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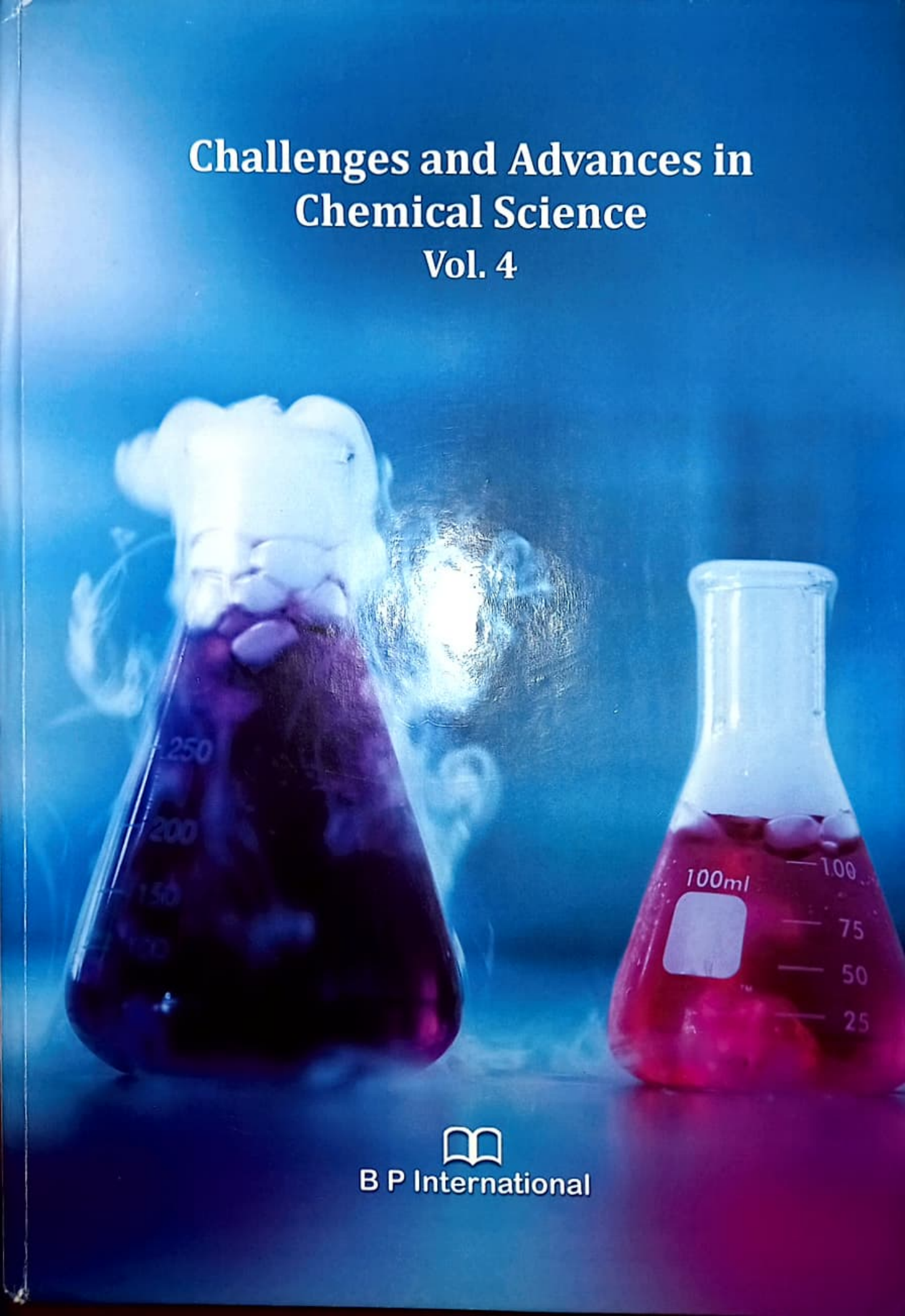

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Chapter 9
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Study on Spectrophotometric Determination of Uranium in Ore and Commercial Samples

