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Application of adsorptive stripping voltammetry to the simultaneous determination of bismuth and copper in the presence of nuclear fast red

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Abstract

A sensitive and selective method for the simultaneous determination of copper and bismuth by adsorptive stripping was developed using nuclear fast red (2-anthracenesulfonic acid, 4-amino-9,10-dihydro-1,3-dihydroxy-9,10-dioxo-, monosodium salt) as selective complexing agent onto hanging mercury drop electrode. In a single scan both metals gave peaks that were distinctly separated by 85 mV allowing their determination in the presence of each other. Optimal analytical conditions were found to be: nuclear fast red concentration of 80 μM, pH of 2.8 and adsorptive potential of −300 mV versus Ag/AgCl. With accumulation time of 180 s the peaks currents are proportional to concentration of copper and bismuth over the 1–100 and 5–60 ng mL^{-1} range with detection limits of 0.2 and 1.2 ng mL^{-1}, respectively. The procedure was applied to simultaneous determination of copper and bismuth in some real samples.

Keywords: Copper and bismuth; Adsorptive stripping voltammetry; Nuclear fast red; Simultaneous determination

1. Introduction

Bismuth and copper are environmentally important [1], and are of biological interest due to their possible binding to thiolate ligands to form metal-thiolate clusters [2]. Many electroanalytical stripping procedures have been proposed for the individual determination of nanomolar concentration of copper [3–10] and bismuth [11–15] on the bases including anodic stripping voltammetry (ASV) and adsorptive cathodic stripping voltammetry (AdCSV). Although these procedures offer the desired sensitivity, they suffer from some practical difficulties such as nearness of reduction peaks potential of bismuth and copper metal ions with oxidation peak potential of the electrode, formation of the intermetallic compound and the overlapping of the anodic stripping voltammograms of these two metal ions [16]. Thus, accurate determination of these two species in the presence of each other is not possible by common electroanalytical methods. In spite of this fact, there are two reports on simultaneous determination of copper and bismuth [16,17]. In one of them, substituted catechols were used for the determination of bismuth, lead, copper and cadmium by adsorptive stripping voltammetry [17]. Although the peak potentials of copper and bismuth are well separated in the presence of resorcinol, simultaneous determination was not possible due to their competition for the ligand [17]. In the other one [16], the simultaneous determination of both metal ions in the presence of morin was reported that in which two accumulation potentials were used. To the best of our knowledge, the simultaneous analysis of bismuth and copper by single scan has not been reported yet.

Nuclear fast red has hydroxyl and amino groups; thus, it has been used to chelate many metal ions for chemical analysis [18–20] and has been proposed as a qualitative reagent for the fluorimetric detection of aluminium [21]. Since quinones play an important part in natural electron transfer systems, they have often been used for modifying electrode surfaces. According to various electrochemical studies [22], anthraquinones are irreversibly adsorbed onto graphite. Of anthraquinone derivatives, nuclear fast red was chosen because it not only has the foregoing characteristics but also has the advantage of a sulfonate group in the molecule, which makes the reagent and its complex with

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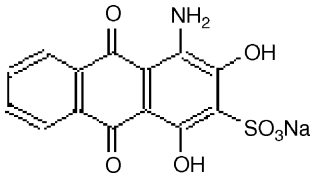

Fig. 1. Chemical structure of nuclear fast red.

metal ions soluble in water. In the AdCSV after accumulation of the complex onto the electrode during the deposition step and the reduction of the adsorbed metal complex by application of a negative going potential scan a reduction current is generated that is a sensitive measure of the concentration of the metal. This paper describes an *AdCSV* procedure for simultaneous determination of bismuth and copper by using nuclear fast red (Fig. 1) as complexing agent. Various factors influencing the simultaneous determination of bismuth and copper were investigated.

2. Experimental

2.1. Chemicals

All chemicals used were of analytical reagent grade. A 0.01 M nuclear fast red (NFR) was prepared by dissolving 0.0357 g NFR (Merck) in water and diluting to 10.0 mL in a volumetric flask. Double distilled water was used throughout. Stock solution of bismuth (100 mg L^{-1}) was prepared by dissolving 0.0232 g of bismuth nitrate [$Bi(NO_3)_3{\cdot}5H_2O$] in 10 mL 1.0 M nitric acid and diluting to 100.0 mL with water. A 1000 mg L^{-1} copper(II) stock solution was prepared by dissolving 0.3802 g of [$Cu(NO_3)_2{\cdot}3H_2O$] (Merck) in water and diluting to 100 mL in a volumetric flask. A 0.1 M of acetic acid solution with pH 2.8 was used as electrolyte. Nitrogen gas with 99.99% purity was used to de-aerate solutions. Metal ions solutions were prepared by dissolving appropriate amounts of their salts (Merck, Germany) in distilled water.

