



Operation of bismuth film electrode in more acidic medium



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ABSTRACT

A new approach for application of bismuth film electrode (BiFE) under more acidic conditions is presented. The BiFE was prepared in-situ on a glassy carbon substrate electrode and employed for anodic stripping voltammetric measurement of Zn(II) in 0.01 mol L⁻¹ hydrochloric acid (pH 2.0) in the presence of dissolved oxygen. The addition of potassium sodium tartrate tetrahydrate into the measurement solution resulted in significant improvement of the electroanalytical performance of BiFE via inhibition of hydrogen evolution. The BiFE revealed an excellent linear response towards Zn(II) in the examined concentration range of 10 to 100 μg L⁻¹ with the calculated LoD of 1.3 μg L⁻¹ associated with 300 s accumulation step and satisfactory repeatability of 4.8% (RSD). A preliminary study of simultaneous detection of selected trace metal ions, i.e. Pb(II) and Cd(II), together with Zn(II) was also carried out. Finally, the applicability of the proposed method was corroborated via measuring Zn(II) in a real tap water sample.

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1. Introduction

For the past six decades mercury has been the most commonly used electrode material for electrochemical (stripping) measurements in its various electrode configurations. Due to its well-known toxicity, there have been numerous attempts to replace mercury with some other non-toxic or less-toxic electrode materials. Since 2000, when it was introduced for the first time [1], the bismuth film electrode (BiFE) has gained a wide acceptance in electrochemical stripping analysis due to its excellent electroanalytical performance, also in the presence of dissolved oxygen, and a similar wide operational potential window to its mercury counterpart [2–5]. Appropriate selection of supporting electrode and optimal operational parameters allow expedient and simultaneous (multi-elemental) analysis of several metal ions in their μg per liter or even lower concentrations levels [6]. In numerous laboratories bismuth-based electrodes have been employed in different combinations, e.g. in-situ and ex-situ BiFE prepared, predominantly on different carbon substrates [7–11], bismuth powder-, bismuth oxide-, and NH₄BiF₄-bulk modified carbon paste electrodes [12–14], bulk bismuth electrode [15], bismuth nanoparticles modified electrodes [16,17], polymer coated BiFEs [18,19], etc. In combination with anodic stripping voltammetric or

stripping chronopotentiometric modes bismuth electrodes are usually used in acetate buffer solution, however, in more acidic solutions, e.g. in 0.01 mol L⁻¹ hydrochloric acid with pH 2.0, the electroanalytical performance becomes hindered, particularly in the case of measuring Zn(II) due to considerable hydrogen evolution reaction.

Tartrates are typically used as strong complexing/stabilizing agents for Bi(III) and Sb(III) in adsorptive cathodic stripping voltammetric measurements of, e.g. trace Ni(II) in mildly alkaline solutions in combination with the in-situ preparation of bismuth or antimony film electrodes [20,21], trace Co(II) in the presence of nitrite at the in-situ prepared bismuth electrode [22], and in anodic stripping voltammetric measurements of selected trace metal ions using antimony film electrode in a saturated solution of hydrogen potassium tartrate with pH 3.6 [23]. It is also well known that numerous bismuth compounds are used in medicine and among them, sodium bismuth tartrate was used in the past as an antibacterial drug for the treatment of, e.g. syphilis [24]. Composition of bismuth(III)-tartrate compounds strongly depends on the tartrate to bismuth molar ratio and when this ratio is 2 or higher, two or more tartrate ligands prevails in the Bi(III)-tartrate chelate. Synthesis and characterization of Bi(III)-tartrate trihydrate was described in detail by Herrmann et al. [25].

In this work we present a successful application of the in-situ prepared BiFE in more acidic medium (pH 2.0) for measuring low concentration levels of Zn(II), also in the presence of Cd(II) and Pb(II), combined with a beneficial effect of potassium sodium tartrate

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providing a wider applicable cathodic operational potential window. Several key parameters were optimized and the elaborated procedure was evaluated for measuring Zn(II) in a real sample of tap water. With respect to the measurement media, the proposed protocol extends the applicability of bismuth film electrode toward more acidic environments, i.e. of $\text{pH} \leq 2$, and thus, the convenience of using bismuth film electrode approaches to those of the antimony- and particularly of the mercury film electrode which both operate excellently in more acidic media. Namely, conducting the measurements under more acidic conditions prevents the hydrolysis of metal ions; consequently, in trace metal analysis, the sample handling/pre-treatment usually involves acidifying for sample stabilization.

2. Material and methods

2.1. Apparatus

Anodic stripping voltammetric (ASV) measurements were carried out using a modular electrochemical workstation (Autolab, Eco Chemie, Utrecht, The Netherlands) equipped with PSTAT10 and driven by GPES software (Eco Chemie). A three-electrode configuration was employed consisting of a bismuth film modified glassy carbon electrode ($d = 2 \text{ mm}$), Ag/AgCl/KCl(satd.), and a platinum rod acting as the working, reference, and counter electrodes, respectively. During the electrochemical deposition, a magnetic stirrer of approximately 300 rpm was employed.