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ABSTRACT

A new Analytical reagent, Acetophenone 2', 4'- dihydroxy semicarbazone [A24DHS] is proposed as a spectrophotometric reagent for U(VI). The reagent A24DHS is synthesized in the laboratory and characterized by NMR, IR and elemental analysis. Spectrophotometric method is presented for the trace determination of U(VI) using A24DHS as spectrophotometric reagent (λ_{max} = 340 nm) in acidic aqueous solution (pH = 7.4). The Beer's law is obeyed in the concentration range from 1 to 10 ppm. The A24DHS forms a 1:2 coloured complex. The Sandell's Sensitivity is 0.0823 µg cm^{-2} with molar absorptivity 2896.43 L mol^{-1} cm^{-1}. The proposed method has been successfully applied to the determination of Uranium in ores and commercial samples. The precision and the accuracy obtained were satisfactory for its use in the concerned industry. This chapter details the method development for determination of Uranium in different commercial samples.

Keywords: Uranium (VI); Spectrophotometry; 1-Butanol; Acetophenone 2',4'-dihydroxy Semicarbazone; A24DHS.

1. INTRODUCTION

Uranium and its decay products are source of radioactive energy. Its long half-life makes possible determination of the age of the earth by measuring the amount of lead. Uranium present in earth crust as ore viz. Pitchblende, Carnotite, Tyuyamunite, Torbernite, and Autunite. Radiological effects are generally local because alpha radiation, the primary form of U-238 decay. Uranyl (UO_2^+) ions, such as from uranyl nitrate and other hexavalent uranium compounds, have been shown to cause birth defects and immune system damage in laboratory animals [1]. Therefore, precise knowledge of the Uranium present in various samples is required. Literature indicates the importance of the element and hence a reliable method is required for its determination at trace level [2,3]. Assessment of the Uranium is an increasing need for analytical methods for the determination of trace level. Many methods have been reported for the determination of Uranium but require expensive instruments and well-trained operators [4]. Analytical reagents are reported for the spectrophotometric determination of Uranium [5,6]. The purpose of this work is to find a selective and simple method for the exact determination of Uranium by using a new analytical reagent. In this paper simple method has been developed using Acetophenone 2',4'- dihydroxy semicarbazone [A24DHS] for estimation of Uranium, which is selective, and sensitive. The proposed method has been applied for the spectrophotometric determination of U (VI) in various samples and offer advantages of simplicity, rapidity and stability.

2. OBJECTIVES

The overall objectives of the study are,
To study various methods available for determination of Uranium.
To find best suitable method for its determination.
To synthesize new reagent (Ligand) for Uranium metal.

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Develop simple, precise method for estimation of Uranium.
To study various aspects of new developed method and its application.

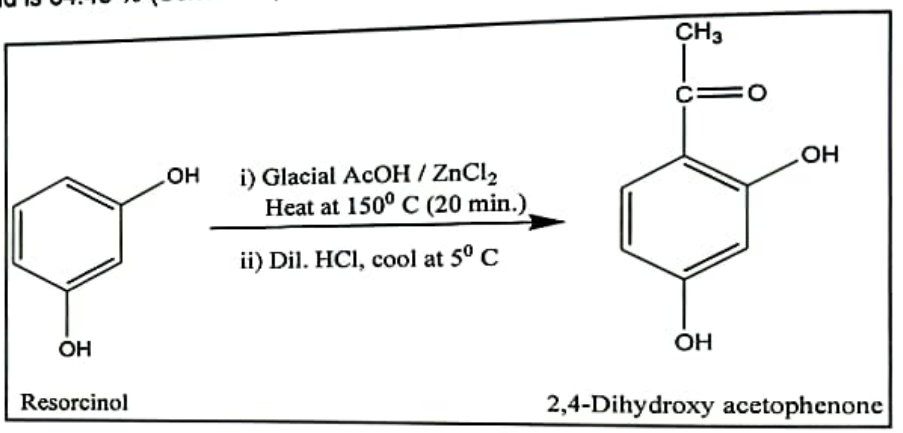
3. MATERIAL AND METHODS

3.1 Synthesis of the reagent Acetophenone 2', 4' - dihydroxy semicarbazone (A24DHS)

Synthesis of ADHS involves two steps.

