

Spectrophotometric Determination of Uranium without solvent extraction in Geomaterials using Arsenazo-III in presence of EDTA

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ABSTRACT

A sensitive and selective spectrophotometric method for the determination of uranium ranging from 100 μ g to 4000 μ g U₃O₈/g of geomaterials (more than 4000 μ g U₃O₈/g of geo-materials is also possible by sub-dilutions), using disodium salt of ethylene diamine tetra-acetic acid (EDTA) and colour development with 2,7-bis(2,2-arseno phenyl azo) 1,8-dihydroxy naphthalene-3,6-disulphonic acid (Arsenazo-III) in phosphoric acid medium at $\lambda_{\text{max}} \sim 642$ nm was developed. Method is basically direct determination of uranium in coloured solution and it does not require solvent extraction for the removal of interferences, however, stoichiometry of the reagents solution is to be followed as per the optimised conditions.

Keywords : Uranium, Arsenazo-III, and Stability of Complex

I. INTRODUCTION

Natural uranium as main source of energy occurs in three isotopic forms as U₂₃₄-0.0056%, U₂₃₅-0.718% and U₂₃₈-99.276%. Uranium occurrence in earth crust is about 0.1-2ppm and in sea water is about 3ppb. The geological distribution of uranium, in India is about 0.046% - 0.265% U₃O₈ [1] and in Canada -high grade of uranium, 18% U₃O₈ in Cigar Lake and 21% U₃O₈ in Mc Arthur River deposit in Athabasca basin.

The largest deposit of the world is a polymetallic deposit in Australia, the Olympic Dam deposit (Cu, U, Au, Ag and REEs) contains low grade uranium (0.023%) along with moderate grades of silver and gold [2].

The reduced form of uranium (IV) occurs in primary uranium minerals, and the oxidised form of uranium (VI) in secondary uranium minerals which are variably soluble in oxygenated water as UO₂(OH)⁺, UO₂(OH)₂^o, (UO₂)₂(OH)₂²⁺, (UO₂)₂(OH)₂F⁺, UO₂Cl⁺,

UO₂(SO₄)^o, UO₂(SO₄)₂²⁻, UO₂(SO₄)₃⁴⁻, UO₂PO₄⁻, UO₂(HPO₄)^o, UO₂(H₂PO₄)⁺, UO₂(CO₃)^o, UO₂(CO₃)₂²⁻, UO₂(CO₃)₃⁴⁻etc [3]

Analytical chemistry as a tool plays an important role in determining uranium in geomaterials. Uranium determination requires high selectivity due to its strong association with other elements [4,5].

Several methods for the spectrophotometric determination of uranium using sodium fluoride, Arsenazo-III, 4-(2-pyridylazo)resorcinol, dibenzoyl methane etc have been reported [6], but most of them require solvent extraction step which entail various disadvantages in terms of reproducibility, simplicity, rapidity and sensitivity. The usefulness of the reactivity of Arsenazo-III lies in the fact that metals whose complex formation depends on high pH, do not interfere with the determination of other elements

such as Th, Zr, Pu and Np which give complexes in strongly acidic media [7].

Arsenazo-III is a commercial product, equally soluble in both water and dilute mineral acids [7,8,9,10]. Arsenazo-III was found to be more stable in acids like H_3PO_4 , HClO_4 and HCl than HNO_3 which can cause oxidation and can easily decompose azo-dyes at room temperature [11,12].

II. METHODS AND MATERIAL

UV/VIS 920 (GBC) with 10mm matched quartz cells equipped with a recording device was employed for the measurement of optical density/absorbance.

