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Talanta 65 (2005) 62–66
Talanta
www.elsevier.com/locate/talanta

Cathodic adsorptive stripping voltammetric determination of uranium (VI) complexed with 2, 6-pyridinedicarboxylic acid

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Received 8 December 2003; received in revised form 8 April 2004; accepted 12 May 2004
Available online 17 July 2004

Abstract

Uranium (VI) (U(VI)) forms a complex with dipicolinic acid (2, 6-pyridinedicarboxylic acid).This complex can be used for a highly sensitive and selective determination of uranium by adsorptive cathodic stripping voltammetry (ACSV) using a hanging mercury drop electrode (HMDE) as working electrode. Influence of effective parameters such as pH, concentration of ligand, accumulation potential and accumulation time on the sensitivity and selectivity were studied. The detection limit (3σ of the blank value) obtained under the optimal experimental conditions is 0.27×10^{-9} M after 150 s of the accumulation time. The peak current is proportional to the concentration of U(VI) in the range of 1×10^{-9} to 1.2×10^{-7} M. The relative standard deviation of 2.5% at the 3.5×10^{-8} M level was obtained. The interference of some metal ions and anions were studied. The application of this method was tested in the determination of uranium in synthetic and natural water samples.

Keywords: Cathodic adsorptive stripping voltametry; Uranium; Dipicolinic acid

1. Introduction

Because uranium is a relatively mobile element in many surface or near-surface environment, its geochemical exploration methods require the measurement of the trace quantities of metal ion in water samples [1,2] along with that in plants, soils, and rocks. The uranium concentration of seawaters is about 3.3 ng ml^{-1} [2,3], in freshwater, even lower. Thus, highly sensitive methods are required for preconcentration and determination of uranium in water samples collected for prospecting purposes. It should be noted that uranium is a chemically toxic as well as being radioactive; the safety profiles for uranium compounds are well established [4,5]. Several techniques have been developed for determination of uranium including α-spectrometry [6], neutron activation [7], spectrophotometry [8], molecular fluorescence spectrometry [9], gas chromatography [10], complexometric titration [11]. These methods are not sufficiently sensitive for the direct determination of uranium; so that a preconcentration stage is necessary. However, the preconcentration step is too much time-consuming and of labor-intensive.

Adsorptive cathodic stripping voltametry (ACSV) is a powerful technique for determination of levels (ng ml^{-1}) of metal ions and organics. The technique is based upon adsorptive accumulation of the metal ion complexed with a suitable ligand at the electrode and then scanning the potential of the electrode in the negative direction. Advantages of ACSV for trace analysis are high sensitivity, low instrumentation and running costs, the possibility of analysis sailing matrices, such as seawater, without the need of prior separation. Several complexing reagent already have been applied to determine uranium by ACSV such as catechol [12], mordant blue 9 [13], oxine [14], cupferron (nitrosoarylhydroxylamines) [15], DTPA [16], propyl gallate [17], 2-TTA-TBP [18], xylidyl blue [19], TTA [20], triphosphineoxide [21], potassium hydrogen phatalate [22], chloranilic acid [23], aluminon [24], PAR [25] and *N*,*N*′-ethylenebis(salicylidenimine) [26] onto the hanging mercury drop electrode prior to the reduction of the adsorbed species, but most of the procedures often suffer

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doi:10.1016/j.talanta.2004.05.019

from interferences due to overlapping stripping peaks (from some coexisting metals [12–21]) or high level of detection [24], long accumulation time (10 min [25]) and short linear range [14,22,26].

This paper describes a sensitive and selective cathodic adsorptive stripping voltammetric procedure for determination of uranium in synthetic and natural water samples. This method is based on the effective accumulation of the uranium (VI) (U(VI)) complexed with dipicolinic acid (DPA) on a hanging mercury drop electrode and then reduction of the adsorbed complex.

2. Experiment

2.1. Apparatus

All polarographic measurements were performed using 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), (size: 7) in a three-electrode arrangement. The auxiliary electrode was a wire of platinum with a considerably larger surface area than that of HMDE. A silver–silver chloride (KCL 3 M) was used as reference electrode. Stirring was carried out by a large Teflon road with 1000 rpm speed. A Metrohm-692 digital pH-meter was used for pH measurement. Solutions were deoxygenated with high-purity nitrogen for 5 min prior to each experiment, and it was performed under a nitrogen atmosphere.

