BISMUTH FILM ELECTRODES FOR ADSORPTIVE STRIPPING VOLTAMMETRY. PREPARATION, PROPERTIES AND ANALYTICAL APPLICATION[1]

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The properties of the bismuth film electrode (BiFE) designed for adsorptive stripping voltammetry were examined by electrochemical and microscopic techniques (optical microscopy, SEM-EDX, AFM). The BiFE was prepared by ex-situ electrodeposition of a Bi film onto a glassy carbon disk support. The composition of the plating solution, the influence of accumulation potential, the stability of bismuth coating as well as the memory effect were investigated. The analytical usefulness of the BiFE obtained by the proposed procedure for adsorptive stripping voltammetric measurement of cobalt traces in a solution of 1×10^{-4} M DMG and 0.1 M ammonia buffer was assessed. It was found that the plating solution containing 0.02 M $Bi(NO_3)_3$, 1 M HCl and 0.5 M LiBr combined with a plating potential of -0.28 V and c.a. 35 s plating time ensure the finest

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quality bismuth film. The electrode-to-electrode reproducibility of the described plating procedure evaluated in terms of the relative standard deviation (RSD) was equal to 12%. The repeatability of the cobalt response for 30 subsequent adsorptive stripping measurements of the same BiFE amounted to RSD = 6 %. The performance of the BiFE for trace cobalt and nickel analysis in geological samples is presented.

Introduction

Adsorptive stripping voltammetry (AdSV) is known to have given excellent sensitivity in the determination of a variety of trace metals at both drop and film mercury electrodes. This method involves complexation of trace metals with metal-specific ligands and adsorbing the formed complex onto the mercury surface. The adsorbed metal complex is subsequently electrochemically removed during a cathodic potential scan. The success of an electrochemical sensing process relies mainly on a careful choice of the working electrode. Film electrodes, which comprise a thin liquid or solid metal coating (liquid or solid) deposited on a support – an electric conductor, have several distinct features: simplicity and lack of any electronic appendages, non-restricted geometry, stability in flow conditions and possibility of modification of their surface [1,2]. The properties of the newly introduced bismuth film electrode (BiFE) are similar to that of mercury electrodes but their use does not require the time-consuming deareation procedure [3–21]. It should be mentioned that papers dealing with BiFEs have been first reviewed recently [22].

Until recently, the plating procedures of the bismuth film presented in literature were optimized mainly for use in anodic stripping voltammetry [3,4,6,7, 9–13]. In most measurements the acetic buffers containing bismuth ions were used as plating solutions because a wide potential window could be obtained with this supporting electrolyte.

To improve the quality of the bismuth film electrode used for AdSV purpose a plating solution containing bismuth and complexing bromide ions was proposed [15, 21]. The aim of the present work is to examine the properties of the bismuth film electrode plated *ex-situ* on glassy carbon from a plating solution containing bromide ions by means of electrochemical and microscopic techniques. The composition of the plating solution, the influence of accumulation potential, and stability of bismuth coating and memory effect is discussed.

Results

Preparation of the Bismuth Film Electrode for Adsorptive Stripping Voltammetry

The glassy carbon support was chosen for the preparation of BiFE due to its analytical properties (chemical and electrochemical stability, low porosity, relatively high hydrogen overpotential) and practical reasons (wide availability, simplicity of surface renewal) [1,2].
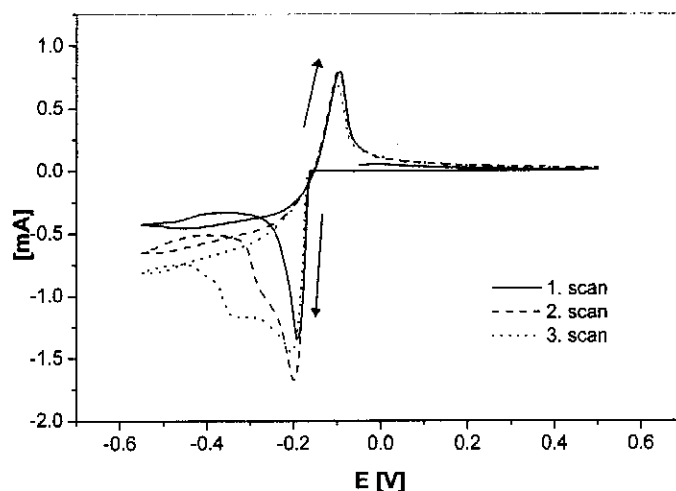

