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POTENTIOSTATIC DEPOSITION OF BISMUTH FILMS AND THEIR PERFORMANCE IN ANODIC STRIPPING VOLTAMMETRY[1]

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The performance of bismuth deposits obtained at different accumulation potentials is discussed in terms of their analytical application in anodic stripping voltammetry. As a test system the lead and zinc ions were chosen and examined by square wave voltammetry in synthetic solution and real samples.

Introduction

Stripping voltammetry has long been recognized as a very powerful technique for the determination of trace metals in a wide range of samples. The practicability, precision, and selectivity of this method are comparable with spectrometric

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techniques, outperforming them, however, in the field applications [1].

Two factors are crucial for the voltammetric analysis, namely the kind of working electrode (bulk or film, prepared ex-situ or in-situ) and the effectiveness of the accumulation stage. As a rule, every conductive material might be used as a working electrode but in practice the choice is far more limited. Only metals such as mercury, gold, platinum, iridium, bismuth and a variety of carbon materials turned out to be useful in stripping voltammetry. A drop of mercury, a metal disc and a very thin layer of metal covering a conductive carbon support (film electrode) are usually used as a voltammetric working electrode. There exist two ways of the preparation of the film electrode, namely the electrolysis of an external solution followed by the electrode transfer to the analysed sample or addition of deposited ions to the sample and the in-situ formation of film.

The processes that lead to analyte accumulation on the working electrode surface are as follows: a) processes of physical nature such as: adsorption of metal complexes or organic compounds, physical attraction (e.g. adhesion forces) of the electrodeposited metal on the electrode surface (e.g. metals deposited on GC, As deposited on Au, Pt), dissolution in electrode material (e.g. Pb, Cd, Zn, Cu at HMDE or MFE, Hg at AuFE); b) chemical reaction with the electrode material such as alloy or intermetallic compounds (e.g. Cu_xAs_y, AsSe) formation.

When the target metal and the electrode-forming material do not react to produce any compound, they can still be deposited together during the in-situ electrode preparation. Then, the electrode material serves as a matrix in which the analyte crystals are embedded.

Among other stripping techniques the anodic stripping voltammetry (ASV) is the most widely used.

Though highly sensitive and versatile, stripping methods are not commonly used in routine analysis. The main factor which discourages scientists from using stripping voltammetry is the high toxicity of electrode material – liquid mercury or mercuric solutions. However, during the last few years, a revival of the interest of researchers in stripping voltammetry was induced by the introduction of bismuth film electrodes into electroanalytical practice. Since the first paper, published in 2000 [2], about fifty contributions dealing with anodic, cathodic and adsorptive stripping voltammetry in batch and flowing sets have been issued.

It has to be said, though, that the papers published up to the present time have shown that so far the scientists' attention has been focused mainly on the practical application of bismuth film electrodes in the voltammetric analysis, while the preparation-structure-performance relationship is still not fully investigated [3–8]. As it was emphasized by Wang [4], to take full advantage of bismuth electrodes in analytical practice it is necessary to obtain further information about their voltammetric behaviour and properties. We found it interesting to examine the properties of bismuth deposits plated potentiostatically in the potential range from –0.7 V to –1.7 V. The influence of plating potential on the co-deposition of bismuth was tested with two model ions Pb(II) and Zn(II). Lead and zinc were chosen since they are widely used in anodic stripping voltammetry utilizing the bismuth film electrode [9–19]. The research was performed in pure acetic buffer with addition of standard solution of lead or zinc and also in the dolomite sample solution. The voltammetric studies were coupled with microscopic observation to obtain information about the deposit topography.

Experimental

Apparatus

All the electrochemical experiments were performed with a μAutolab potentiostat (Eco Chemie BV, The Netherlands) controlled by a PC kitted out with GPES 4.9 software. All the experiments were carried out in a three-electrode cell with an Ag/AgCl/3M KCl reference electrode and a platinum wire auxiliary electrode. A glassy carbon electrode of diameter ⌀ = 3 mm (BAS, USA) was used as a support for the bismuth film electrode. The surface of the electrode was polished with alumina powder Micropolish II (Buehler, USA) of two sizes of grains (0.3 μm and 0.05 μm) on the polishing cloth (Buehler, USA) to the mirror-like finish.

