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

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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.
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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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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

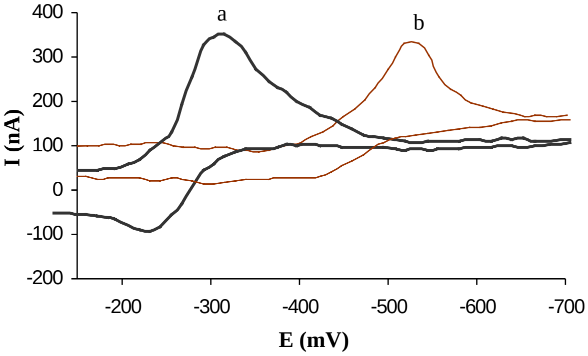

Fig. 1. Cyclic voltammograms of acetate buffer 0.05 M (pH = 6.7) containing 1×10^{-4} M $UO_2{}^{2+}$ (curve 'a') plus 4×10^{-3} M DPA with scan rate of $0.4\,V\,s^{-1}$.

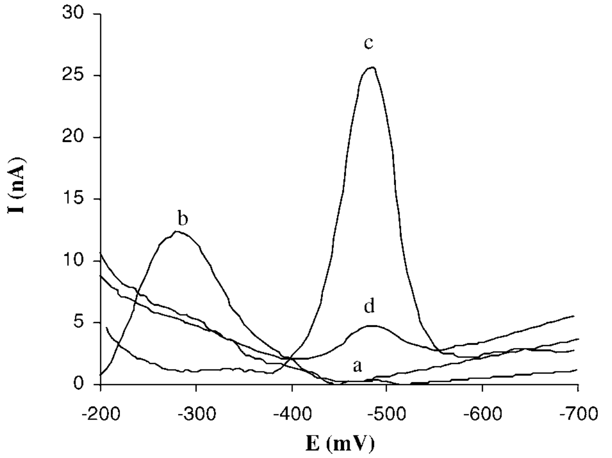

Fig. 2. Adsorptive stripping voltammograms of: (a) 5×10^{-5} M DPA; (b) 1×10^{-5} M UO_2^{2+}; (c) 5×10^{-8} M UO_2^{2+} in the presence of 5×10^{-5} M DPA in 0.05 M acetate buffer, pH = 6.7, with accumulation time = 150 s, accumulation potential = −0.20 V, and scan rate = 30 mV s^{-1}; (d) 5×10^{-8} M UO_2^{2+} and 5×10^{-5} M DPA without accumulation time.

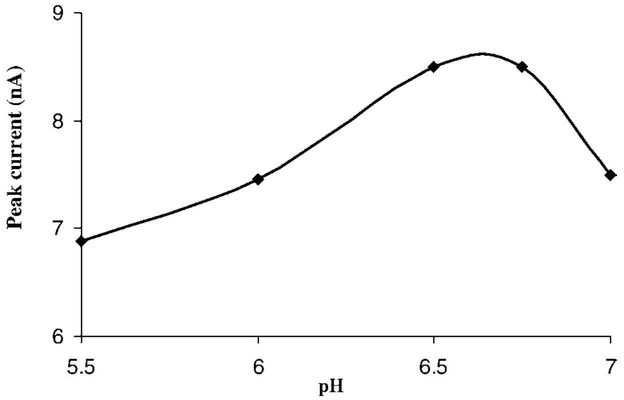

Fig. 3. Effect of pH on the peak current of 2×10^{-8} M U(VI), with [DPA] = 5×10^{-5} M in acetate buffers, accumulation time = 150 s, and accumulation potential = −0.20 V.

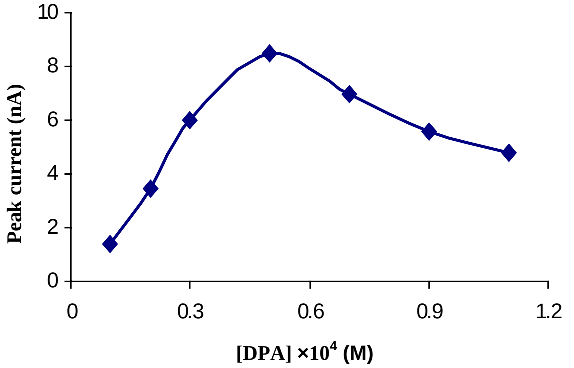

Fig. 4. Effect of DPA concentration on the peak current of 2×10^{-8} M U(VI), acetate buffer, pH = 6.7; other conditions as in Fig. 2.

on the presence and absence of DPA, which reveals the adsorptive nature of the response.

3.3. Optimizations

3.3.1. Effect of pH

Various electrolytes were tested as a supporting electrolyte (sodium acetate, sodium nitrate and sodium perchlorate). Of these, 0.05 M sodium acetate gave the best response. The effect of pH in the system was also studied in the range 5.5–7.5 (Fig. 2). It was observed that the height of reduction peak increase by raising the pH of the medium. This is due to complexed uranyl species adsorbed onto the electrode surface. The peak height reached its maximum at pH range 6.5–6.8. A decrease in response was observed at pH > 6.8 due to formation of hydroxocomplexes. Therefore, pH = 6.7 was chosen for subsequent experiments.

