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Determination of lead and cadmium by anodic stripping voltammetry at bismuth film electrodes following double deposition and stripping steps

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ABSTRACT

The double deposition and stripping steps were proposed to increase the sensitivity in anodic stripping voltammetry of lead and cadmium. Two in situ plated bismuth film electrodes at drastically different surface areas were used for the measurements. Cadmium and lead were at first deposited at the electrode with a large surface area. When the deposition step at the electrode was finished, the electrode was placed at a short distance opposite the small one. Then Cd(II) and Pb(II) stripped from the first electrode were deposited at the second electrode. Taking into account the small volume of space between the electrodes, the concentration of Pb(II) and Cd(II) between the electrodes was drastically higher than that in the bulk solution. The deposition step at the second electrode was performed from the solution with a higher concentration of the determined ions, and so the detection limit was lowered. Calibration was performed following deposition times of 300 and 120 s at the first and the second electrode, respectively. Under such conditions the detection limits of 1.8×10^{-10} and 4.5×10^{-11} mol L^{-1} for Pb(II) and Cd(II) were obtained, respectively.

1. Introduction

Cd(II) and Pb(II) which occur in close association in nature are known to be hazardous environmental pollutants with toxic effects on living organisms. These metal ions are continuously added to air, water and soil as a consequence of human activity. There has been growing concern about heavy-metal contamination which led to increasing needs to monitor trace metals in a variety of matrices [1]. Anodic stripping voltammetry (ASV) has been proved to be a useful and versatile technique for the determination of trace metal ions in various samples of environmental, clinical, and industrial origin [2]. Its remarkable sensitivity is attributed to the 'built-in' preconcentration step, during which the target metals are deposited onto the working electrode. In the literature a large number of procedures of Cd(II) and Pb(II) determination by ASV were reported. The electrodes made from various materials such as: mercury [3–11], bismuth [12–31], antimony [32], tin [33] and others [34–36] were used for determination of these ions. Among them mercury and bismuth were most frequently used. Taking into account lower toxicity of bismuth and elimination of removing oxygen from solutions in the case of application of bismuth electrodes new procedures for determination of Cd(II) and Pb(II) by ASV were frequently reported. In recent years in order to decrease the detection limit of these ions determination various types of bismuth containing electrodes were reported. The most popular were bismuth film electrodes plated on different substrates [12–21]. Bismuth film electrodes additionally containing the ion exchange polymer and/or other components [22–28], bulk bismuth electrodes [29,30] and arrays of bismuth film electrodes [13,31] were proposed. So far the detection limits obtained using mercury containing electrodes for Cd(II) and Pb(II) have been lower than those reported for bismuth electrodes, so further studies are required to decrease the detection limit with the application of bismuth electrodes.

In the investigations described in this paper, in order to obtain a low detection limit for Pb(II) and Cd(II) by ASV at bismuth film electrodes two working electrodes of very different surface areas were used and the double deposition and stripping steps were exploited. Owing to a decrease of the detection limit one can avoid the additional preconcentration step outside the voltammetric cell before the analysis of low concentrations of Cd(II) and Pb(II) by ASV at a bismuth film electrode as proposed in [37].

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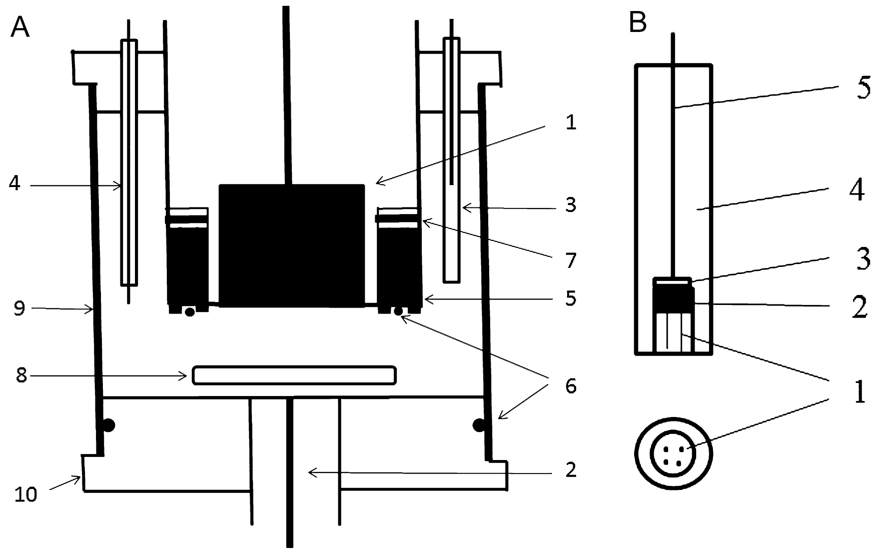

Fig. 1. (A) Schematic diagram of voltammetric cell: 1, the first working electrode; 2, the second working electrode; 3, reference electrode; 4, auxiliary electrode; 5, Teflon ring; 6, Teflon foil; 7, O-rings; 8, magnetic stirring bar; 9, quartz tube; 10, Teflon bottom. (B) Schematic diagram of ensemble of multifiber carbon microelectrodes: 1, carbon multifibers; 2, graphite powder; 3, copper plate; 4, epoxy resin; 5, copper wire.