A. Conversion of Resorcinol to 2,4-Dihydroxy acetophenone [7,8].

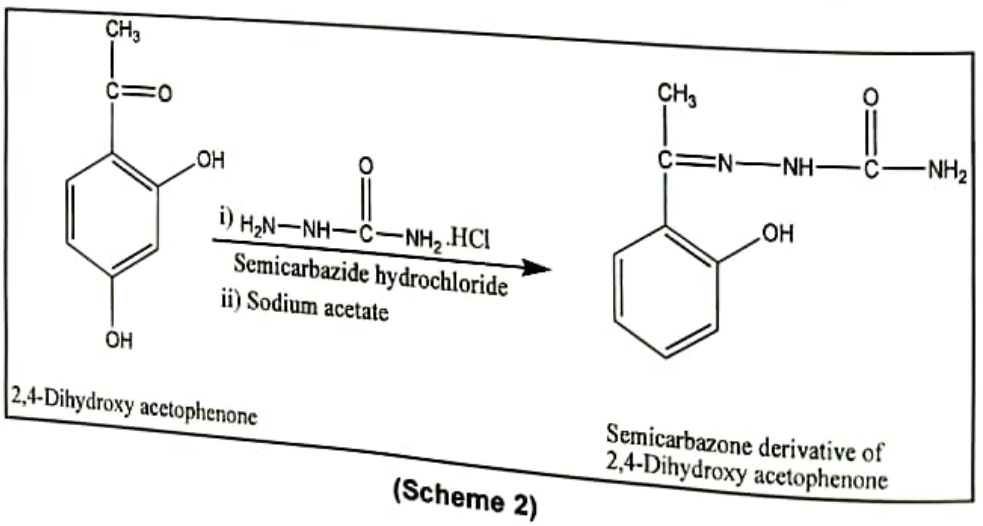
Freshly fused and powdered Zinc chloride (0.24 mole) is dissolved in glacial acetic acid (32 mL) by heating in a beaker on a sand bath. Dry Resorcinol (0.2 mole) is added with stirring to the mixture at 140°C. The solution is heated until it just begins to boil and kept for 20 min. At 150°C dilute Hydrochloric acid (1:1) is added to the mixture and solution cooled (5°C). The separate product is filtered and washed with dilute HCl (1:3). It is recrystallized from hot water containing little HCl. M.P. is 142°C [7]. Yield is 84.45 % (Scheme 1).



(Scheme 1)

B. Synthesis of Acetophenone 2', 4' - dihydroxy semicarbazone from 2,4-Dihydroxy acetophenone [8,9].

Equimolar mixture of sodium acetate and semicarbazide hydrochloride is dissolved in minimum quantity of water and then it is added to methanolic solution of 2',4'-Dihydroxy acetophenone. After addition warm the solution and stir the solution about one hour. The pink colored compound is precipitate out, which is washed and then recrystallized by using 50% ethyl alcohol as solvent (Scheme 2)



(Scheme 2)

3.2 Instrumentation

The pH measurements were made using a pH meter Elico, Model LI-129, India in conjugation with a combined glass and calomel electrode. Shimadzu UV-Visible 2100 spectrophotometer with 1.0 cm matched quartz cells were used for all absorbance measurements.

3.3 Reagents

The stock solution of hexavalent Uranium was prepared by dissolving weighed amount of Uranyl nitrate in doubly distilled de-ionized water containing 1–2 mL of nitric acid. More dilute standard solutions were prepared from this stock solution as and when required.

