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Adsorptive stripping voltammetric measurements of trace uranium at the bismuth film electrode

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Abstract

Bismuth-coated carbon-fiber electrodes have been successfully applied for adsorptive stripping voltammetric measurements of trace uranium in the presence of cupferron. The new protocol is based on the accumulation of the uranium–cupferron complex at a preplated bismuth film electrode held at −0.30 V (versus Ag/AgCl), followed by a negatively-sweeping square-wave voltammetric waveform. Factors influencing the stripping performance, including the film preparation, solution pH, cupferron concentration, adsorption potential and time have been optimized. The resulting performance compares well with that observed for analogous measurements at mercury film electrodes. A detection limit of 0.3 μg/L is obtained in connection to a 10 min adsorption time. The response is linear up to 50 μg/L and the relative standard deviation at 50 μg/L uranium is 3.8% ($n = 15$; 2 min adsorption). Potential interferences are examined. Applicability to seawater samples is demonstrated. The attractive behavior of the new 'mercury-free' uranium sensor holds great promise for on-site environmental and industrial monitoring of uranium.

Keywords: Bismuth film electrode; Uranium; Cupferron; Adsorptive-cathodic stripping voltammetry

1. Introduction

Uranium is found in the ground water of numerous nuclear energy sites. Extensive efforts have thus been devoted for developing highly sensitive analytical procedures for trace measurements of uranium. However, most techniques, such as spectrometry [1–3], gas chromatography [4,5], complexometric titration [6], neutron activation [7,8] and pulse polargraphy [9,10] are not sufficiently sensitive for its direct determination in relevant environmental samples. Voltammetric techniques are especially suitable for on-site monitoring of uranium owing to their portable character and low power requirements [11,12]. In particular, adsorptive-cathodic stripping voltmmetry (AdCSV), involving the interfacial accumulation of surface-active complexes of uranium onto a hanging mercury drop electrode, has been shown useful for monitoring sub-nanomolar levels of trace uranium in different natural water systems [12–15]. Uranium complexes with oxine [12], catechol [13], chloranilic acid [14], or cupferron [15] have been particularly useful for this task. A limitation of these AdCSV procedures, particularly for field screening applications, is their reliance on a mercury drop detector. While these mercury electrodes offer an attractive AdCSV performance, new alternative electrode materials—with a similar performance—are urgently desired for addressing growing concerns regarding the toxicity, handling, and disposal of mercury. The development

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of a reliable 'non-mercury' uranium sensor should particularly benefit on-site (and especially in situ) measurements of uranium.

This article reports on an effective AdCSV protocol for trace measurements of uranium at a bismuth-coated carbon electrode. Recently introduced bismuth electrodes have been shown useful alternatives to commonly used mercury electrodes in connection to anodic stripping measurements of heavy metals [16–18]. Bismuth is an environmentally-friendly element, with very low toxicity, and a widespread pharmaceutical use [19]. Several recent studies have demonstrated the suitability of bismuth film electrodes for AdCSV measurements of nickel [20], cobalt [21] and chromium [22]. Similarly, in the following sections we will describe the favorable AdCSV behavior of uranium–cupferron complexes at bismuth-coated carbon-fiber electrodes.

2. Experimental

2.1. Apparatus and electrodes

Square-wave AdCSV measurements were conducted using a multi-potentiostat Electrochemical Analyzer 1030 (CH Instruments, Austin, TX) connected to a Pentium 2240X computer. The cell assembly consisted of bismuth-coated carbon-fiber working electrode, Ag/AgCl reference (Model CHI111, CH Instruments), and a platinum wire counter electrode. The carbon-fibers (Alfa Aesar 10451, Johnson Matthey Co., Ward Hill, MA) were pretreated first by a 12 h immersion in ethanol. Subsequently, the fibers were dipped into a 6 M nitric acid solution for 30 s, and rinsed with distilled water. Another wash with acetone was followed by a thorough rinse with distilled water after which the fibers were allowed to air dry. A bundle of ca. 20 fibers (each of 8 μm diameter) was attached to a copper wire with silver conductive paint (SPI Supplies Inc., West Chester, PA). Subsequently, the bundle of carbon-fibers was inserted into the 100 μL plastic pipette tip, exposing a 3 mm length of the fibers at the narrow end of the tip. The copper wire was used to provide the electrical contact. The narrow end of the pipette tip was then sealed with a nail polish. These electrodes were inserted into the 3 mL electrochemical cell (BAS, Model VC-2). All glassware was soaked in 1 M nitric acid and rinsed several times with deionized water prior to use.

2.2. Reagents

Sodium acetate, 1000 μg/mL stock solutions of uranium(VI), bismuth, and mercury were purchased from Aldrich. The cupferron (Aldrich), or chloranilic acid (Sigma) solutions (0.05 M) were prepared by dissolving the appropriate amount of the ligand in nanopure water. A solution of 50 μM propyl gallate (Aldrich) was prepared with 1:1 ethanol/nanopure-water solution. The seawater sample, collected from the San Diego Bay, CA, was used without any pretreatment. The water was adjusted to pH 4.6 with acetate buffer before measurement. All experiments were carried out at room temperature.

2.3. Deposition of the bismuth or mercury film

The bismuth or mercury-coated electrodes were prepared by a 300 s deposition at −0.8 V from a 0.1 M acetate buffer (pH 4.5) solution containing 50 mg/L bismuth or 10 mg/L mercury, respectively.

2.4. Procedure for the detection of uranium

The supporting electrolyte contained 0.1 M acetate buffer (pH 4.6) and 75 μM cupferron (or 200 μM chloranilic acid or 50 μM propyl gallate in comparative studies). The electrode was poised for 2 min at a potential of −0.3 V to adsorb the U(VI)–ligand complex. The stirring was then stopped and after 10 s the square-wave voltammogram (SWV) was recorded over the −0.30 to−1.25 V range (using a step potential of 4 mV, amplitude of 25 mV and a frequency of 25 Hz). Before each measurement, a pre-cleaning step was applied with a potential of −1.25 V for 15 s.

3. Results and discussion

Initial work involved comparison of the uranium response at the bismuth film electrode in the presence of different ligands commonly used for AdCSV measurements of uranium [12–15], including similar levels of propyl gallate, oxine, chloranilic acid and cupferron. The most favorable uranium response (in term of signal-to-background characteristics) was observed in the presence of cupferron. Fig. 1 illustrates typical cyclic voltammograms at the bismuth-film electrode for 350 μg/L uranium in the presence of 75 μM

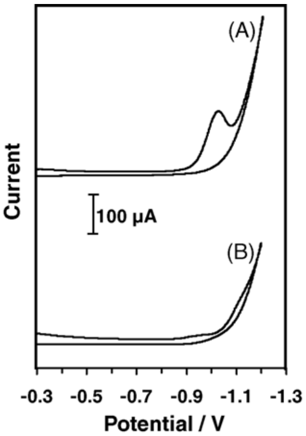

Fig. 1. Cyclic voltammograms for 350 μg/L uranium in the presence of 75 μM cupferron following 120 s (A) and 0 s (B) accumulation at −0.3 V (vs. Ag/AgCl). Scan rate, 50 mV/s; supporting electrolyte, 0.1 M acetate buffer (pH 4.6).