



# A Rapid Sensitive Voltammetric Determination of Ultra Trace Level Uranium in Sea Waters

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## Abstract

A simple and convenient voltammetric method is described for the determination of low concentration uranium in aqueous matrices. It is based on the electrochemical reduction of uranium (VI) in a complexing medium of thioglycolic acid in acetate buffer. The interference of possibly associated metal ions was examined and ruled out. It was observed that on increasing the concentration of uranium the peak current increased linearly up to a concentration of 20 ppm. Limit of determination was observed to be 0.005 ppm. The method has been successfully applied for the trace level estimation of uranium in sea water samples.

**Keywords:** Differential pulse polarography, uranium, sea water samples, uranium, DPP, waste water analysis.

## Introduction

Uranium is a white/black metallic element belonging to the actinide series of the periodic table. From the point of view of nuclear energy production, uranium and its isotopes are of tremendous importance. Other applications include its use in photographic chemicals (especially uranium nitrate as a toner)<sup>1</sup>, in lamp filaments and to improve the appearance of dentures. It is also used in leather and wood industries for stains and dyes<sup>2</sup>. In nature uranium is present in various minerals [autunite, tobernite, uraninite (UO<sub>2</sub>) etc], soil and sea waters. In view of rapid growth of industrialization and energy production, various toxic metals<sup>3</sup> are used and finally disposed causing water pollution.

Pulse polarography and stripping voltammetry are sensitive electroanalytical techniques; comparable with atomic absorption spectroscopy (AAS)<sup>4,5</sup>, XRD<sup>6</sup>, neutron activation analysis<sup>7</sup>, for the analysis of trace metals. The different ionic forms of an element can be characterized and determined by voltammetric methods due to the selectivity of the redox potential as in case of gallium (III) which is stable in solution<sup>8</sup>. Therefore the suitability of differential pulse polarography (DPP) is envisaged in present studies.

The first study of polarography of uranium was carried out by Herasymenko where he observed that in neutral or weakly acidic media uranyl ion undergoes a stepwise reduction to produce a polarogram comprising of three waves for subsequent reduction to +5, +4 and +3 states<sup>9</sup>. Preconcentration of trace uranium from seawater with solid phase extraction followed by differential pulse polarographic determination in chloroform eluate has been reported by Dj Dojozan, M.H Pournaghi-Azar and J Toutouchi-Asr<sup>10</sup>. M.H. Pournaghi-Azar, R. Zargharian

systematically investigated adsorptive pulse polarographic determination of uranium (VI) oxinate in chloroform and its use for the analysis of uranium mineral ores<sup>11</sup>. In another method determination of U (VI) in organic extraction phases: hydrocarbon-diethyl-2-hexyl phosphoric acid-trioctylphosphine oxide and hydrocarbon-tri-*n*-octylamine, diluted by an alcohol have been studied by direct current polarography and differential pulse polarography (DPP)<sup>12</sup>. The electrochemical investigations of complexes of uranium with, nitrilo triacetic acid, cupferron, salicylic acid and succinic acid have also been reported<sup>13-16</sup>. Kim et al has carried out electrochemical studies on [UO<sub>2</sub> (DMF)<sub>5</sub>] (ClO<sub>4</sub>)<sub>2</sub>, UO<sub>2</sub> (acac)<sub>2</sub> DMF and UO<sub>2</sub> (salen) DMF<sup>17</sup>.

The electrochemical data on uranium reveals that its aqueous chemistry predominates with +6 oxidation state in the form of uranyl ion (UO<sub>2</sub><sup>2+</sup>). A complexing medium of thioglycolic acid (TGA) in acetate buffer was therefore used where the reduction potential of complexed ion would be shifted to a sufficiently negative potential as to be measurable at a dropping electrode. The suitability of differential pulse polarography (DPP) is envisaged in present studies. The DPP determinations of thorium, selenium, gallium have also been reported<sup>18-20</sup>.

