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Differential Pulse Polarographic Determination of Uranium (VI) in rocks by adsorptive cathodic stripping voltammetry

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Abstract

Uranium (VI) forms a complex with potassium hydrogen phthalate. 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). The reduction current of adsorbed complex ions of differential pulse cathodic stripping voltammetry (DPCSV), preceded by a period of preconcentration onto the electrode surface. As low as 2×10^{-9} mol dm⁻³ (0.5 mg:l) and 2×10^{-8} mol dm⁻³ (4.8 mg:l) with accumulation time 240 and 120 s using DPCSV, respectively, have been determined successfully. The relative standard deviation of 2.2% at the 5 ppm level was obtained. The interferences of some metal ions and anions were studied. The concentration of the analyte was estimated by the standard deviations (n = 10) indicated the good precision and reproducibility of the selected procedure. The concentration of U (VI) found ranged from: 1.23 – 21.422 ppb in the sample. The stripping voltammetry method was shown to be simple and accurate for detecting U (VI) in rock samples.

Keywords: Cathodic adsorptive stripping voltammetry; Uranium (VI) , rocks

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Introduction

Uranium is a toxic element that occurs naturally in most rocks in concentrations of 2–4 $\mu\text{g kg}^{-1}$, and, in much lower concentrations, in surface (0.03–2.1 $\mu\text{g L}^{-1}$) and ground (0.003–2.0 $\mu\text{g L}^{-1}$) water. In seawater the concentration is about 3.0 $\mu\text{g L}^{-1}$ [1]. Uranium, can, also, enter the environment as a consequence of several technogenic processes, such as burning of fossil fuels, nuclear weapons fabrication and testing, nuclear fuel cycle processes, radioisotopes production and application and nuclear accidents. Due to the uranium intake in human body, especially from water, vegetables, cereals and table salt, its monitoring in the environment is essential [2].

Radiometric techniques (alpha-, gamma spectrometry and liquid scintillation counting) [3], inductively coupled plasma-mass spectrometry (ICP-MS) [4] and neutron activation analysis [5] can be successfully used for the determination of uranium; however, these methods are not cost-effective and are, mostly, available in centralized laboratories. On the other hand, electroanalytical techniques are simpler in means of equipment and expenditure and yet are potent tools for the determination of uranium in water samples.

Among them, various procedures based on solution-phase voltammetry on mercury electrodes have been proposed [6,7] However, sensitivity issues do not allow their application to the direct monitoring of uranium in environmental samples. Contrary to these methods, adsorptive stripping voltammetry (AdSV), which relies on complexation of uranium with a surface-active ligand and adsorptive preconcentration of the complex on the surface of the working electrode, offers low limits of detection and so far it has been extensively used for the determination of uranium in environmental samples. Reagents that have been proposed for the complexation of U(VI) ions, among others, include oxine [8], hydroxyethyl piperazine ethane sulfonic acid [9], cupferron [10], propyl gallate [11], chloranilic acid [12], catechol [13], potassium hydrogen phthalate [14], aluminon [15], 8-hydroxyquinoline [16], pyromellitic acid [17], arsenazo (III) [18] and humic acid [19]. However, mercury, onto which all the above uranyl complexes are absorbed, is not recommended because of its toxicity, and thus, a new type of electrodes, based on less toxic bismuth [20] has been alternatively proposed for the determination of uranium [21,22]. In general, the performance of these electrodes is good, although reported values for both limit of detection and preconcentration time are higher compared with those have been reported at mercury electrodes. Other electrode materials based on lead-coated glassy