2. Experimental

2.1. Apparatus

The measurements were performed using an μAutolab analyzer made by Eco Chemie, the Netherlands. The four-electrode voltammetric cell of a 30 mL volume consisted of two working electrodes, a Pt electrode and an Ag/AgCl reference electrode. As a working electrode with a large surface area (the first electrode) a GC electrode with 12 mm diameter was used. An ensemble of four multifiber microelectrodes made from carbon fibers was used as the second electrode. A real view of microelectrodes was taken by MA200 Inverted Metallographic Microscope Nikon (Japan).

2.2. Construction of voltammetric cell

A schematic diagram of the used cell is shown in Fig. 1A. The working electrodes were placed on opposite sides. The position of the first electrode was different in the course of the first and the second deposition steps. Briefly, in the course of the first deposition step the first electrode was placed about 15 mm above the bottom of the cell. As the deposition step at the first electrode was finished the electrode was moved to a short distance near the second working electrode. To control the distance between two working electrodes that was about 100 μm Teflon foil was placed between the electrode body and the Teflon ring as shown in Fig. 1A. On the basis of a distance between two working electrodes and diameter of O-ring a volume of space between electrodes was estimated at about 25 μL. In order to assure electrical contact between the electrodes the channel with a 1-mm high triangular cross-section was drilled under the O-ring placed on the casing of the first electrode. The single multifiber microelectrode sensor was constructed by gluing under vacuum about forty carbon fibers with an epoxy resin in chromatographic capillary. Schematic diagram of ensemble of multifiber carbon microelectrodes is shown in Fig. 1B, while a real view of one multifiber microelectrode is presented in Fig. 2A. To characterize electrode ensemble cyclic voltammogram recorded in 1×10^{-3} mol L^{-1} $K_3Fe(CN)_6$ + 1 mol L^{-1} KCl are presented in Fig. 2B. The sigmoidal shape of voltammogram confirms microelectrode properties of the used ensemble.

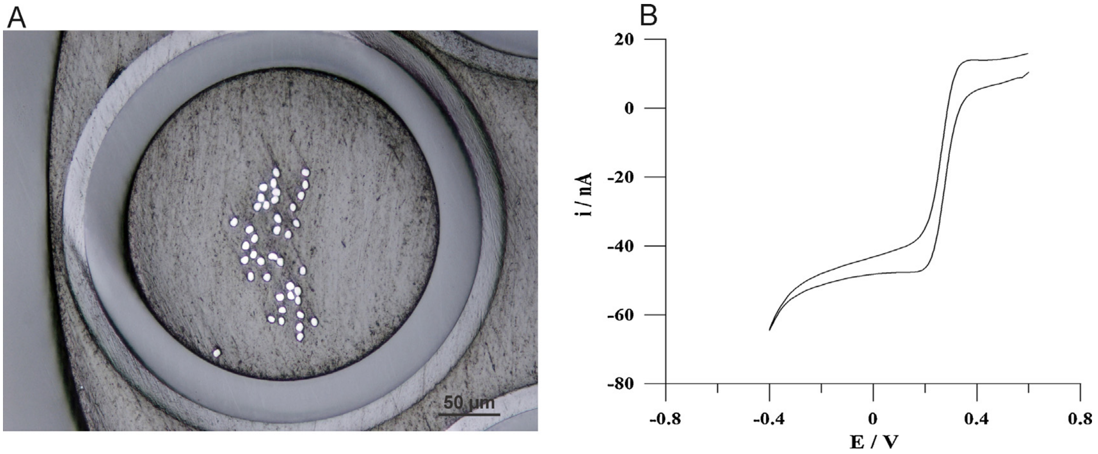

Fig. 2. (A) A real image of one multifiber microelectrode. (B) Cyclic voltammogram recorded in 1×10^{-3} mol L^{-1} $K_3Fe(CN)_6$ + 1 mol L^{-1} KCl obtained with multifiber microelectrode ensemble. Scan rate of 20 mV s^{-1}.