## Material and Methods

**Instrumentation:** A microprocessor based pulse polarographic analyzer (Model CL-362) in combination with a drop-timer assembly, all from Elico Limited, Hyderabad, India, was used for polarographic measurements. Current voltage curves were recorded by an Epson printer (Epson-LX-300+II). The instrumental settings for DPP were as follows: a dropping mercury electrode (DME) as the working electrode; pulse amplitude, 50 mV; pulse duration, 57ms; clock time of pulse,

0.5s; scan rate, 12mV/sec and charging current compensation, 20%. Potentials were measured against a saturated calomel electrode (SCE). Platinum wire was used as auxiliary electrode. Polarographic medium employed was 0.01 M  $\text{KNO}_3$ .

An atomic absorption spectrophotometer (Model – AA 2380, Perkin Elmer) USA, was also used for sample analysis. The instrument has a Czerny tuner grating monochromator with a wavelength range of 1900-9000Å°. Slit-Width is selectable in three modes of 1.9, 3.8 and 9.5Å°. Sample aspiration flow control is adjustable by variable 3-line flow system. Chemicals used in this work were of analytical grade purity.

The pH studies were made by a systronics digital pH meter (Model – 355).

**Sea Water Sample Preparation:** The marine samples were collected from Arabian Sea, near nuclear power plant. The contents of uranium were separated by selective extraction with di-2-ethyl hexyl phosphoric acid in carbon tetrachloride solution. It was followed by uranium purification by extraction of uranyl nitrate into ethyl acetate. Finally sample was made upto the requisite volume<sup>21</sup>.

Above pretreated sea water samples were deaerated for 20 minutes by passing purified nitrogen. All of the experiments were carried out in an air-conditioned laboratory where the temperature was maintained at  $25 \pm 1^\circ\text{C}$ . Nitrogen was purified by passing the gas through a vanadous chloride scrubbing solution kept in contact with amalgamated zinc to remove traces of oxygen.

## Results and Discussion

**Direct Current Polarographic Characteristics:** A well-defined wave corresponding to U(VI)/U(V) was obtained at  $-1.26\text{ V}$  in complexing medium of thioglycolic acid (TGA) in 0.01 M acetate buffer (figure 1). The wave current increased with the concentration of thioglycolic acid upto  $1 \times 10^{-1}\text{ M}$ .

**Effect of pH:** The influence of pH on electroreduction of U(VI) was observed by recording current-voltage curves at different pH in between 3.5 and 5.8 at a fixed concentration of TGA ( $6 \times 10^{-2}\text{ M}$ ). It was noticed that at a pH of 4.1 a distinct wave was obtained.  $E_{1/2}$  values changed slightly on varying the pH. The effect of pH on wave current is shown in figure 2.

Dependence of Limiting Current on the Height of Mercury Column.

The influence of mercury pressure on the limiting current was observed by recording the magnitude of limiting current at various height (h) of the mercury column. The linearity of  $I_l$  versus  $\sqrt{h}$  illustrated that the uranium (VI) – thioglycolic acid reduction in acetate buffer (pH 4.1) was diffusion controlled. Results are described in table 1.

The nature of electrode process of uranium (VI)–thioglycolic acid reduction in acetate buffer (pH 4.1) was studied by plotting  $\log i/(i_d-i)$  values against corresponding potential as shown in figure 3. A slope value of 0.066 was obtained which indicated that the electrode reaction was reversible.

**Differential Pulse Polarographic Studies:** U (VI)–thioglycolic acid electroreduction in acetate buffer (pH 4.1) gave a sharp DP peak at  $-1.26$  as shown in figure 4. It was observed that on increasing the concentration of uranium the peak current increased linearly upto a concentration of 20 ppm (table 2).

**Interference:** DP polarogram of uranium were also recorded in presence of some common metal ions such as lead and zinc. DP peaks of these ions were distinguishable from each other [Ep : Pb(II),  $-0.54\text{ V}$ ; Zn (II),  $-1.05\text{ V}$  Vs SCE], thus displayed no interference. The interference of coexisting metals i.e. nickel and vanadium with uranium in mineral ores was also examined. The peak potentials of Ni(II) and V(V) were measured at  $-0.609\text{ V}$  and  $-0.743\text{ V}$ , respectively which were well separated from that of U(VI) at  $-1.26\text{ V}$ . Similarly, Mn (II), Th (IV) and Ca (II) did not gave DP peak in these conditions.