carbon electrodes [23], mercury film silver-based electrodes [24], and iridium-based mercury electrodes [25] have also been proposed; however, in these approaches as well, issues related to environmental considerations are still unsolved. Despite the excellent in some cases figures of merit of the above electroanalytical techniques, the development of solid-state sensors is also in parallel progress, as, in principle, the latter hold promise for routine, on-site environmental monitoring of uranium. A number of sensors based on solid-state electrodes modified with propyl gallate [26], N-phenylcinnamohydroxamic acid [27], carbamoyl phosphonic acid [28], self-assembled monolayers of thiols functionalized with phosphate groups [29,30], nafion [31], calixarenes [32,33], carbon nanotubes [34], and electrochemically produced 4-carboxyphenyl moieties onto graphite electrodes [35], has been proposed the last two decades. In general, the uranyl sensors proposed so far are inferior, in terms of sensitivity and rapidity, compared with the AdSV-based methods. Limits of detection near nM level are usually achievable at prolonged incubation times (>13 min [34,35]; >20 min [28]), whereas, in some cases, the reported limit of detection values are higher than 10 ppb [33], or even, 100 ppb [26,29]. In addition, multistage sensor fabrication or special electrochemical pre-treatment employed in some of the reported methods [29,30,32,35] are not really compatible with cost effective, mass production techniques of sensor fabrication. In this work, we have explored the possibility of determining uranium in inoculated tap and lake water samples by using a preconcentrating sensor based on PAA-modified GRA electrodes. The proposed sensors exhibit a high selectivity towards U(VI) ions and the way of their fabrication is compatible with mass production techniques. Application to real matrices, rich in organic matter, was successfully tested by passing the sample through a C-18 microcolumn. Following this simple and fast procedure, the total time of analysis was shortened from several hours (following a common UV-digestion based treatment) to less than 30 min.

2. Experimental

2.1. Instrumentation.

differential pulse stripping voltammetry were recorded by polarographic Analyzer stripping voltammeter Model 264 A (EG&G, Princeton Applied Research; Princeton, NJ, USA), coupled with a PAR 303 A Static Mercury Drop Electrode (SMDE; drop size: medium, area of the drop:0.014 cm²). The polarographic cell bottom (PAR Model K 0060) was fitted with a saturated Ag: AgCl, reference electrode, and platinum wire used as a counter electrode. A PAR 305 stirrer was connected to the 303 SMDE. A PAR Model RE 0089 X-Y recorder was used for recording the voltammograms.



2.2. Chemicals

The following reagents were prepared. A 0.01- mol dm⁻³ aqueous stock solution of U(VI) was prepared by diluting the appropriate volume from uranyl perchlorate (prepared in our laboratory) [41]. A 0.01-mol dm⁻³ solution of the ligand; potassium hydrogen phthalate (Merck) was prepared by dissolving the appropriate amount in bidistilled water. The solution was used for a few days only to avoid the bacterial effects. Solutions of 0.1 mol dm⁻³ sodium perchlorate, potassium nitrate, potassium chloride, and 0.2 mol dm⁻³ sodium dihydrogen phosphate were used as supporting electrolytes. Sodium hydroxide solution (0.1 mol dm⁻³) was used to adjust the pH of the supporting electrolytes using an Orion 601 A precision Research Ion analyzer digital pH meter.

2.3. Analysis of mineral rock samples.

Transfer about 0.6 g of dried and powdered ore sample into a 100 ml beaker, add about 15 ml of 12 M hydrochloric acid, and boil on a hot plate, then add 5 ml of 16 M nitric acid and boil the solution almost to dryness. Take the residue with a solution (1:1) of nitric acid and boil for 15 mm, filter and wash with a 5% hot nitric acid solution, transfer the filtrate into a 100 ml flask, and dilute to volume. Take five 10 ml flasks and pipet 1 ml portions of the sample solution into each, and add 0, 0.2, 0.4, 0.6, and 0.8 ml of 1W5M U(VI) nitrate standard solution, respectively. Add 1 ml of 0.5 M EDTA solution for each flask, dilute to volume, Extract the U(VI) oxinate into chloroform as described above for pure uranium solutions. Transfer each chloroform extract into a polarographic cell, add 0.25 g of tri-BAP as supporting electrolyte, record the pulse polarograms as described above, construct the standard addition graph to determine uranium