Reagents

- i. Uranium Standard Solution- $5\mu\text{g U}_3\text{O}_8$ / ml without maintaining acidity was prepared from $100\mu\text{g U}_3\text{O}_8$ / ml stock solution { prepared from $\text{UO}_2(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ } containing 5% HNO_3 acid using distilled water.
- ii. 1M. H_3PO_4 acid- 63.5ml of 88% ortho phosphoric acid (GR-pro analysis, Merk Ltd) was taken and made it up to 1litre with distilled water.
- iii. 0.5M. $\text{HONH}_2\cdot\text{HCl}$ - 8.686g of hydroxylamine hydrochloride (GR, Merk Ltd) was dissolved in 250ml of distilled water.
- iv. 0.05M. Na_2EDTA - 9.306g of disodium salt of ethylene diamine tetra-acetic acid(BDH, GPR, Merk Ltd) was dissolved in 500ml of distilled water.
- v. 10% TEA- 50ml of triethanolamine (Emparta-R, Merk Ltd) was dissolved in 500ml of distilled water.
- vi. Complexing Reagent, 0.025% Arsenazo-III- 0.05g of 2,7-bis(2,2-arsenophenylazo)1,8-dihydroxy naphthalene-3,6-disulphonic acid (GR, Merk Ltd) was dissolved in 200ml of distilled water and it was maintained with 0.05M. H_3PO_4 acid (0.64ml of 88% ortho phosphoric acid in 200ml).

Procedure

0.5g of geomaterial (-200mesh) was weighed in teflon beaker and was treated three times on hot plate with 10ml of 1:1 mixture of HNO_3 and HF acid, followed by two times treatment with 5ml of HNO_3 for complete dissolution [12]. Finally, sample was dissolved in 4% HCl acid and made up to 50ml.

Uranium standards in the range from $2.5\mu\text{g}$ to $40\mu\text{g U}_3\text{O}_8$ and 1ml aliquot for each sample were taken in 25ml flasks. Added 1ml of 1M. H_3PO_4 acid ($\sim 40\text{mM}\cdot\text{dm}^{-3}$), 0.5ml of 0.5M. $\text{HONH}_2\cdot\text{HCl}$ ($\sim 10\text{mM}\cdot\text{dm}^{-3}$), 2.5ml of 0.05M. Na_2EDTA ($\sim 5\text{mM}\cdot\text{dm}^{-3}$), 5ml of 10%TEA ($\sim 2\%$) and 1ml of 0.025% Arsenazo-III ($\sim 0.001\%$). The solution was made up to 25ml with deionised water. pH of the final solution was found to be in between 7.5 and 8.0. The solution was kept for 10-15 minutes for complete colour development and absorbance was measured at 642nm.

III. RESULTS AND DISCUSSION

Purple colour developed for uranium-Arsenazo-III complex is stable for more than two weeks at these conditions. Optimization of U_3O_8 standards 0.1-1.6ppm at wavelength range 400-700nm is shown in **Fig-1**. Maximum absorbance was observed at 642nm.

The absorbance of standards and samples was measured against blank/ zero absorbance and calibration graph was plotted upto 1.6ppm of U_3O_8 passing through zero absorbance. The linearity was observed upto 1.6 ppm of U_3O_8 as shown in **Fig-2**. The accuracy and precision determined for this range of standards was found excellent and the results showed that the percentage recovery of uranium was quantitative with good precision, 96.0-98.6% (Table-3).

It was also tested that similar results were obtained by

using perchloric acid or hydrochloric acid in place of ortho phosphoric acid. However, absorbance measurement with phosphoric acid was quite stable.