A DP polarogram of U (VI) in presence of Pb(II), Ni(II), V(V) and Zn(II) is shown in figure 5.

**Limit of Determination:** The limit of determination of uranium in these conditions achieved was 0.005ppm.

**Accuracy and precision:** The DPP determination of uranium was evaluated for its precision and accuracy in terms of standard deviation and percentage error as described in table 3.

**Analytical Applications:** The thioglycolic acid sensitized DP reduction of U (VI) in acetate buffer (pH 4.1) was made the basis for trace level determination of uranium in sea water samples.

**Voltammetric measurement:** The prepared sample was taken into the polarographic medium and DP polarograms were recorded between  $-0.8\text{ V}$  to  $-1.4\text{ V}$ . Peak currents were measured at  $-1.26\text{ V}$  after making the blank correction. The results of uranium determination in sea water samples are summarized in table 4.

**Validation:** The validity of DPP measurements was further established by comparing the results with Atomic Absorption Spectrophotometric method. The comparative data are included in table 5.

## Conclusion

The complexation of uranium with thioglycolic acid in acetate buffer at pH 4.1 has enabled its determination at trace level with enhanced sensitivity of  $0.005\text{ }\mu\text{g/ml}$ . Further, the results obtained by DPP method are in good agreement with that obtained by Atomic Absorption Spectrophotometric method.

**Table-1**  
**Influence of Mercury Pressure on Limiting Current U (VI) = 0.75 x 10<sup>-4</sup> M, Thioglycolic Acid = 0.06 M, Acetate Buffer (pH = 4.1)**

S.No.	Height of Hg column (h) (cm)	$\sqrt{h}$ (cm)	I <sub>l</sub> (μA)	I <sub>l</sub> / h	I <sub>l</sub> / $\sqrt{h}$
1	55	7.41	3.91	0.0710	0.527
2	60	7.74	4.12	0.068	0.532
3	65	8.06	4.25	0.065	0.527
4	70	8.36	4.45	0.063	0.532
5	75	8.66	4.58	0.061	0.528
6	80	8.94	4.72	0.059	0.527
7	85	9.21	4.91	0.057	0.533
8	90	9.48	5.08	0.056	0.535
9	95	9.74	5.3	0.055	0.544
10	100	10.0	5.38	0.053	0.538

**Table-2**  
**Relationship Between Uranium (VI) Concentration and Peak Current, Thioglycolic Acid = 0.06 M, Acetate Buffer (pH 4.1)**

S.No.	U (VI) concn. (ppm)	i <sub>p</sub> (μA)
1	0.005	0.17
2	0.007	0.20
3	0.05	0.25
4	0.1	0.27
5	0.5	0.3
6	1	0.35
7	2	0.47
8	4	0.78
9	6	0.95
10	8	1.42
11	10	1.82
12	12	2.1
13	14	2.4
14	16	2.8
15	20	3.47

**Table-3**  
**Precision and Accuracy of Uranium (VI) Determination**

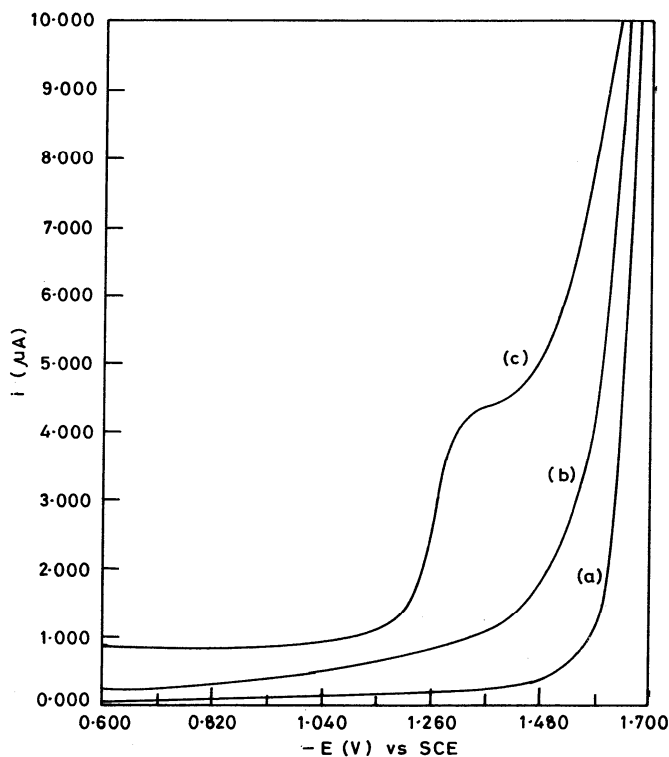
S. No.	U (VI) concn. (μg/ml)		S.D. (±)	R.S.D. (%)	Percentage Error (%)
	Present	Determined			
1	1.0	0.8314			
2	1.0	0.9956			
3	1.0	0.9957	0.0717	0.0745	4.48
4	1.0	0.9998			
5	1.0	0.9537			

