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Evaluation of carbon paste electrodes modified with 1-furoylthioureas for the analysis of cadmium by differential pulse anodic stripping voltammetry

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Abstract

Two series of 1-furoylthioureas (FTHD) were used as modifiers of carbon paste electrodes (CPEs) for the analysis of Cd(II). The capacities of the newly FTHD-modified CPEs were calculated and the surface reactions during the preconcentration of Cd(II) were studied by cyclic voltammetry. The analyte was accumulated on the surface of the modified CPEs by complexing with FTHD 3,3-disubstituted (series 1) and 3-monosubstituted (series 2) and reduced at a negative potential $(-1.0 \, \text{V})$. It was then quantified by differential pulse anodic stripping voltammetry (DPASV) in Britton–Robinson buffer at pH 4. Experiments were conducted to establish the optimal carbon paste composition, electrolyte and pH of the determination, accumulation potential and time, and instrumental parameters. Under the optimized working conditions good linear correlations were obtained for the calibration graphs in the concentration ranges studied. For 5 min of accumulation time, detection limits using modified CPEs with ligands of series 2 were lower than that of series 1 $(6 \times 10^{-5} \, \text{mg L}^{-1}$ versus $3 \times 10^{-3} \, \text{mg L}^{-1}$, respectively, for the CPEs modified with 1-furoyl-3-p-tetradecylphenylthiourea and 1-furoyl-3-benzyl-3-phenylthiourea taken as models of both series). For a series of seven determinations of Cd(II) at $0.5 \, \text{mg L}^{-1}$ relative standard deviations below 3.9% were achieved for CPEs with ligands of both series. Only Pb(II) and Cu(II) apparently affected the electrochemical response of Cd(II).

Keywords: Chemically modified carbon paste electrode; Differential pulse anodic stripping voltammetry; Cadmium(II); 1-Furoylthioureas

1. Introduction

Cadmium is one of the most toxic heavy metals of prime environmental and health concern. Cadmium toxicity may be manifested by a variety of syndromes and effects on human health [1,2]. Sensors for obtaining real time ppb-level cadmium concentration would reduce time and costs associated with the most common methods for the characterization and treatment of hazardous waste sites. Stripping voltammetric techniques are favourable methods for the determination of heavy metal ions, including Cd(II), because of their speed, remarkable analytical sensitivity, relative instrumental simplicity and minimum sample pre-treatment required prior to analysis. These attractive

features have resulted in rapid development and wide application

of stripping voltammetry [3-5]. A number of analytical determinations of Cd(II) based on stripping voltammetry at hanging mercury drop electrode have been reported [6-8]. However, mercury drop electrodes have the disadvantage of being mechanically unstable during various steps of the assay procedure and issues related to the use and disposal of toxic mercury, thus they are less desirable than solid-state sensors in routine field applications [9,10]. In the past two decades, more and more works has been performed at mercury free modified electrodes [11–16]. Carbon paste electrodes chemically modified are endowed with many good qualities, such as easy fabrication and renewal, low background current, low cost, ease of handling and applicability to anodic oxidations [3–5]. Different modifiers for carbon paste have been reported in the last years for the electrochemical stripping analysis of Cd(II): bismuth-powered [17], carbamoylphosphonic acid [18], organofunctionalized amorphous

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