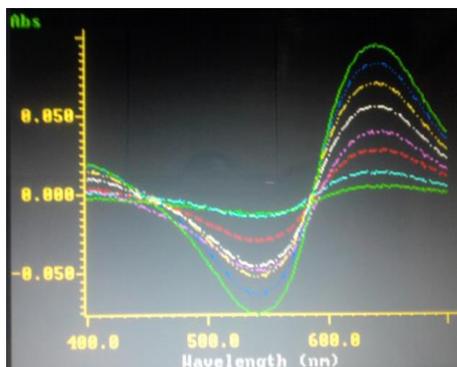
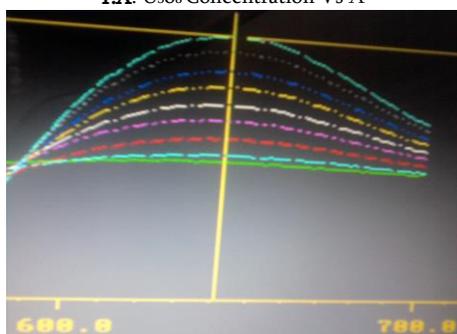
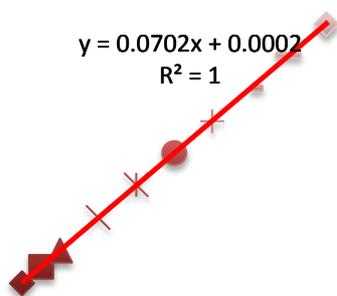


Figure-1: Wavelength, λ Optimization For U_3O_8
1.A. U_3O_8 Concentration Vs λ



1.B. Fixation Of λ_{max}
Figure-2: Calibration Graph For U_3O_8

Absorbance



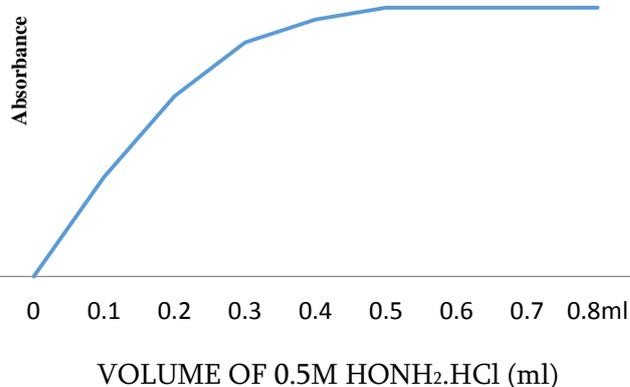
U_3O_8 (ppm)

Sl. No.	U_3O_8 (ppm)	Absorbance	RSD (%)
1.	Blank	0.0000	0.00
2.	0.1	0.0071	1.52
3.	0.2	0.0141	1.53
4.	0.4	0.0284	1.52
5.	0.6	0.0426	1.52
6.	0.8	0.0563	1.53
7.	1.0	0.0701	1.54
8.	1.2	0.0844	1.53
9.	1.4	0.0987	1.53
10.	1.6	0.1121	1.54

Determination of uranium(VI) without using hydroxylamine hydrochloride ($HONH_2.HCl$) is also

possible, however, absorbance for $U(VI)$ -Arsenazo-III complex is lowered 10-15% in comparison to using $HONH_2.HCl$. It reduces $U(VI) \rightarrow U(IV)$ which makes more sensitive $U(IV)$ -Arsenazo-III complex.

Optimization of 0.5M $HONH_2.HCl$ is as follows



Interference study for various cations such as Ca, Mg, Al, Sc, Ti, V, Cr, Mn, Fe, Co, Ni, Cu, Zn, Pb, Mo, Th, Zr and rare earth elements was carried out and its effect on uranium determination was seen using disodium salt of ethylene diamine tetra-acetic acid and triethanolamine. It was observed that optimum quantity of each elements added along with $25\mu g U_3O_8$ standard in 25ml flask has shown negligible absorbance against U_3O_8 standard as shown in Table-1. Thus, uranium determination in geomaterials is possible without any interference.