**Table-4**  
**Results of U (VI) Determination in Sea Water Samples**

Sample	U(VI) Concn. (μg/ml)	Ave.	S.D. (±)	R.S.D. (%)
A	3.380	3.375	0.027	0.8088
	3.400			
	3.384			
	3.336			
B	4.196	4.118	0.052	1.261
	4.091			
	4.086			
	4.102			

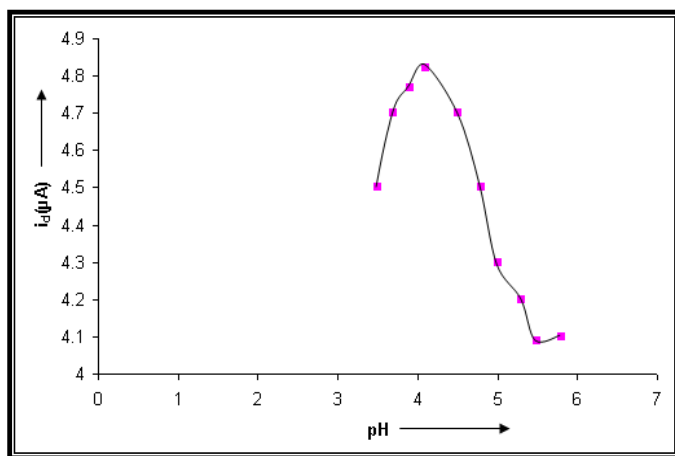
**Table-5**  
**Determination of Uranium (VI) by DPP and Atomic Absorption Spectrophotometry**

S. No.	Sample	Uranium ( $\mu\text{g/ml}$ )		
		Added	DPP	UV-VIS
1	Sea Water Sample A	–	3.375	3.270
2	Sea Water Sample B	–	4.118	4.20



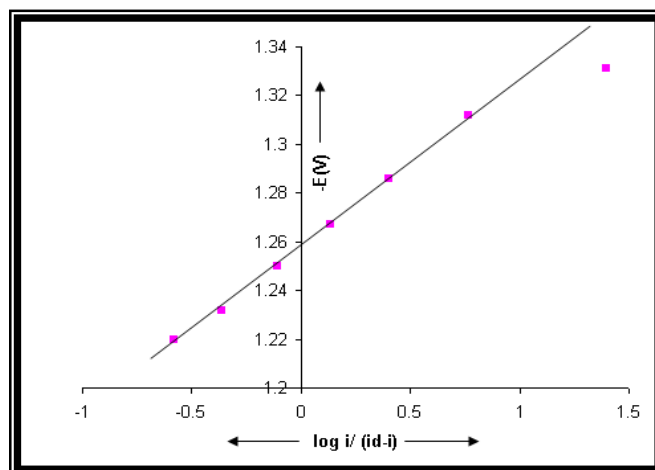
**Figure-1**

DC Polarogram of Uranium (VI): i. Blank Solution of 0.01 M Acetate Buffer (pH 4.1), ii. Blank Solution of  $6 \times 10^{-2}$  M Thioglycolic Acid (TGA) in 0.01 M Acetate Buffer (pH 4.1), iii.  $0.6 \times 10^{-4}$  M U (VI) -  $6 \times 10^{-2}$  M TGA IN 0.01 M Acetate Buffer (pH 4.1)