Fig. 1   Cyclic voltammogram (3 scans) for a solution containing 0.02 M Bi(NO$_3$)$_3$, 0.5 M LiBr and 1 M HCl recorded on GC

The crucial parameter which influences the quality of bismuth coating is the composition of the plating electrolyte. The non-complexed Bi(III) ions very easily hydrolyse [23] forming insoluble compounds e.g. BiOCl, which redissolve in concentrated HCl. Because of the risk of hydrolysis, only acidic media (HCl, HNO$_3$, acetic buffer) can be considered as potential plating solutions for the bismuth film preparation. The cyclic voltammetric curve of the solution containing 0.02 M Bi(NO$_3$)$_3$, 0.5 M LiBr and 1 M HCl (Fig. 1) indicates that the reduction process of Bi(III) complexes reaches the maximum rate at a potential of –0.24 V. In order to efficiently coat the glassy carbon support with metallic bismuth a plating potential more negative than –0.24 V should be applied. To obtain the highest reproducibility of the bismuth film surface, the plating procedure was performed without stirring and by inspection of the electrolysis current and shape of chronoamperograms recorded during the plating process (Fig. 2). Monitoring

the changes of current during the plating procedure allows evaluating the quality of the bismuth film and is used to identify faults related to the electrode itself or the plating procedure. The reproducibility of the plating procedure was tested as electrode-to-electrode reproducibility, and the recorded signals on average differ from each other by 12 %. The deposition of bismuth coating on GC (Q = 10 mC, E_{plat} = -0.28 V) is a quick process. In spite of lack of convective transport, the whole process takes ca. 35 s, and as early as after 5 s the bismuth coating achieves 30 % of the total mass.
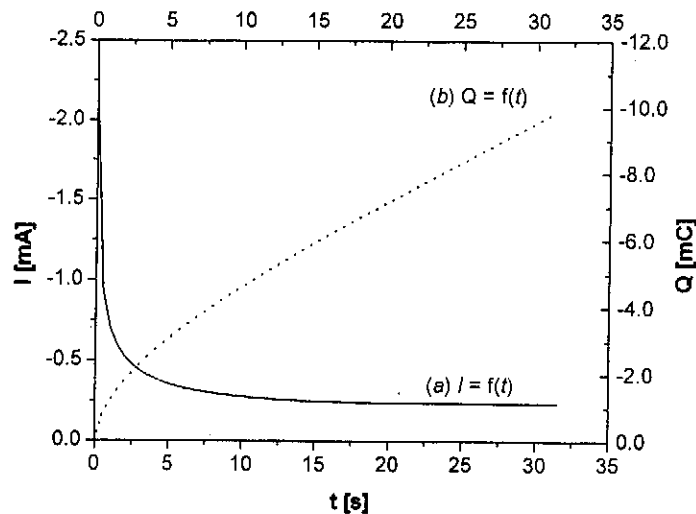

Fig. 2 Chrono- (a) amperometric and (b) coulometric curve recorded in solution containing 0.02 M Bi(NO$_3$)$_3$, 1 M HCl, 0.5 M LiBr; E_{plat} = -0.28 V, Q = 10 mC

Electrochemical Study of Properties of Bismuth Film Electrode

The working potential range of the electrode is determined by the composition of the supporting electrolyte . In case of the bismuth film electrode the accessible potential window is restricted by the oxidation of bismuth at the positive potential region and by the reduction of hydrogen ions at the negative potential region (Fig. 3). The oxidation process of the metallic bismuth depends strongly on the pH of the solution. The obtained potential window is wider for neutral and basic solutions. The composition of supporting electrolyte also affects the background current behaviour. In case of application of buffered solutions the background current value does not change in a wide potential range. However, for supporting electrolytes containing salts (e.g. KCl, KNO$_3$) the background current does not

