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Electrochemistry Communications 7 (2005) 1185–1189

electrochemistry communications

www.elsevier.com/locate/elecom

Adsorptive stripping voltammetry of nickel and cobalt at in situ plated lead film electrode

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Received 15 July 2005; received in revised form 10 August 2005; accepted 16 August 2005
Available online 26 September 2005

Abstract

In situ plated lead film electrode was proposed for adsorptive stripping voltammetric determination of nickel and cobalt in the presence of dimethylglyoxime. The stabilisation of lead at mild alkaline pH used for determination of these elements was achieved by increasing the concentration of dimethylglyoxime in the supporting electrolyte and so ensuring complexation of Pb(II) by dimethylglyoxime. At such conditions, Bi(III) ions undergo hydrolysis and so bismuth film cannot be plated in situ. The application of an in situ plated lead electrode leads to a shortening of the time of the measurements and requiring no pre-plating with medium exchange. The Ni(II) and Co(II) signals at lead film electrode are better resolved than at bismuth film electrode. The linear calibration graphs for Ni(II) and Co(II) in the range from 5×10^{-9} to 1×10^{-7} mol L^{-1} and from 1×10^{-9} to 1×10^{-7} mol L^{-1} were obtained, respectively. The method was applied to Ni(II) and Co(II) determination in certified reference materials.

Keywords: Lead film electrode; Adsorptive stripping voltammetry; Nickel; Cobalt

1. Introduction

Adsorptive stripping voltammetry (AdSV) is a well-established method for determination of trace metals which do not form amalgams, e.g., Ni, Co and Cr. In the case of determination of Ni(II) and Co(II) usually these ions are complexed with dioximes and accumulated on a mercury drop [1–7] or mercury film electrode [8–10]. Recently, bismuth film electrodes were introduced in anodic stripping [11–13], adsorptive stripping [14,15], catalytic adsorptive stripping [16] voltammetry and chronopotentiometry [17]. The most notable advantages of bismuth film electrodes are lower toxicity and lower background current in the presence of dissolved oxygen as compared to mercury film electrodes. In the case of Ni(II) and Co(II) determination by AdSV the measurements were carried out in ammonia buffers. In such buffers, bismuth salts undergo hydrolysis and so the measurements cannot be performed at an in situ plated bismuth film electrode. The bismuth film electrodes applied till now for Ni(II) and Co(II) determination are formed ex situ usually from bismuth salts dissolved in an acetate buffer [17] or in a LiBr + HCl solution [18]. Preplating influences total analysis time and requires an exchange of solution before determination.

In the present study, we used a lead film electrode formed in situ and applied it to Ni(II) and Co(II) determinations by AdSV. Lead can be easily stabilised at mild alkaline pH in the form of Pb(II)–DMG (dimethylglyoxime) complexes. The application of an in situ formed lead film electrode simplifies measurements and is of particular interest when determinations are carried out in the flow system.

2. Experimental

Measurements were performed using μAutolab, Eco Chemie, the Netherlands. A three electrode cell containing a glassy carbon working electrode ($d = 1$ mm), a Pt wire as

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doi:10.1016/j.elecom.2005.08.022

a counter electrode and Ag/AgCl as a reference electrode was used. The glassy carbon electrode was polished daily using 0.3 µm Al_2O_3 paste on a polishing pad (Buehler). After polishing the electrode was cleaned in a water ultrasonic bath for 30 s. Solid certified reference material was digested with a Mars-5 microwave digestion system (CEM, USA). Liquid samples were mineralised using a UV-digester made by Mineral, Poland.

2.1. Reagents

0.5 mol L^{-1} PIPES buffer (pH 7.0) was prepared from piperazine-*N*,*N*′-bis(ethanesulfonic acid) and Suprapure NH_4OH, Merck. A solution of 0.1 mol L^{-1} DMG was prepared by a dissolution of the reagent in 0.2 mol L^{-1} NaOH. Standard solutions of Ni(II) and Co(II) at concentration 1 g L^{-1} were obtained from Fluka. Certified reference materials, rain water TMRAIN-95 and tea leaves INCT-TL-1 were obtained from the National Research Council, Canada, and the Institute of Nuclear Chemistry and Technology, Poland, respectively. Suprapure HNO_3 was used for the digestion of solid samples. Other reagents were obtained from POCh Poland, and used as received. All solutions were prepared in triply distilled water.