The morphology of deposits was examined with AFM images obtained for the grain samples using a NanoScope E microscope (Digital Instruments, USA) in the contact mode.

Reagents

All the solutions were prepared from distilled and further deionized water of conductivity below 0.1 μS cm^{-1}. A 1 M stock solution of acetic buffer was prepared by mixing appropriate amount of CH_3COONa (per analysis grade, POCH, Poland) with 99.5 % acetic acid (per analysis, POCH, Poland). Stock solution of bismuth (1 g l^{-1}) was prepared by dissolving bismuth nitrate ($Bi(NO_3)_3 \cdot 5H_2O$, per analysis, POCH, Poland) in 10 % nitric acid (per analysis grade, POCH, Poland) and diluting with water. Stock solutions of zinc and lead of 1 g l^{-1} were Merck standard solutions. The dolomite sample was SRM of DWA1 Laboratoires Associes de Geologie, Belgium.

Procedure

The electrochemical deposition of a bismuth film on the glassy carbon electrode surface was done according to an *in situ* procedure. The electrochemical cell was filled to the final volume of 10 ml with 0.1 M acetic buffer with addition of bismuth salt solution to the appropriate concentration with addition of lead and zinc salts solutions or sample solution. The solutions were not deareated. Usually, the accumulation was carried out for 30 s at the deposition potential followed by 15 s of equilibration and then positive-going polarization was applied in the SW mode up to potential of 0.3 V.

Results and Discussion

Before the study of the metal/bismuth deposition process the selection of the optimal mode of electrode polarisation was undertaken. Two techniques widely applied in analytical voltammetry were considered: square wave voltammetry (SWV) and differential pulse voltammetry (DPV). The preliminary tests were performed in a solution containing 40 $\mu g\ l^{-1}$ Pb, 10 μM $Bi(NO_3)_3$ and 0.1 M acetic buffer. For both techniques the same amplitude, $\Delta E = 25$ mV and scan rate $v = 50$ mV s^{-1} ($f = 10$ Hz, $E_s = 5$ mV, $t_{int} = 0.1$ s) were applied. The SWV lead peak currents are twice as high compared to the DPV currents (Fig. 1). The application of higher frequencies, such as the routinely used 50 Hz, will result in a further increase of the signal and, at the same time, will shorten the analysis time. To have all the potential advantages of working with SWV, the optimisation of two main factors has to be done, i.e. amplitude and frequency perturbation. Square wave

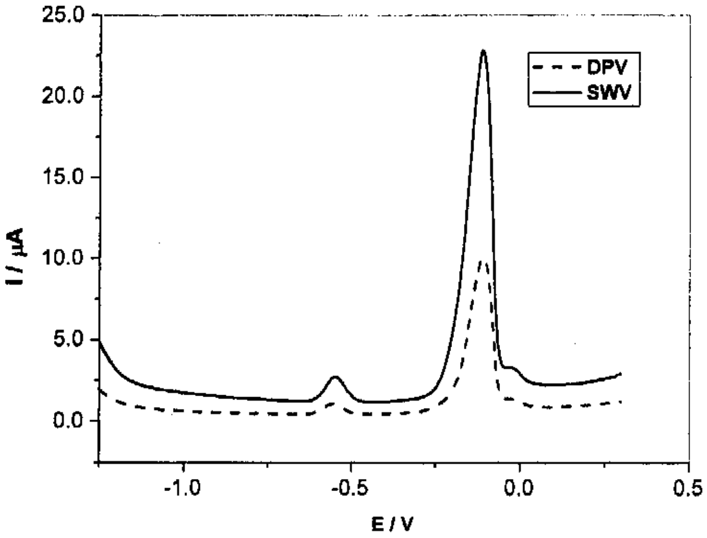

Fig. 1 DPV and SWV stripping voltammograms developed in the solution containing 40 $\mu g\ l^{-1}$ Pb, 10 μM $Bi(NO_3)_3$ and 0.1 M acetic buffer. Instrumental parameters: $E_{acc} = -1.5$ V, $t_{acc} = 60$ s, $E_{fin} = 0.3$ V, $\Delta E = 25$ mV, $v = 50$ mV s^{-1} ($f = 10$ Hz, $E_s = 5$ mV, $t_{int} = 0.1$ s)