**Figure-2**

Effect of pH on U (VI)-Thioglycolic Acid System



**Figure-3**

Log Plot Analysis of Uranium (VI) – Thioglycolic acid Reduction in Acetate Buffer (pH 4.1)

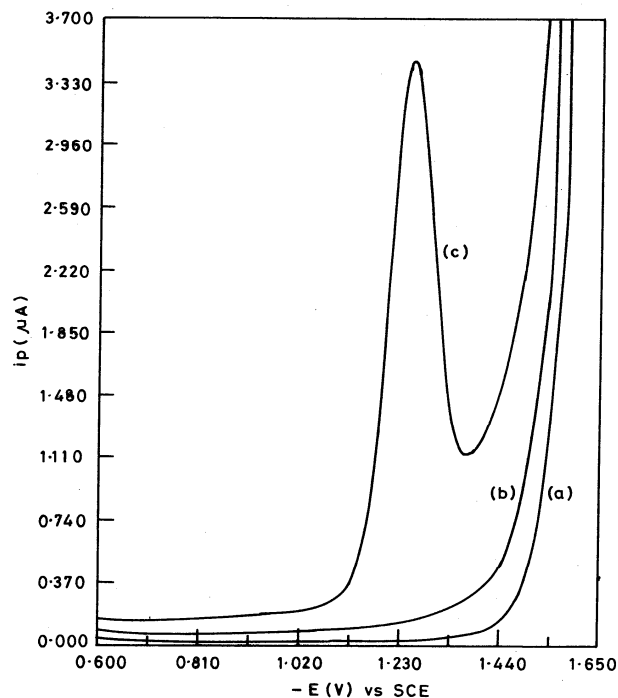


Figure-4

DP Polarogram of U (VI)-TGA in Acetate Buffer (pH 4.1)  
i. Blank Solution of Acetate Buffer (pH 4.1),  
ii.  $6 \times 10^{-2}$  M Thioglycolic Acid in Acetate Buffer (pH 4.1),  
iii. U (VI) - TGA in Acetate Buffer (pH 4.1), U (VI) = 20ppm

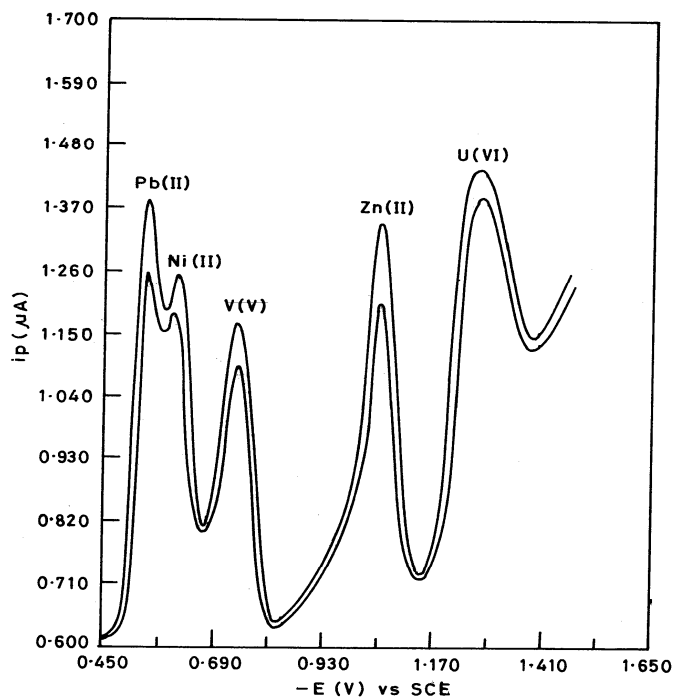


Figure-5

DP Polarogram of U (VI) in Presence of Pb (II), Ni (II), V (V) and Zn (II), Medium = 0.06 M TGA IN Acetate Buffer (pH=4.1), Pb (II) = 18ppm; Ni (II) = 12ppm; V (V) = 8ppm; Zn (II) = 8 ppm and U (VI) = 6ppm

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