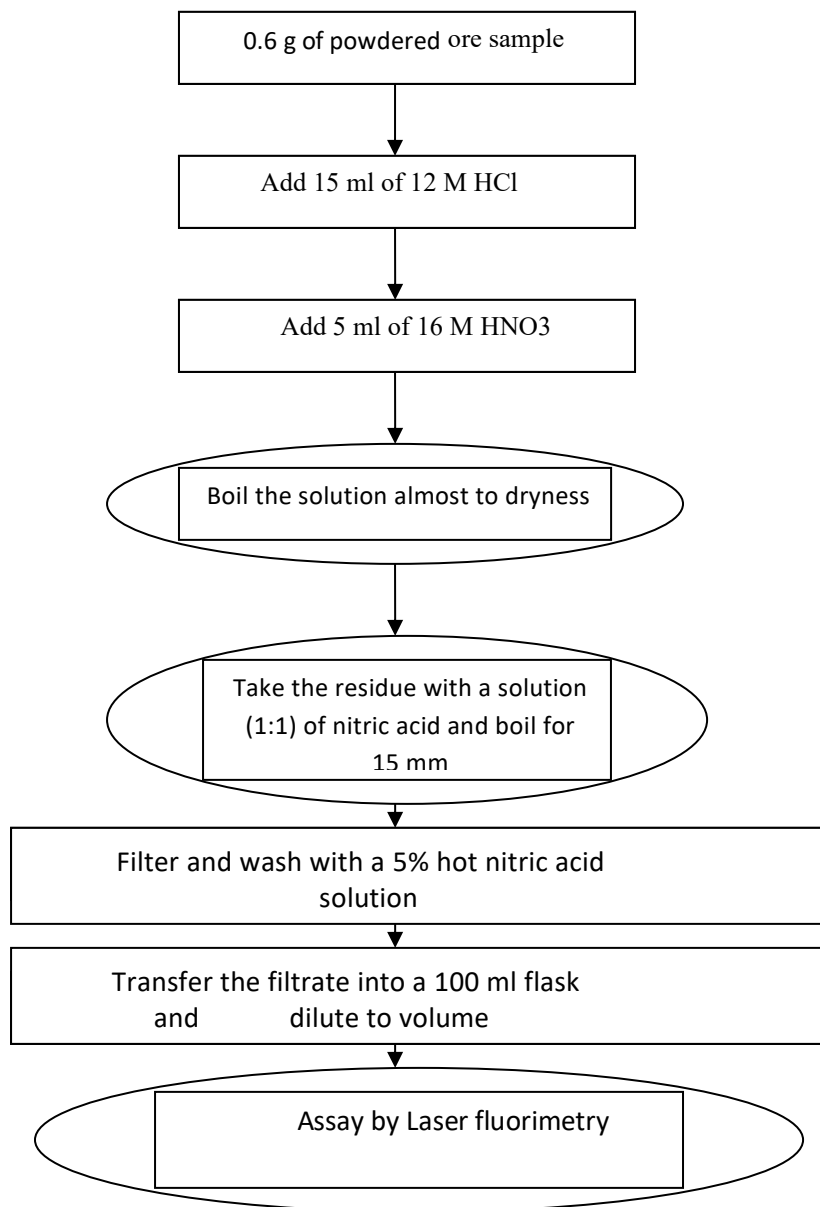


Figure 2. Chart of sample digestion of sample

2.4. Procedure

A known volume (10 ml) of 0.01 mol dm⁻³ sodium perchlorate (pH:7) as supporting electrolyte was deaerated with nitrogen for 16 min then for 30 s before each adsorptive stripping cycle. The preconcentration potential of -0.1 V (vs. Ag:AgCl); was applied to the electrode for a period of time, while the solution was stirred at 400 rpm. The stirring was then stopped as controlled by the microprocessor and after 15 s (equilibrium time) the voltammogram with negative potential scan was recorded. The scan rate was 100 mVs⁻¹ for direct current stripping (DCSV) and 5 mVs⁻¹ for differential pulse stripping voltammetry (DPSV) with 50 mV pulse amplitude and pulse duration of 1 s. The same procedure was repeated after spiking the ligand and uranyl perchlorate. All data were obtained at room temperature 10⁻⁶ mol dm⁻³ UO₂²⁺ preceded by quiescent period of 15 s (without preconcentration time) at deposition potential -0.1 V in the presence of 10⁻⁵ mol dm⁻³ potassium hydrogen phthalate at pH:7, 0.01 mol dm⁻³ sodium perchlorate shows that the U(VI)-U(V) reduction peak is located at -0.6 V Fig. 1. There is a 0.31 V difference in the cathodic and anodic peak potentials. The peak heights of scans 1, 2, and 3 are almost the same, whereas subsequent cycles show an increase in the peak signal. Thus, reduction of this complex is irreversible as demonstrated by differential pulse stripping voltammetry Fig. 1. Complex ions of U(VI) are reduced to U(V), which is oxidized initially to the free uranyl ion, followed by relatively slow complex reformation. Then, some of the U(VI) formed by reoxidation remained on or near the electrode surface and was reduced again in the next cathodic scan. This behavior illustrates the increase of the cathodic peak height. As well as, some part of U(V) formed in cathodic scan is reoxidized to U(VI), this may be leads to a very small anodic peak appears in the opposite scan (anodic) direction. This mechanism was confirmed by van Den Berg and Huang. [20].