2.2. Chemicals

All chemicals used were of analytical reagent grade. Doubly distilled deionized water was used for all electrochemical experiments. A 0.001 M stock solution of uranium was made from $UO_2(CH_3COO)_2{\cdot}2H_2O$ (BDH) (acidified with 1 mL concentrated nitric acid). A 0.01 M stock solution of dipicolinic acid (Fluka) was prepared by dissolving appropriate amount of compound in double distilled water. Supporting electrolyte 0.05 M acetate buffer (pH = 6.7).

2.3. Procedure

Ten milliliters of the supporting electrolyte solution, 50 μL of 0.01 M DPA solution and different amount of 5×10^{-5} M UO_2^{2+} solution were pipetted into the cell and purged with nitrogen for 5 min. An accumulation potential of −0.20 V was applied to a fresh mercury drop electrode, while the solution was stirred for an accumulation time of 150 s at 1000 rpm. Following the preconcentration, stirring was stopped, and after equilibrium time of 10 s, the differential pulse voltammograms were recorded from −0.20 to −0.70 V, at a scan rate of 30 mV s^{-1}, and pulse amplitude of 80 mV. All the results were obtained at room temperature with nitrogen maintained over the solution surface.

3. Results and discussion

3.1. Cyclic voltammetry

Preliminary studies of the electrochemical behavior of uranyl (VI), and its complexes with DPA were performed by cyclic voltammetry. Fig. 1 shows the cyclic voltammograms obtained for 1×10^{-4} M UO_2^{2+} (curve 'a') and after the addition of 4×10^{-3} M DPA (curve 'b') in an unstirred 0.05 M acetate buffer (pH = 6.7). The forward potential scan commences at an initial potential of −0.1 V, and its direction was reversed at −0.7 V. As it is seen, U(VI) is reduced on the HMDE producing one cathodic peak with $E_{pc} = -0.30$ V and one anodic wave at peak potential of −0.23 V. The peak separation (0.07 V)was close to the theoretical value of 0.059 V for a one electron-reversible wave [27]. This result indicated that the cathodic reduction peak is due to the reduction of U(VI) to U(V). After the addition of DPA, the cyclic voltammogram shows a new reduction peak in the forward scan at −0.53 V due to the reduction of the complex UO_2^{2+}–DPA, and an anodic peak was observed in reverse scan at peak potential of −0.46 V. There is a 0.07 V difference in the cathodic and anodic peak potentials. This result also shows the reduction of U(VI)–DPA complex to its U(V) complex.

3.2. Cathodic adsorptive 'c' stripping voltammetry

Fig. 2 display differential pulse voltammograms of uranium–DPA system between −0.20 and −0.70 V (versus Ag/AgCl). Curve 'a' shows differential pulse voltammograms of DPA in the absence of uranium (blank solution) after 150 s of accumulation at −0.20 V. The voltammograms of uranium in the absence (curve 'b') and presence (curve 'c') of DPA after 150 s of accumulation time at −0.20 V, versus Ag/AgCl are also shown. Curve 'd' shows differential pulse voltammogram of uranium in the presence of DPA, without preconcentration. Comparison of the voltammograms shows that the height of uranium reduction peak depends on the duration of preconcentration step and also

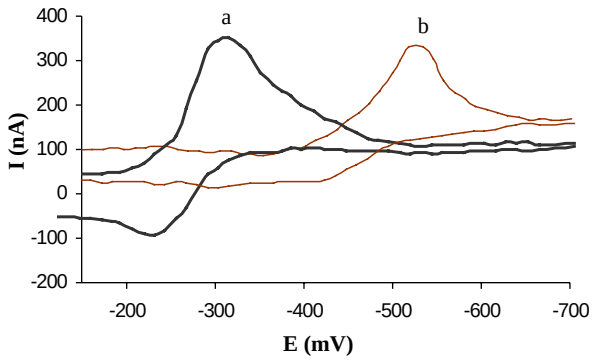

Fig. 1. Cyclic voltammograms of acetate buffer 0.05 M (pH = 6.7) containing 1×10^{-4} M UO_2^{2+} (curve 'a') plus 4×10^{-3} M DPA with scan rate of 0.4 V s^{-1}.