3.3.2. Effect of ligand concentration

The reduction current of 2×10^{-8} M U(VI) was measured in the presence of various concentrations of DPA at pH = 6.7 using a collection time of 150 s at the potential of −0.20 V. The results are shown in Fig. 3. As it is seen, maximum current was obtained for a concentration of 5×10^{-5} M of DPA; so, this concentration was selected for subsequent experiments.

3.3.3. Effect of accumulation potential, accumulation time and scan rate

The influence of the accumulation potential on the U(VI) peak current was also tested between 0 and −0.30 V. The plot of stripping peak current as a function of preconcentration potential (Fig. 4) indicates that the peak current increased with changing the potential from 0 to −0.20 V probably due to the increased accumulation of U(VI)–DPA complex on the electrode surface. The peak current decreased at potential more negative from −0.20 V. The best results, judged from the overall signal to background characteristics, were obtained at an accumulation potential of −0.20 V. For subsequent work −0.20 V was selected. The effect of accumulation time on the peak current was also studied. Fig. 5 shows a plot of peak current versus

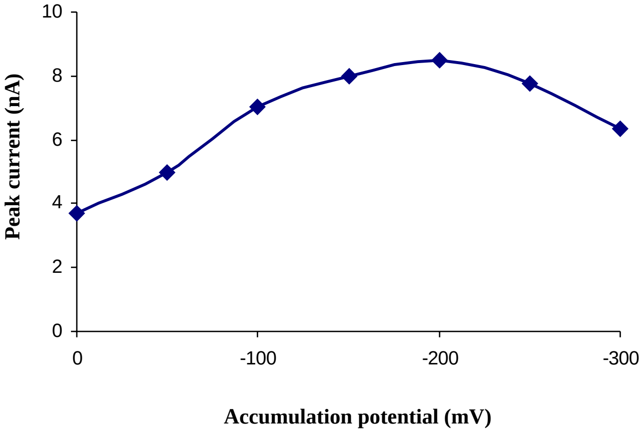

Fig. 5. Effect of accumulation potential on the peak current, in the presence of 5×10^{-5} M DPA; other conditions as in Fig. 3.

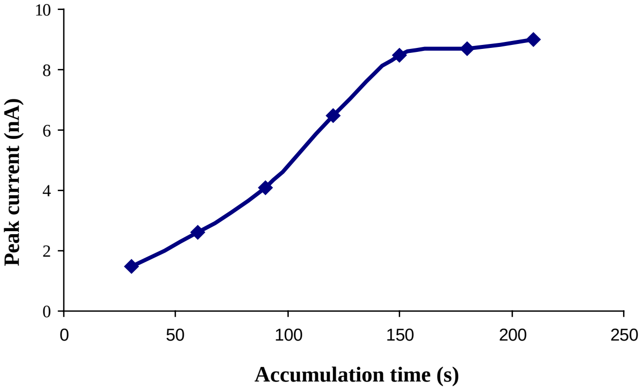

Fig. 6. Effect of accumulation time on the peak current, at accumulation potential = −0.20 V; other conditions as in Fig. 4.

accumulation time. For times longer than 150 s the current was constant, illustrating that adsorptive equilibrium was achieved. The effect of scan rate on the stripping peak current was tested in the range 10–50 mV s^{-1}, the current was found constant at scan rates higher than 30 mV s^{-1}. Therefore, a scan rate of 30 mV s^{-1} and accumulation time of 150 s was selected for subsequent studies.

3.4. *Linear range, detection limit and reproducibility of method*

Under the selected conditions, the reduction peak current of the uranium complexes yields well-defined concentration dependence. Fig. 6 shows voltammograms for solutions of increasing U(VI) concentration after 150 s accumulation, sharp and well-defined peak are observed. The calibration equation obtained by the least squares method is $y = 1.81X + 0.061$ ($R^2 = 0.9991$) where y is peak current (nA) and X is the concentration of U(VI) in nM. The reduction peak current of uranium complex was found to be directly proportional to the uranium concentration in the range of 1×10^{-9} to 1.2×10^{-7} M following 150 s of accumulation time. The detection limit calculated as (3s) [28] of the blank value obtained under the optimal experimental conditions is 0.27×10^{-9} M ($n = 7$). Ten successive measurement of 3.5×10^{-8} M uranium after 150 s of accumulation showed the relative standard deviation of 2.5% (Fig. 7).