level off but increases when approaching the negative potential region. Among the investigated supporting electrolytes HNO_3 is not recommended for stripping voltammetry as the background current for this electrolyte is the most parabolic in shape, having a very narrow potential window. This phenomenon is caused by the oxidative properties of HNO_3 towards the metallic bismuth.
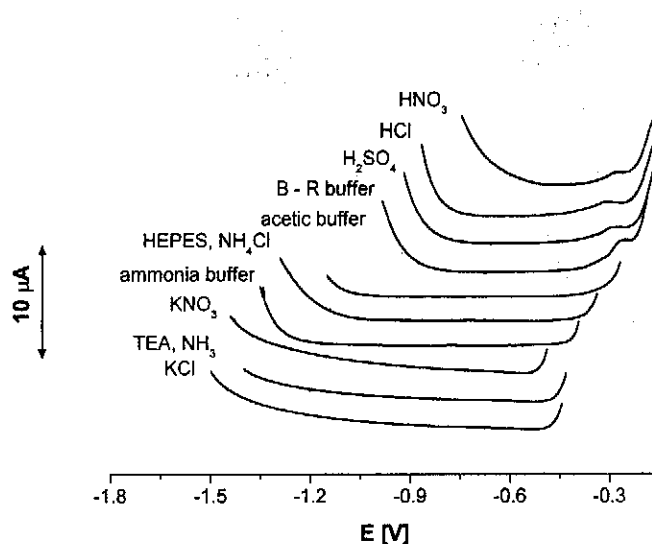

Fig. 3 Potential ranges for BiFE in various supporting electrolytes

Microscopic Examination of the Properties of the Bismuth Film Electrode

The changes of the GC surface after plating can be noticed with the naked eye. After plating with bismuth the electrode surface is no longer shiny but is evenly covered with black deposit. The inspection of the microscopic image reveals that the surface of the film is not homogeneous. The bismuth crystallites deposited at E_{plat} = -0.28 V are built of large, lumpy and black crystallites which consist of fine (1 mm thick) sheet metal perpendicular to the GC surface and can be described as a pyramid with a shape polygon base. Bismuth films of this kind were adhesive and it was difficult to wipe them off. As the plating potentials become more negative (< -0.35 V), the process of reduction of bismuth ions becomes quicker, and the microstructure of bismuth film changes to small, pure shaped crystallites, which dye the film grey. The grey bismuth film is oxidised when exposed to air. At even more negative potentials of the plating process (E_{plat} < -0.6 V) the obtained bismuth coating is transformed to a non-adhesive powder.

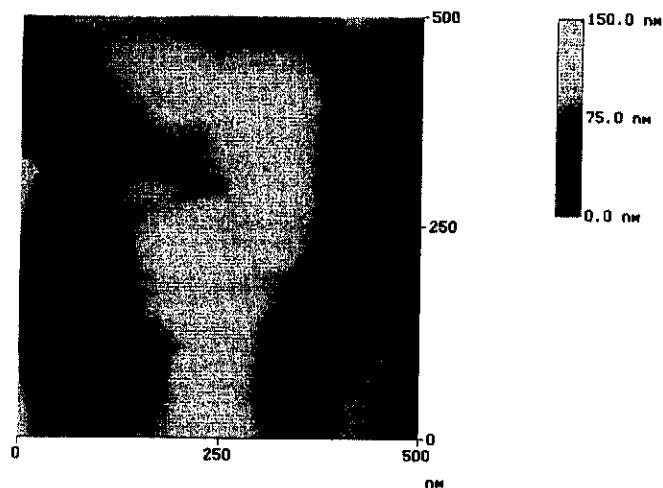The thickness of the bismuth film layer estimated from Faraday's law

Fig. 4 AFM image of the surface of GC covered by bismuth according to the procedure described in Fig. 1

(Q = 10 mC, Φ = 3 mm) is 1.04×10^{-5} cm. This value should be treated as the average value because it is obvious from Fig. 4 that the bismuth film is not a flat disc. From the atomic force microscopy (AFM) study the height of the larger crystallites was estimated to be 1.5×10^{-5} cm, which corresponds to the maximum thickness of the bismuth coating (Fig. 4).

The background current and the hydrogen overpotential observed on the BiFEs depends on the thickness of the bismuth layer. Removal of a certain amount of metallic bismuth by polarizing the BiFE working electrode using LSV mode from −1.3 V up to the potential of 0 V causes the decrease of the hydrogen overpotential by ca +0.08 V.

