surface as Bi and Sn continued to be deposited. Reproduced from [38] with permission

Conclusion

As shown in this overview, recent research in the field of metal film electrodes applied in electrochemical stripping analysis has brought some interesting new insights that have a chance to be further developed. First, according to the authors' opinion, an unexpected property of SbFEs should be utilized in a search for new electroanalytical procedures in the range of more positive potentials. Also, a research on the apparent catalytic effect of the presence of less noble metals in samples containing more noble ones indicates that further studies might be worth of pursuing because — as can be expected — not only cadmium(II) is the right cation.

As discussed in the last example, a combination of *ex situ* and/or *in situ*

electroplating techniques in the presence of reversibly deposited mediator(s) results in electrodes with the increased coverage of their working surfaces coated by metal films, which facilitates accumulation of the target analytes in stripping analysis. But, is zinc(II) the only one that can be used? As it seems, there are still many questions for further research in this area.

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