frequency is the most important parameter in SWV since it determines the intensity of the signal and, consequently, the sensitivity of the technique. The lead oxidation peak current is a linear function of frequency ($z = 0.1365x + 0.12$, $r^2 = 0.9998$). The lead peak potential varied linearly with the logarithm of the frequency, following the equation $y = 0.0191x - 0.5671$ ($r^2 = 0.9589$).

The pulse amplitude is another parameter that strongly influences the peak current in SWV. The lead peak current depended linearly on the pulse amplitude lower than 40 mV and reached a plateau at values higher than $\Delta E = 60$ mV. The use of increasingly higher frequency and amplitude caused not only an enhancement of the peak current but broadened the peak. The perturbation amplitude higher than 80 mV caused a peak splitting (Fig. 2).

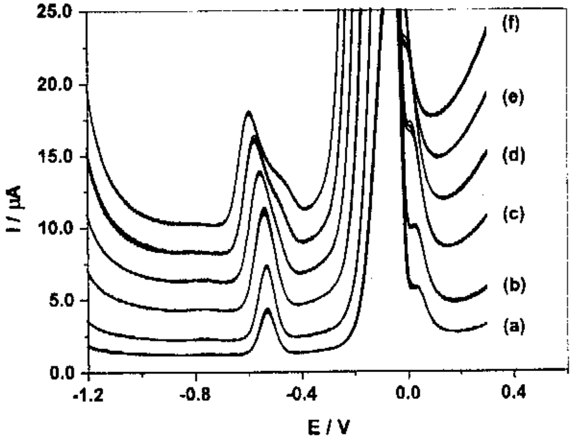

Fig. 2 SWV stripping voltammograms developed in the solution containing 80 µg l^{-1} Pb, 10 µM $Bi(NO_3)_3$ and 0.1 M acetic buffer for different values of perturbation amplitude (ΔE). Instrumental parameters: $E_{acc} = -1.5$ V, $t_{acc} = 60$ s, $E_{fin} = 0.3$ V, $f = 50$ Hz, $E_s = 5$ mV, ΔE: (a) 10, (b) 20, (c) 40, (d) 60, (e) 80, (f) 100 mV

The next stage after the choice of the stripping voltammetric technique was the investigation of the properties of GC support for the bismuth film. GC is typically the substrate of choice where a making film electrode is concerned. This material is chemically inert, non-porous and easy to maintain. The surface of the mechanically polished glassy carbon electrode is smooth and has a mirror-like finish when examined by the naked eye, which can be deceptive. The optical and scanning electron microscopes show that the GC surface is rough, covered with a network of scratches. A more detailed analysis of the surface topography was possible by the use of the AFM technique (Fig. 3a).

The support surface condition is very important as the surface defects are the centres where crystallization of the deposits starts. A strong preference for the formation of new nuclei along the scratches was observed for mercury [20] and for lead and silver [21] at the glassy carbon support. The competition between the