RESULTS AND DISCUSSION

Uranium is a component of practically all rocks and therefore it is classified as a lithophilic element. Its relative abundance compares to silver, gold and the light rare earths elements and it is more common than tin, mercury and lead. It occurs in numerous minerals and is also found in lignite, monazite sands, phosphate rock and phosphate fertilizers, in which

the uranium concentration may reach as much as 200 mg kg⁻¹ Voltammetric techniques are known to show unique advantages both economical (low initial and running costs) and strictly analytical (the ability to determine low levels of metal in different matrixes). In particular, stripping techniques are perfectly suited for trace and ultratrace metal determination. Adsorptive cathodic stripping voltammetry (ACSV) is based upon adsorptive accumulation of metal ion complex with a suitable ligand at the electrode and then scanning the potential of the electrode in the negative direction. A single sharp adsorption peak was observed in presence of 10 mM sodium perchlorate and 0.1 mM potassium hydrogen phthalate, pH~7at preconcentration potential -0.4V vs. Ag, AgCl/Cl⁻ (sat'd) electrode. Uranium species is accumulated onto the electrode surface as phthalate complex. The current signal may be considered as the result of reduction of U(VI) to U(V). The optimum accumulation time were tested to determine U(VI) in all samples under investigation. Fig. 26 represents the differential pulse cathodic stripping voltammograms for U(VI) ions in sample G1 at different accumulation times. The linear relation must verify between accumulation time and the current signal as shown in Fig. 27. It's noticed that the peak height increases by increasing accumulation time. The optimum accumulation times are 30, 30, 30, 120, 90, 120, 30, 30, 60 and 120 sec. for determination of uranium (VI) ions in samples C1, C2, C3, C4, C5, P1, P2, P3, G1 and G2 respectively. Fig's 28, 29 and 30 represent DPCSV of U(VI) ions in samples C1, P3 and G1 in presence of different concentrations of standard solution of U(VI). On plotting of *i*_p against concentration of U(VI) added, straight lines are obtained as shown in Fig's. 31 and 32. From the interception of the line with the concentration axis at zero current signal, gives the concentration of the analyte in the voltammetric cell for each sample. The uranium content of different rock samples and its statistical parameters by linear regression method are tabulated in Table 7. The values reveal the accuracy of the proposed method. The results show that the concentrations are ranging from 0.167 to 3.637 mgKg⁻¹ in rock samples.