3.4 Procedure for the Extraction

1 mL of aqueous solution containing 5 µg of Uranium metal and 2 mL of reagent was mixed in a 50 mL beaker. The pH of the solution adjusted to 3.4, it must be noted that the total volume should not exceed 10 mL. The solution was transferred to 100 mL separatory funnel. The beaker was washed twice with 1-Butanol and transferred to the same funnel. The two phases were shaken for two minutes and allowed to separate. The organic phase was passed through anhydrous sodium sulphate in order to absorb trace amount of water from organic phase and then collected in 10 mL measuring flask and made up to the mark with organic solvent if required. The amount of Uranium present in the organic phase determined quantitatively by spectrophotometric method by taking absorbance at 340 nm and that in the aqueous phase was determined by thiocyanate method [10-15].

4. RESULTS AND DISCUSSION

The results of various studies are discussed below.

4.1 Extraction as a Function of pH

The extraction of Uranium with Acetophenone 2',4'-dihydroxy semicarbazone has been studied over the pH range 1-10 and was observed that percentage extraction of U (IV) is maximum at pH range 7.2-7.6. Hence, further extraction and determination carried out at pH 7.4.

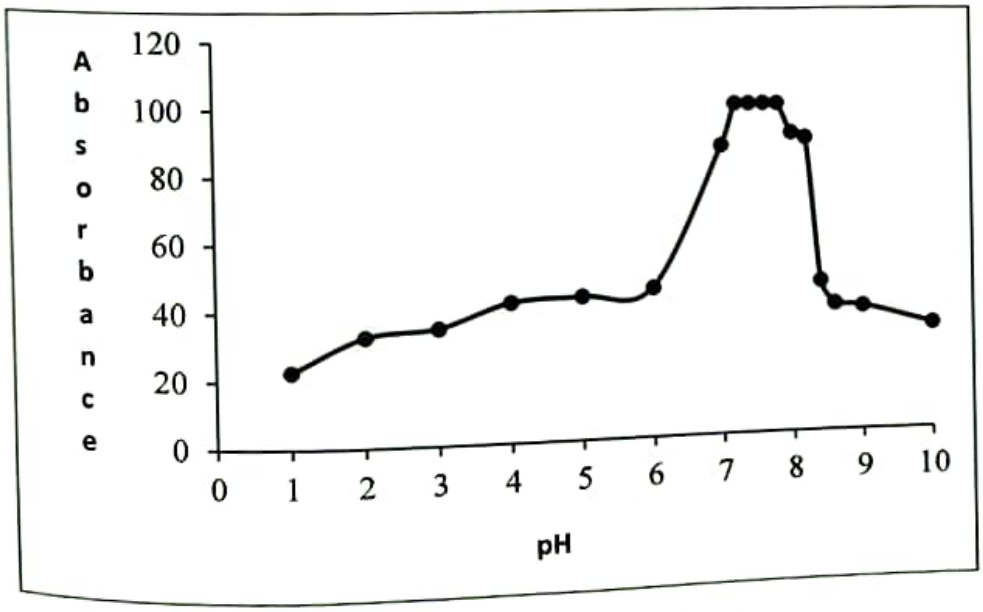


Fig. 1. Extraction as a function of pH

4.2 Absorption Spectrum

The absorption spectrum of U (IV): A24DHS in 1-Butanol shows the maximum absorption at 340 nm. The absorption due to reagent at this wavelength is nearly negligible. Hence the absorption measurements were carried out at 340 nm.