TABLE-1. EFFECT OF VARIOUS INTERFERING ELEMENTS ON THE DETERMINATION OF URANIUM

Elements	Conctn. of each Element /25ml	Absorbance	(Conctn. of U_3O_8 Std. + Conctn. of each element) /25ml	Absorbance
Blank	---	0.0000	---	0.0000
U_3O_8 Std.	$25\mu g$	0.0695 to 0.0720	$25\mu g$ + ---	0.0695-0.0720
Ca, Mg	1.0mg	-0.0004	$25\mu g$ + 1.0mg	0.0703
Al, Fe	2.0mg	-0.0001	$25\mu g$ + 2.0mg	0.0713
Mn, Co, Ni Zn, Pb	0.8mg	0.0004	$25\mu g$ + 0.8mg	0.0707
Cu	0.2mg	0.0010	$25\mu g$ + 0.2mg	0.0711
Mo, V	0.5mg	0.0017	$25\mu g$ + 0.5mg	0.0716
Ti	0.5mg	-0.001	$25\mu g$ + 0.5mg	0.0695

Cr	0.1mg	0.003	25µg +0.1mg	0.0719
Th	0.5mg	-0.0003	25µg +0.5mg	0.0698
Zr	0.5mg	-0.0002	25µg +0.5mg	0.0696
La, Ce, Pr, Nd,Sm,Eu, Gd,Tb, Dy, Ho, Er,Tm, Yb, Lu, Y, Sc	0.2mg	-0.0001	25µg +0.2mg	0.0700

4.	Z-3599	2476	2459	3.2	0.13	0.69
5.	Z-3600	702	708	2.6	0.37	0.86
6.	Z-3601	201	204	1.5	0.73	1.49
7.	B-904	144	141	1.5	1.06	2.08
8.	B-905	164	167	1.3	0.80	1.83
9.	B-906	450	456	2.4	0.52	1.33
10.	B-907	273	277	1.2	0.42	1.47
11.	SY-2	335	329	2.2	0.66	1.79

Applications

Proposed spectrophotometric method was applied in geomaterials (rock/soil samples) containing 100µg-4000µg U₃O₈/g of sample. However, more than 4000µg U₃O₈/g of a sample is also possible using sub-dilutions without maintaining acidity in final test solution. Results were also compared with inductively coupled plasma optical emission spectrometer and pellet fluorimeter techniques.

Validation of the method was also carried out using CRM (SY-2).The results were found reproducible and good agreement with those obtained values by standard technique at the 95% confidence level as shown in-**Table-2**. Accuracy/relative error and precision achieved for samples and CRM is shown in **Table-3**.

TABLE-2. COMPARISON OF THREE DIFFERENT ANALYTICAL METHODS FOR THE DETERMINATION OF URANIUM

Spectrophotometric Method using Arsenazo-III			ICP-OES Method	Pellet Fluorimeter Method
Sl. No.	Sample Code	U ₃ O ₈ (%)	U ₃ O ₈ (%)	U ₃ O ₈ (%)
1.	Z-3595	0.221	0.220	0.220
2.	Z-3597	0.096	0.099	0.098
3.	Z-3598	0.185	0.187	0.185
4.	Z-3599	0.246	0.248	0.248
5.	Z-3600	0.071	0.072	0.070
6.	Z-3601	0.020	0.020	0.020
7.	B-904	0.014	0.015	0.014
8.	B-905	0.017	0.017	0.016
9.	B-906	0.046	0.049	0.045
10.	B-907	0.028	0.029	0.027
CRM	U ₃ O ₈ (ppm) by Arsenazo-III		U ₃ O ₈ (ppm) Certified Value	
SY-2	329		335±1.8%	

TABLE-3 ACCURACY AND PRECISION ACHIEVED FOR SAMPLES AND CRM (CERTIFIED REFERENCE MATERIAL)

Sl. No	Sample Code	Assigned Value (Fluorimetry) U ₃ O ₈ (ppm)	Spectro-photo-metry Mean (n=10)	Std. Dev.	CV (%)	Accuracy ±(%)
1.	Z-3595	2201	2210	2.5	0.11	0.41
2.	Z-3597	978	962	2.2	0.23	1.64
3.	Z-3598	1854	1845	2.8	0.15	0.49

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