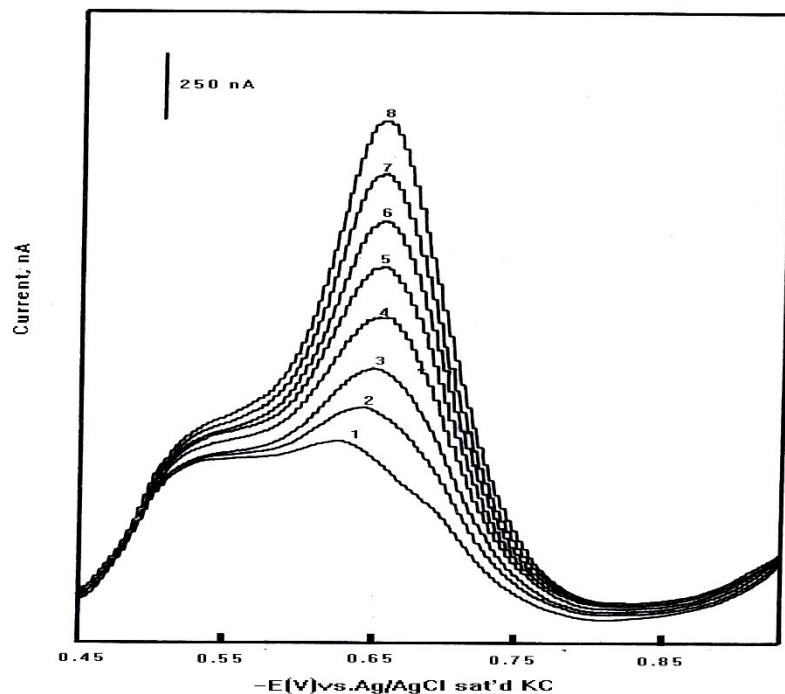


Fig. (26):DPCS Voltammograms for U(VI) ions in sample G₁ in 10 mM sodium perchlorate and 0.1 mM potassium hydrogen phthalate, pH ~7at preconcentration potential -0.4V and different accumulation times.

- | | | | |
|---------|--------|--------|-----------------|
| 1) zero | 2) 30 | 3) 60 | 4) 90 |
| 5) 120 | 6) 150 | 7) 180 | and 8) 210 sec. |

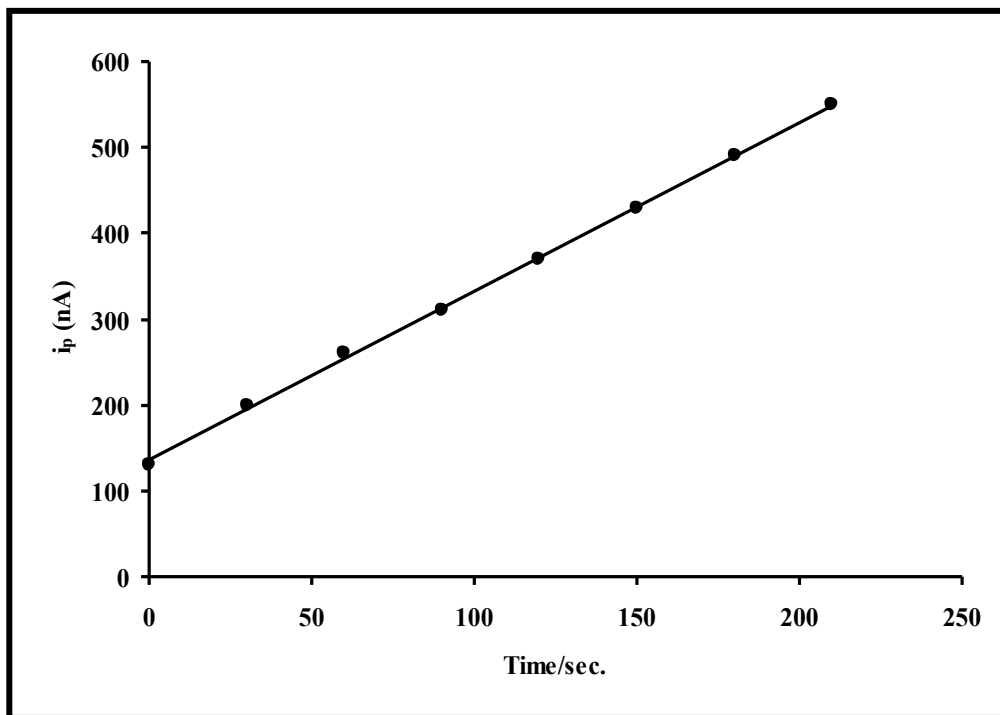


Fig. (27): Effect of accumulation time on the i_p for U(VI) ions in sample G₁.