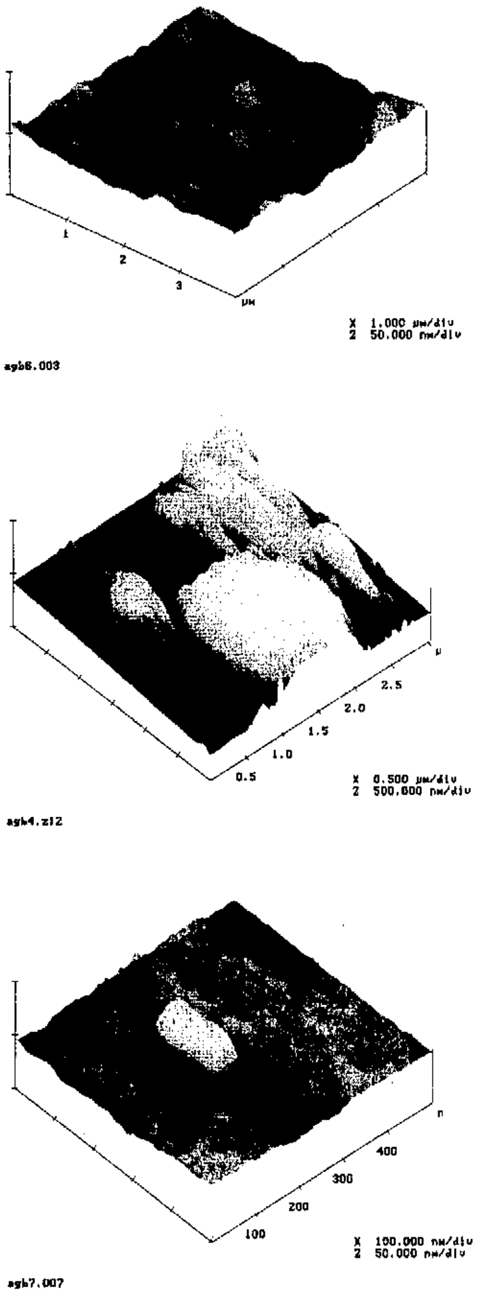

Fig. 3 AFM images of GC electrode: (a) bare, (b) covered with bismuth layer obtained after 30 s electrolysis of the solution containing 0.1 M acetic buffer and 10 μM $Bi(NO_3)_3$ at potential of −1.2 V, (c) 'cleaned' by stripping of bismuth deposit obtained as described in (b) by positive going potential in the SWV mode (E_{fin} = 0.3 V, f = 50 Hz, ΔE = 25 mV, E_s = 5 mV)

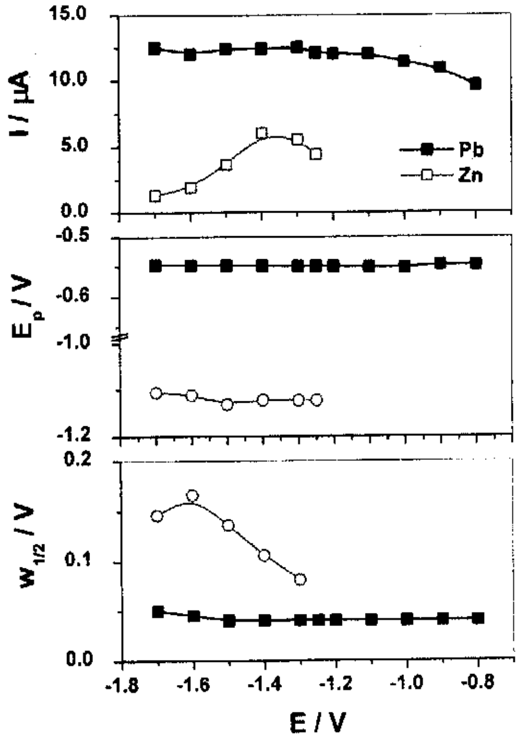

Fig. 4 Parameters of lead and zinc peaks (peak potential (E_p), peak current (I), a width at half peak height ($w_{1/2}$)) recorded in SWV mode after accumulation at different accumulation potentials. Solution composition: 80 μg l^{-1} Pb, 36 μg l^{-1} Zn, 0.1 acetic buffer, 10 μM Bi(NO$_3$)$_3$. Instrumental parameters: t_{acc} = 30 s, E_{fin} = 0.3 V, f = 50 Hz, ΔE = 25 mV, E_s = 5 mV

crystal growth and nuclei formation determines the morphology of the deposit and its chemical and electric properties.