2.2. Reagent and solutions

Standard stock solutions of Bi(III), Cd(II), Pb(II) and Zn(II) (1000 mg L^{-1} , atomic absorption standard solutions) were obtained from Merck and diluted as required. A 0.01 mol L^{-1} HCl solution with $\text{pH} 2.0$ was used as the supporting electrolyte without and in the presence of potassium sodium tartrate tetrahydrate as described below. All other chemicals were of analytical grade purity. Water used to prepare all solutions throughout the work was first deionized and then further purified via Elix 10/Milli-Q Gradient unit (Millipore, Bedford, MA).

2.3. Procedures

ASV measurements were conducted usually using an accumulation potential of -1.4 V for 120 s, and after an equilibration period of 15 s, the anodic stripping voltammogram was recorded in the quiescent solution by applying a positive-going square-wave potential scan. Before each measurement a cleaning step was carried out by keeping the working electrode potential at $+0.3 \text{ V}$ for 30 s.

3. Results and discussion

Preliminary experiments revealed surprisingly broader applicable potential window (cathodic part) of the in-situ prepared BiFE operating in more acidic medium, i.e. in 0.01 mol L^{-1} HCl with $\text{pH} 2.0$, when potassium sodium tartrate tetrahydrate was added into the measurement solution containing bismuth ions. The observed effect can be beneficially exploited for measuring low concentration levels of Zn(II) due to significant shift of the hydrogen evolution reaction toward more negative potentials. Fig. 1 clearly shows the comparison of measuring Zn(II) using BiFE in the presence (a) and absence (b) of tartrate ions; in the latter case, a poorly developed signal of Zn(II) could be observed at ca. -1.1 V coinciding with the hydrogen evolution reaction, thus precluding an efficient quantification of low concentration levels of Zn(II). Evidently, in the presence of tartrate ions a well-developed anodic stripping voltammetric signal of $70 \mu\text{g L}^{-1}$ Zn(II) was observed along with a hydrogen evolution reaction shifted considerably toward more negative potentials. This effect might be attributed to changes of the BiFE surface structure when the crystallization of Bi proceeds from Bi-tartrate complex; this presumption can be supported with the observation of an attenuated stripping signal of bismuth in the presence of tartrate, i.e. ca. $35 \mu\text{A}$ in Fig. 1a vs. ca. $60 \mu\text{A}$ in Fig. 1b. At the same time, the effect of tartrate can be reflected also via a slight shift of the re-oxidation potential of bismuth toward more negative potentials.

Further investigations were aimed at attaining better understanding about the effect of tartrate ions upon the electroanalytical performance of BiFE. For this purpose, the effect of boric acid was examined and compared, since it is known as a complexing agent and a buffer for Ni(II) and Fe(II) deposition, and may also affect the composition of interfacial layer at the electrode [26]. Surprisingly, and as shown in Fig. 2, under these conditions the addition of 0.5 mmol L^{-1} boric acid into the measurement solution did not improve/change the performance of BiFE. Namely, according to the reference [26], a neutral H_3BO_3 molecule can be adsorbed on the electrode surface causing a net decrease in the active surface area. In Fig. 2, only a barely-developed shoulder could be observed for Zn(II) without any improvement considering the shift of hydrogen evolution (dashed line) resembling that shown in Fig. 1b (without tartrate). Also, there was no significant shift of the bismuth re-oxidation/stripping signal in the negative direction. On the other hand, the same concentration of tartrate (0.5 mmol L^{-1}) provided a strong stripping signal of Zn(II) and at the same time resulted in considerably decreased and shifted stripping signal of bismuth. This phenomenon has still not been explained completely, however, it is obvious that it can be exploited effectively for measuring low concentration levels of Zn(II) in more acidic media. Additionally, it has to be mentioned that the chosen amount of

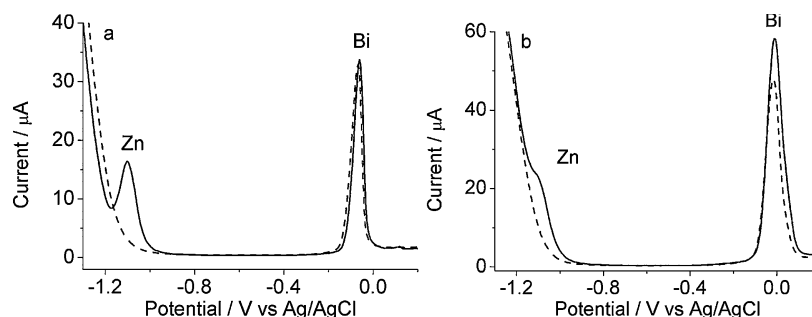


Fig. 1. ASVs at the in-situ prepared BiFE with (a) and without (b) 0.6 mmol L^{-1} tartrate in 0.01 mol L^{-1} HCl with $\text{pH} 2.0$ containing 1 mg L^{-1} Bi(III) with (solid line) and without (dashed line) $70 \mu\text{g L}^{-1}$ Zn(II); accumulation potential of -1.40 V for 120 s, equilibration period of 15 s, step potential of 4 mV, frequency of 25 Hz, amplitude of 50 mV, and cleaning step at $+0.3 \text{ V}$ for 30 s.

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