2.2. Apparatus

Differential pulse stripping was conducted with a Metrohm multifunction instrument model 693 VA Processor equipped with a 694 VA stand. Measurements were carried out with a hanging mercury drop electrode (HMDE), in a three-electrode arrangement. The auxiliary electrode was a wire of platinum with a considerably larger surface area than that of HMDE. An Ag/AgCl (KCl 3 M) was used as reference electrode. Stirring was carried out using a large Teflon road with 2000 rpm speed. Solutions were deoxygenated with high-purity nitrogen for 5 min prior to each experiment, and followed under a nitrogen atmosphere. A Metrohm-692 digital pH-meter was used for pH measurement.

2.3. Procedure

Ten milliliters of 0.1 M acetic acid solution (pH 2.8) was pipetted into the voltammetric cell. Then, 80 μL of 0.01 M NFR was added, giving a final concentration of 80 μM. The solution was purged with water-saturated nitrogen for 5 min in the first cycle and 30 s for each successive cycle. The preconcentration (adsorption) potential (usually −300 mV) was applied for 180 s to a fresh mercury drop while the solution was stirred. The stirring was stopped for a period of 10 s (equilibration time) and then, the potential was scanned from +200 mV toward more negative values using differential pulse (DP) modulation (modulation time, 40 ms; modulation amplitude, −50 mV; interval time, 0.2 s; potential step, 8 mV, resulting in a scan rate of 40 mV s^{-1}). Each scan was repeated three times with a new drop for each analyzed solution and the mean of these voltammograms obtained. Bismuth and copper stripping peaks were registered at about +50 and −50 mV, respectively, and their currents used as a measure of bismuth and copper concentrations. All experiments were carried out at room temperature.

3. Results and discussion

3.1. Adsorptive characteristics of the Cu–NFR and Bi–NFR complexes

Preliminary experiments were carried out to identify the general features, which characterize the behavior of the metal ion–NFR systems on hanging mercury drop electrode. Fig. 2 displays the stripping voltammograms of 20 ng mL^{-1} of each metal ion (bismuth and copper) in the presence of NFR at pH 2.8 after 180 s accumulation at −300 mV. Curve 'a' shows the anodic stripping voltammogram of Bi(III) and Cu(II) complexes with NFR when stripped by scanning the potential from −300 mV toward more positive values. As seen the peak separation cannot take place due to overlapping of the oxidation peaks of bismuth and copper. The adsorptive stripping voltammogram of the same system after accumulation at −300 mV and stripping by scanning the potential from +200 mV toward more negative values is shown in curve 'b'. Two separated peaks for reduction of bismuth and copper complexes with NFR were observed that is due

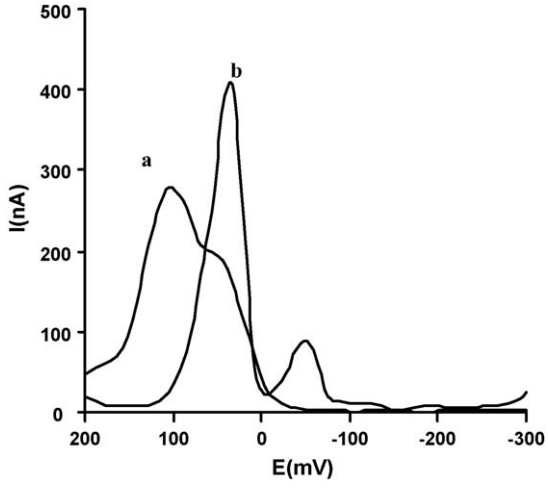

Fig. 2. Stripping voltammograms of 20 ng mL^{-1} each of bismuth and copper in 0.1 M acetic acid, pH 2.8, Tac = 180, E_{acc} = −300 mV and scan rate = 40 mV s^{-1}; (a) anodic stripping of Bi^{3+} and Cu^{2+} and (b) adsorptive cathodic stripping of Bi^{3+} and Cu^{2+} in the presence of 80 μM [NFR].