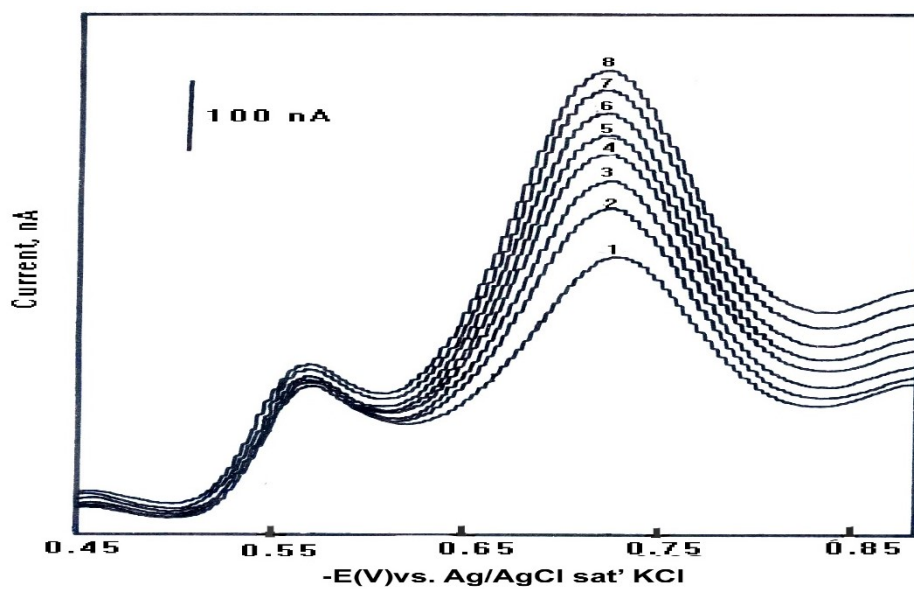


Fig. (28): DPCS Voltammograms for determination of U(VI) ions in sample C₁ spiked with different concentrations of U(VI); accumulation time 210 sec.

1) sample, S 2) S + 5x10⁻⁶ 3) S + 10x10⁻⁶ 4) S + 15x10⁻⁶ 5)
S + 20x10⁻⁶ 6) S + 25x10⁻⁶ 7) S+30x10⁻⁶ and 8) 35x10⁻⁶M
U(VI).

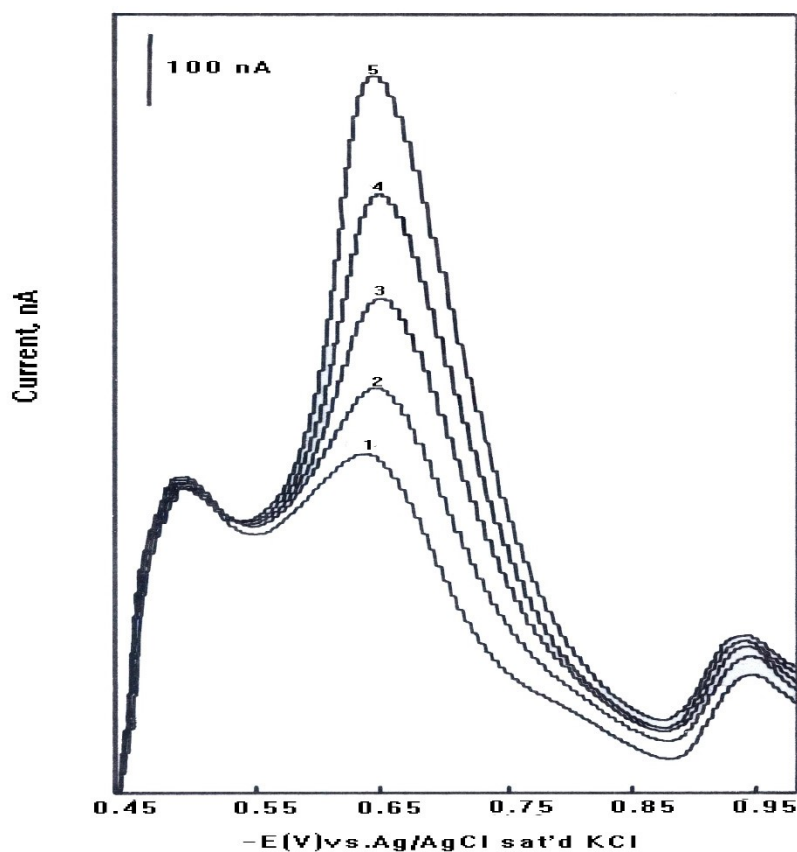


Fig. (29): DPCS Voltammograms for determination of U(VI) ions in sample P₃ spiked with different concentrations of U(VI); accumulation time 210 sec.

1) sample, S 2) S + 5 x10⁻⁶ 3) S + 10x10⁻⁶

4) $S + 15 \times 10^{-6}$ and 5) $S + 20 \times 10^{-6}$ M U(VI).