Table 1
Effect of divers' ions on the estimate of uranium

Ions	Tolerance concentration (ng ml^{-1})
Na^+, Cl^-, K^+, NO_3^-, CN^-, SO_4^{2-}[a] K^+, HPO_4^{2-}[a] Ca(II), Ba(II), Mg(II), Li^+, Cs^+	20000[a]
Ag(I)	5000
Cu(II), Co(II), Cd(II), Cr(III), Ni(II)	2000
Mn(II), Br^-	1000
Zn(II), Fe(II), Hg(II), Tl^+	500
Pb(II)	10
Pb(II)[b], V(III), $Cr_2O_7^{-2}$	300
Fe(III), Al(III)	150

[U(VI)] = 4.2×10^{-8} M, [DPA] = 5×10^{-5} M, pH = 6.7, accumulation potential = −0.20 V, accumulation time = 150 s.

[a] Maximum concentration of foreign species tested.

[b] After addition of 20 μL of 0.001 M EDTA solution as masking agent.

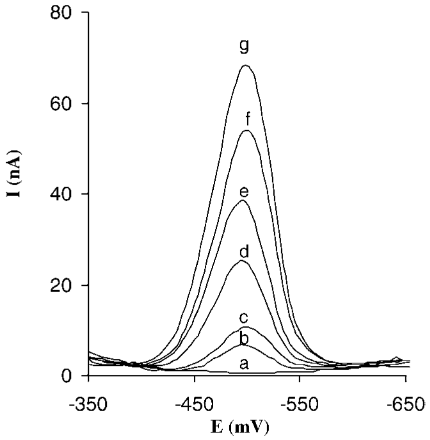

Fig. 7. Adsorptive stripping voltammograms for concentration of U(VI): curves 'a' = 0, 'b' = 1×10^{-8}, 'c' = 2×10^{-8}, 'd' = 5.3×10^{-8}, 'e' = 7.6×10^{-8}, 'f' = 1×10^{-7} and 'g' = 1.2×10^{-8} M, at optimal conditions of 0.05 M acetate buffers (pH = 6.7), [DPA] = 5×10^{-5}, accumulation potential = −0.20 V, accumulation time = 150 s, and scan rate = 30 mV s^{-1}.

3.5. *Interference studies*

The effect of co-exiting ions on the determination of uranium was investigated. More than 30 ions were examined for their possible interferences in the determination of 4.2×10^{-8} M uranium under optimized conditions. The tolerance limit was defined as the concentration, which gave an error at <3.0% in the determination of 4.2×10^{-8} M uranium. The results are presented in Table 1. It was found that only Pb(II) interfered in determination of uranium, which interference can eliminated by the addition of 20 μL EDTA (0.001 M) to the solution containing uranium. It have been reported that interference of some metal ions had some effect on the determination of uranium using different ligand such as catechol [12], mordant blue 9 [13], oxine [14], cupferron (nitrosoarylhydroxylamines) [15], and other ligands [16–24]. The cathodic adsorptive stripping determination of uranium in the presence of dipicolinic acid is highly selective and sensitive.

3.6. *Application*

In order to examine the performance of AdCSV in a practical situation, the method was used in the determination of trace amount of uranium in real water samples and some synthetic mixtures (Table 2). The data obtained for water samples spiked with uranium showed good recoveries. The method was also applied for the determination of synthetic mixtures. The results are shown in Table 2.

Table 2
Determination of U(VI) in synthetic and natural water samples ($n = 5$)

Sample UO_2^{2+}	Added[a]	Found	Recovery (%)	RDS (%)
Tap water	10	9.9 ± 0.3	99	2.6
	2	11.8 ± 0.3	98	2.5
Mineral water	10	9.8 ± 0.3	98	2.5
	2	11.7 ± 0.3	97	2.2
Synthetic sample[b]	10	10.2 ± 0.3	102	2.8
	2	12.1 ± 0.3	101	2.7
Synthetic sample[c]	10	9.8 ± 0.2	98	1.9
	2	11.8 ± 0.3	98	2.2

[a] ng ml^{-1}.

[b] A solution containing: Ag(I), Cu(II), Co(II), Cd(II), Cr(III), Ni(II), (500 ng ml^{-1}) and Pb(II), Fe(II), Zn(II), (200 ng ml^{-1}) and 5×10^{-5} M EDTA.

[c] A solution containing CN^-, SO_4^{2-}, HPO_4^{2-}, Cu(II), Ag(I), (500 ng ml^{-1}) and Cd(II), Fe(II), Mn(II), (200 ng ml^{-1}).

The good recoveries indicate the successful applicability of the proposed method for the determination of uranium in the presence of other metal ions and anions.

4. Conclusion

The present study demonstrates that cathodic adsorptive striping voltammetric determination of uranium based on accumulation of uranium–DPA complexes can be used to determine trace amount of this element in the presence of other ions. The method offers a practical potential for trace determination of uranium with high selectivity, sensitivity, simplicity and speed that have not been present together in the previously reported systems [12–26]. In determination of U(VI) by Berg [12], it is reported that complex ions of catechol with Fe(III) and V(V) have reduction potential near that of U(VI). Therefore, the interferences due to overlapping stripping peaks of these metal ions are possible. Also, the shorter accumulation time in comparison with report of Farias et al. [25] causes to reduce the analysis time.

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