The mechanically polished GC support was electrochemically activated by cycling the potential from –1.3 V to 0.3 V and afterwards plated potentiostatically with metallic bismuth. The bismuth deposits were obtained at a potential varying from –0.7 V to –1.7 V in the plating solution containing 0.1 M acetic buffer (pH = 4.5) and 10 μM of bismuth ions. The comprehensive investigations of the plating potential influence on the bismuth film performance in accumulating lead and zinc were carried out by chronoamperometric and square wave voltammetric techniques. The GC electrode was held at the –0.7 to – 1.7 V plating potential bracket for 30 s and, simultaneously, the electrolysis current was monitored. Afterwards, the accumulated bismuth was dissolved by the polarization of the electrode in the SWV mode from the plating potential up to 0.3 V.

The influence of plating procedure parameters was tested on Pb(II) and Zn(II) ions. They were introduced into the 0.1 M acetic buffer at concentrations of 80 μg l^{-1} and 36 μg l^{-1}, respectively. The signal parameters of tested metals (peak potential, E_p; peak current, I_p; a width at half peak height, $w_{1/2}$) are shown in Fig. 4. The signals of Pb obtained after accumulation at potentials from –0.7 V to –1.3 V showed a moderate increase in the stripping peak currents for more negative deposition potential values. When going into more negative potentials, the more pronounced the increase of oxidation current for Pb becomes. The behaviour of the Zn peak current was strikingly different; it rose steeply up to the accumulation potential of –1.2 V and then dropped sharply. The application of more negative deposition potentials also caused a broadening of both peaks. In the case of lead in the accumulation potential range from –0.7 V to –1.5 V the peak width is almost constant (ca. 40 mV) but at more negative potentials broadens up to 50 mV. The peak width of zinc changed dramatically, it is twofold larger at potential of –1.7 V than that observed at –1.2 V.

The total ionic strength also plays a role during the accumulation process and its increase causes the amplification of the undesirable processes such as hydrogen generation or peak splitting. Figure 5 shows SWV anodic stripping curves recorded in the dissolved dolomite sample solution. In this case, the peak splitting is noticeable at the accumulation (plating) potential –1.5 V, which is more positive than that observed in pure acetic buffer.

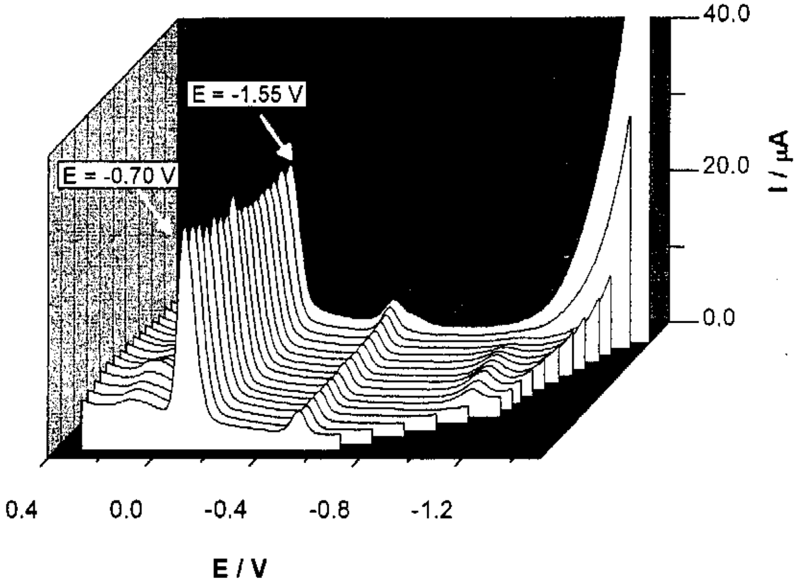

Fig. 5 SWV voltammograms recorded in a sample solution containing: 0.1 M acetic buffer, 10 μM $Bi(NO_3)_3$, and 80 μg l^{-1} Pb and 36 μg l^{-1} Zn spiked from dissolved SRM DWA1 for different accumulation potential (E_{acc}). Instrumental parameters: t_{acc} = 30 s, E_{fin} = 0.3 V, f = 50 Hz, ΔE = 25 mV, E_s = 5 mV, E_{acc}: –0.7, –0.8, –0.9, –1.0, –1.2, –1.22, –1.23, –1.25, –1.27, –1.3, –1.33, –1.25, –1.38, –1.4, –1.45, – 1.5, –1.55 V