2.2. Sample preparation

Certified reference material INCT-TL-1 was digested under pressure with concentrated HNO_3. Next, the digest was additionally mineralised by UV-irradiation to eliminate the interference of residual organic matter on Ni(II) and Co(II) determination. Certified reference material TMRAIN-95 was mineralised by UV-irradiation for 3 h.

2.3. Standard procedure

An aliquot of the analysed sample was pipetted into the electrochemical cell and triply distilled water was added to the volume 7.475 mL. Then, 2 ml 0.5 mol L^{-1} PIPES buffer, 0.5 mL 0.1 mol L^{-1} DMG and 25 µL 0.01 mol L^{-1} $Pb(NO_3)_2$ were added. If the pH of the solution was different from 7.4 ± 0.1, NH_4OH or HNO_3 was added to obtain the required value. In the course of Ni(II) and Co(II) determination the potential of the electrode was changed in the following sequence: −1.25 V for 10 s; 0.2 V for 10 s; −1.25 V for 60 s and −0.675 V for 120 s. The first two steps were applied to clean the electrode after the preceding measurement. The film was reduced to the metallic state and then was stripped from the electrode. During the third and fourth step, a lead film was plated and Ni(II) and Co(II) complexes with DMG were accumulated on the electrode, respectively. During all these steps, the solution was stirred using a magnetic stirring bar. Then, after a rest period of 5 s a square wave voltammogram was recorded at frequency 200 Hz in the potential range −0.675 to −1.2 V. The amplitude was 50 mV. The measurements were carried out from undeaerated solutions.

3. Results and discussion

Ni(II) and Co(II) are commonly determined by AdSV at HMDE and mercury film electrodes. Recently, bismuth film electrodes have been proposed as they are not toxic, unlike the mercury ones. However, bismuth film electrodes cannot be plated in situ at the pH usually used for Ni(II) and Co(II) determination, because at mild alkaline pH bismuth salts undergo hydrolysis. Taking into account, the above data attempts to apply new electrode material suitable for AdSV of Ni(II) and Co(II) at an in situ plated electrode were carried out. Acceptable preliminary results were obtained at an in situ plated lead electrode so the optimisation of parameters of determinations was performed to obtain a low detection limit of Ni(II) and Co(II) determination. Toxicity of lead is lower as compared to mercury and slightly higher than bismuth. Additionally, lead and inorganic lead salts are not so volatile as mercury and mercury salts.

3.1. Composition of the supporting electrolyte and the material of the working electrode

Three buffer solutions, ammonium chloride/ammonia, ammonium sulfate/ammonia and PIPES/ammonia, were chosen for study. Stable signals for Ni(II) and Co(II) were obtained only for the PIPES buffer and it was used in subsequent study. The fact that the presence of high concentrations of chloride or sulfate ions in the supporting electrolyte deteriorates the reproducibility of measurement can be explained by the formation on the electrode of sparingly soluble Pb(II) compounds in the course of the electrochemical cleaning of the electrode. The supporting electrolyte contained DMG at a concentration of 5×10^{-3} mol L^{-1}. Such a high concentration of DMG led to a fast formation of complexes with Ni(II) and Co(II) and additionally prevented precipitation of Pb(II). Pb(II) was added to the electrolyte at a concentration 2.5×10^{-5} mol L^{-1}, although the peaks of Ni(II) and Co(II) were observed also at lower concentrations of Pb(II). At lower concentrations of Pb(II), the Ni(II) and Co(II) peaks increased from measurement to measurement and so for further study Pb(II) concentration of 2.5×10^{-5} mol L^{-1} was chosen as it ensures a stable peaks for studied ions. The influence of pH was investigated for a solution containing 1×10^{-8} mol L^{-1} Co(II) and 1×10^{-7} mol L^{-1} Ni(II). The pH was changed in the range from 6.0 to 9.4. The results obtained are presented in Fig. 1. As can be seen, the Co(II) peak increases as the pH increases in the whole range of pH studied, while the Ni(II) peak increases as pH increases to 8.0 and then decreases. For further study a pH 7.4 ± 0.1 was chosen. The different influence of pH on Ni(II) and Co(II) signals can be exploited for example to decrease the Ni(II) influence on the Co(II) signal or to obtain a lower detection limit of Co(II) determination by choosing the pH of the supporting electrolyte close to 9.0. Voltammograms obtained for three different pH values of the supporting electrolyte are presented in Fig. 2. As can be seen, Ni(II) and Co(II) peaks obtained at