Analyte Accumulation Assessment

The inspection of AFM image (Fig. 4) allow the user to assess whether the bismuth layer is well developed. A highly developed surface is required in adsorptive accumulation procedures because on a larger surface a greater amount of analyte can be accumulated. With such an electrode the linear range of adsorption isotherm is expanded to higher concentrations of the analyte. The ability of the bismuth layer to accumulate cobalt complexes was confirmed by the SEM-EDS analysis [21]. It was shown that on the bismuth crystals the amount of cobalt is significantly higher than on bare GC. The results of LSV investigation of the influence of the voltage scan rate ($\Delta \log I_p / \Delta \log v$ = 1.19 ± 0.2, r^2 =
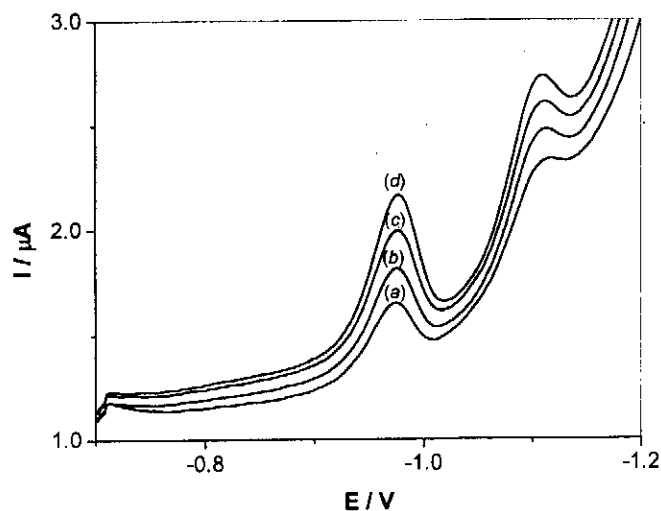
Fig. 5 AdSV quantification of cobalt and nickel procedure in the solution of dissolved dolomite using standard addition: (a) sample; (b) (a) + 0.5 μg l^{-1} Ni and 0.2 μg l^{-1} Co; (c) (a) + 1 μg l^{-1} Ni and 0.4 μg l^{-1} Co; (d) (a) + 1.5 μg l^{-1} Ni and 0.6 μg l^{-1} Co. Supporting electrolyte: 0.1 M ammonia buffer l 1×10^{-4} M DMG, E_{acc} = −0.7 V, t_{acc} = 60 s

0.9978) indicates that the reduction of [Co(DMG)$_2$] process occurs from the adsorbed layer. This was also confirmed by the study of the out-phase AC voltammetric curves (phase angle Φ = 90) recorded within − 0.5V and −1.3V. The decrease in capacity of the double layer was observed in the out-phase AC voltammogramms when cobalt was introduced into the ammonia buffer solution containing DMG, which confirms surface active behaviour of the investigated dioximate complex on the BiFE.

The durability of the BiFE and the risk of deactivating its surface by the products of the electroreduction of Co complexes were also examined. The products of electroreduction of [Co(DMG)$_2$] which can remain on the BiFE surface could influence the long term applicability of the sensor by changing its adsorptive activity.

The storage of the BiFE obtained ex-situ in such media as air, water, ammonia buffer, 0.1 M HCl and the plating solution causes a gradual decrease in the electrode sensitivity. This effect was observed when the Co signal was recorded in the test solution containing the ammonia buffer and DMG. The signal drop was most visible when the electrode was kept in hydrochloric acid and in the plating solution. After 150 minutes of contact of the BiFE with laboratory air the signal of Co reduction reaches only 65 % of its initial value, and the peak potential is shifted by 0.04 V to the more negative potential.

Analytical Application

Under the optimised conditions (a deposition potential of E_{acc} = −0.7 V and a deposition time of t_{acc} = 60 s) and using the BiFE prepared *ex-situ* according to the described protocol (0.02 M Bi(NO$_3$)$_3$, 1 M HCl, 0.5 M LiBr, E_{plat} = −0.28, Q = 10 mC, Φ = 3 mm) the detection limit of the AdSV determination of cobalt in a solution containing 0.1 M ammonia buffer (pH 9.5) was equal to 0.3 µg l^{-1} (E_{acc} = −0.7 V, t_{acc} = 60 s). The elaborated AdSV procedure was successfully employed for the quantification of the Co traces in geological samples (Fig. 5).

Conclusion

The results of the investigation confirm the usefulness of the new bismuth plating procedure. The application of bromide modified plating solution and the use of strongly acidic media (1M HCl) allow to use a concentrated Bi(III) solution (0.02M) and minimize the risk of hydrolysis of Bi ions. Such a plating solution eliminates the necessity of stirring during the plating and improves the reproducibility of AdSV signals. Additionally, the monitoring of the electroplating current enables the elimination of defective electrodes as soon as they are produced. The proposed procedure is especially recommended for AdSV measurements in alkaline solutions because of the durability of the generated films in these media. The BiFEs prepared according to the examined procedure are also characterized by good electrode-to-electrode reproducibility (RSD = 12 %) and excellent signal-to-signal repeatability (RSD = 6 %, n = 30).

Acknowledgements

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