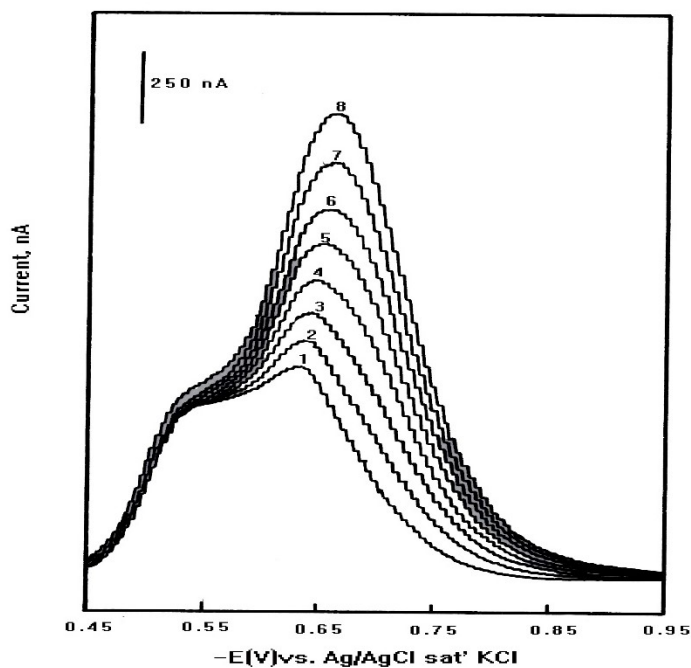


Fig. (30): DPCS Voltammograms for determination of U(VI) ions in sample G_1 spiked with different concentrations of U(VI); accumulation time 210 sec.

1) sample, S 2) $S + 2 \times 10^{-6}$ 3) $S + 4 \times 10^{-6}$ 4) $S + 6 \times 10^{-6}$
5) $S + 8 \times 10^{-6}$ 6) $S + 10 \times 10^{-6}$ 7) $S + 12 \times 10^{-6}$ and 8) $S + 14 \times 10^{-6}$
 6 M U(VI).

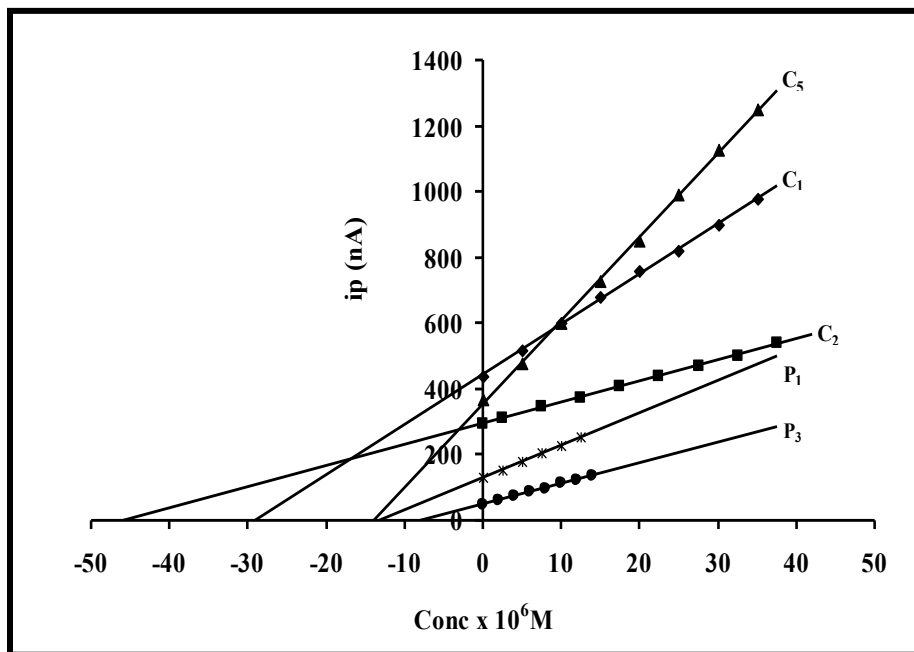


Fig. (31): Standard addition plots for determination of U(VI) ions in samples C₁, C₂, C₅, P₁ and P₃ at accumulation potential - 0.4V and accumulation time 30, 30, 90, 120 and 30 sec. respectively.