The oxidation signals of Zn and Pb obtained after accumulation in the very negative potential range are non-reproducible and become smaller from scan to scan, even when the electrode was cleaned electrochemically. Figure 3 shows successive AFM images of GC during in-situ deposition of bismuth from the solution of 10 µM $Bi(NO_3)_3$ in 0.1 M acetic buffer and after its stripping in the SWV mode. The first image shows the surface of the CG before plating the bismuth. The second one depicts the deposit obtained after 30 s of electrolysis at –1.2 V. Finally, the third one, made after the SWV polarization of the electrode from the deposition potential to 0.3 V, shows some amount of residual covering the surface. The incomplete stripping is more evident at higher concentrations of the plating solution. The same observations were reported in Refs [22,23]. An addition of bromide ions, complexing the ions produced during the stripping stage, was made to try to improve the reproducibility of in-situ plated mercury films [24,25]. The presence of 10 to 100 µM of bromide ions resulted in a small increase of lead peak current (Fig. 6) and reached the highest value (ca. 28 %) for 15 µM of bromide ions. However, the improvement of the reproducibility was not satisfactory and the study was eventually conducted in pure acetic buffer.

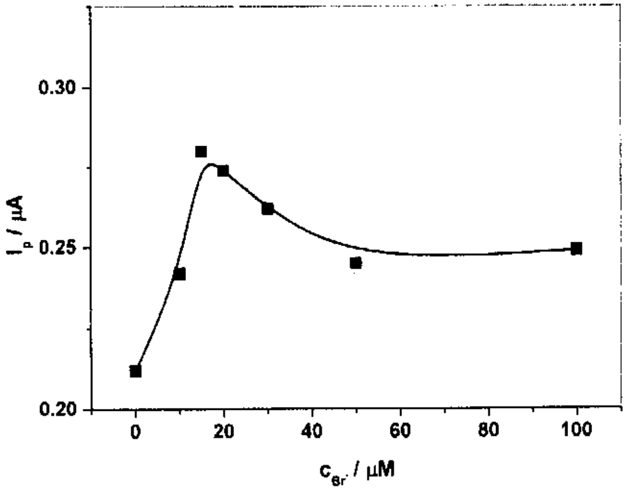

Fig. 6 The bromide ions effect on the lead peak current. Solution composition: 80 µg l^{-1} Pb, 10 µM $Bi(NO_3)_3$ and 0.1 M acetic buffer. Instrumental parameters: E_{acc} = –1.5 V, t_{acc} = 60 s, E_{fin} = 0.3 V, f = 50 Hz, ΔE = 25 mV, E_s = 5 mV

Conclusion

The results obtained in this paper show that the plating potential significantly influences the response of zinc and lead signals by anodic stripping voltammetry. The influence on the lead deposition is moderate but it could not be ignored during the work with zinc. Applying very negative deposition potentials made the ASV signal of zinc diminish despite its high concentration in the solution. Additionally, in the very negative potential range the subsequent oxidation signals of Zn and Pb are not reproducible, getting lower from scan to scan because of the poisoning of the electrode surface by the metal oxidation debris or the products of bismuth hydrolysis. When the amount of the deposited metals is high, the drop of signals from run to run is very pronounced due to the presence of the high amount of their oxidation products. Within this range hydrogen evolution occurs and the hydrogen bubbles partly destroy the layer of deposited metals [6]. Moreover, the vigorous evolution of hydrogen ions increases pH in the vicinity of the electrode surface. This in turn causes the hydrolysis of bismuth ions, and the blockage of the electrode surface is observed. The addition of substances which could form soluble compounds with electrode reaction products could improve the electrode cleaning process. Unfortunately, the addition of bromide to the plating solution did not improve the reproducibility to a satisfactory extent.

The deposition of bismuth and lead or zinc on the energetically non-identical sites explains the widening and splitting of their voltammetric peaks.

Finally, the results obtained in the pure acetic buffer and in the real sample solution show that it is essential to perform the optimisation of deposition parameters for the real sample and not for a synthetic solution.

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