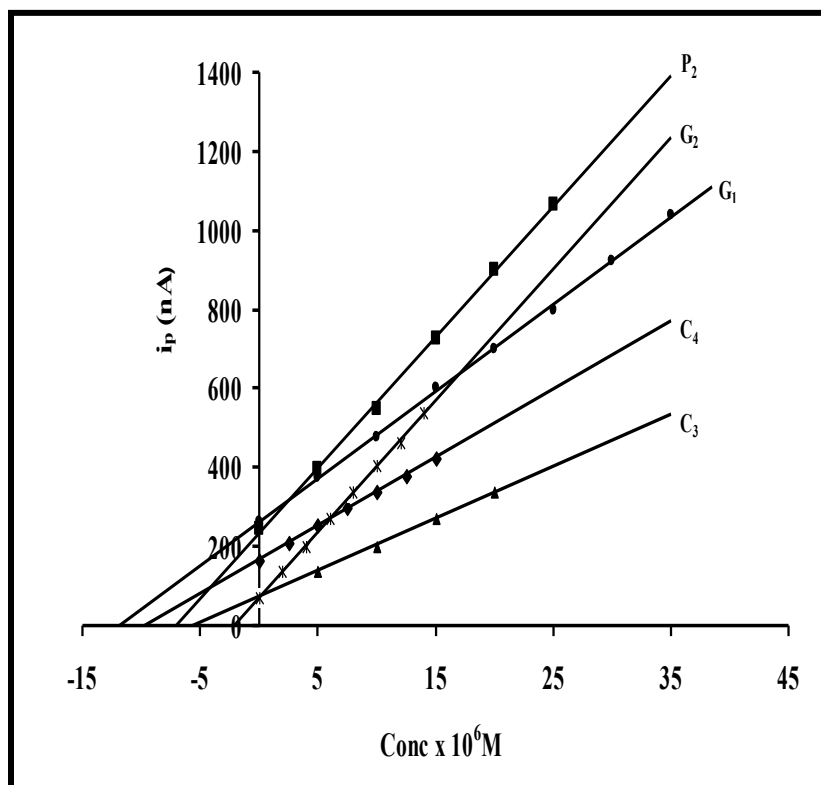


Fig. (32): Standard addition plots for determination of U(VI) ions in samples C₃, C₄, G₁, G₂ and P₂ at accumulation potential - 0.4V and accumulation time 30, 120, 60, 120 and 30 sec. respectively.

Table (7): Uranium content in rock samples.

Sample Number	T _{ac} Sec.	Uranium content (mean±SD) mgkg ⁻¹	Regression parameter				Confidence	
			Slope	Intercept / (10 ⁻⁹ mol dm ⁻³)	Corr. Coef.	Highe	Lower	
C ₁	30	2.310±0.201	0.065	29.07	0.9991	2.559	2.060	
C ₂	30	3.637±0.301	0.155	45.84	0.9992	4.010	3.263	
C ₃	30	0.770±0.3298	0.058	9.71	0.9995	1.179	0.361	
C ₄	120	1.100±0.115	0.039	13.86	0.999	1.243	0.957	
C ₅	90	1.055±0.102	0.101	13.29	0.9994	1.181	0.928	
P ₁	120	0.633±0.96	0.160	7.98	0.999	1.825	0.558	
P ₂	30	0.557±0.040	0.030	7.02	0.999	0.607	0.507	
P ₃	30	0.453±0.027	0.076	5.71	0.999	0.486	0.419	
G ₁	60	0.941±0.081	0.045	11.85	0.999	1.041	0.839	
G ₂	120	0.167±0.001	0.03	2.10	0.999	0.168	0.166	

a mean value ± standard deviation for n=5 at the 95% confidence level

CONCLUSIONS



The concentration of uranium in the geological sample was determined using the voltammeter. The method of voltammeter can be used for other types of matrices containing uranium. This method is sensitive and selective determination of uranium.

It is recommended to use voltammeter method for verification of uranium in samples of small weight, showed accurate indication and determination of uranium concentration in the samples.

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