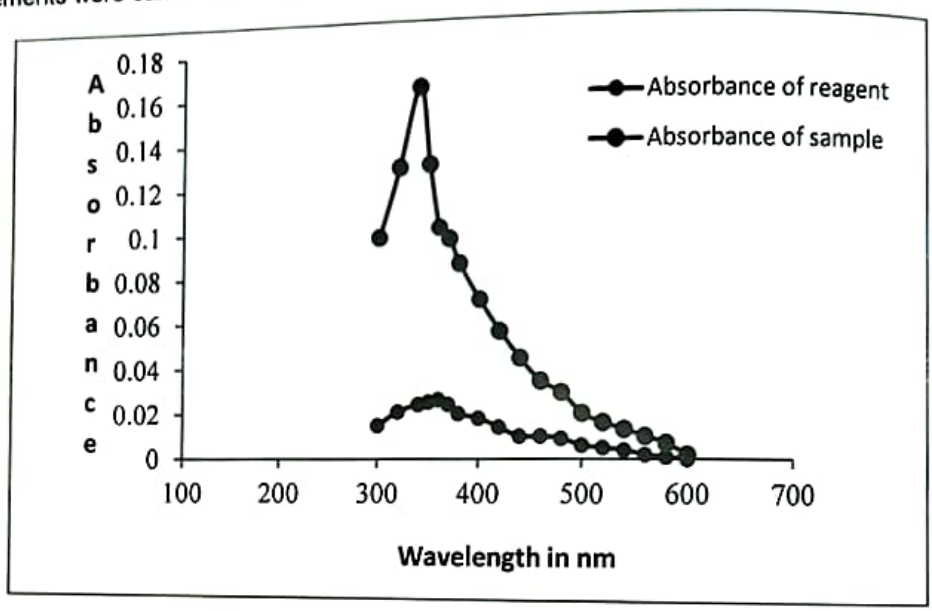


Fig. 2. Absorption spectrum

4.3 Effect of Solvent

The suitability of solvent was investigated using various organic solvents and the extraction of U (IV): A24DHS was quantitative in 1-Butanol. Hence, 1-Butanol was used for further extraction studies as it gave better and quicker phase separation.

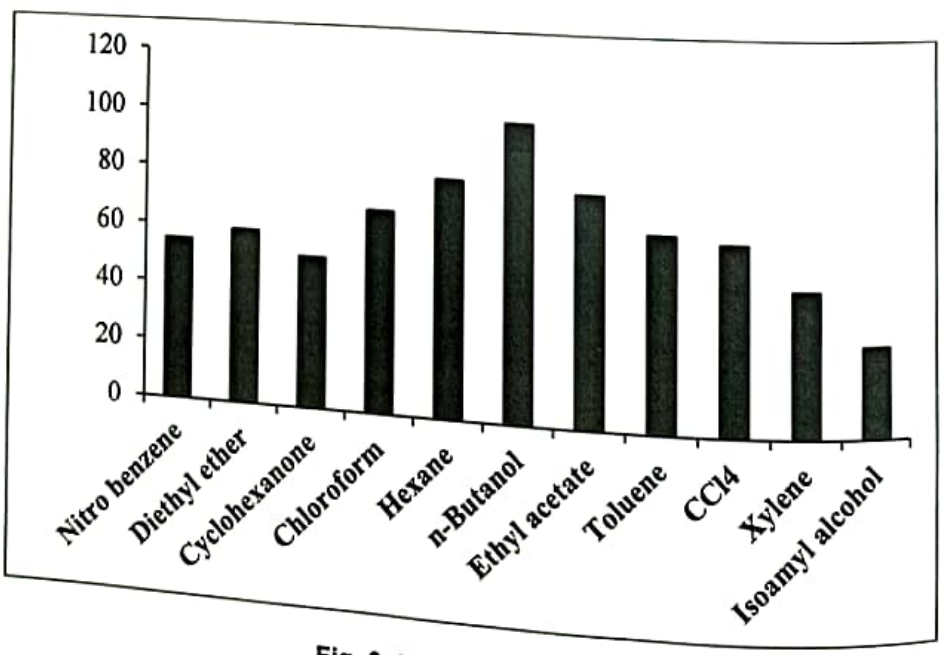


Fig. 3. Effect of solvent

4.4 Effect of Reagent Concentration

It was found that 2 mL of 0.1% reagent is sufficient for the colour development of the metal U (IV) in 10 mL of aqueous solution at pH 7.4.

4.5 Effect of Equilibration Time and Stability of the Complex

The equilibration time of 1 minute is sufficient for the quantitative extraction of Uranium. The stability of colour of the U (IV): A24DHS complex with respect to time shows that the absorbance due to extracted species is stable up to 32 hours, after which slight decrease in absorbance is observed.

4.6 Calibration Plot

The Beer's law is obeyed from 1 to 10 ppm. The molar absorptivity and Sandell's sensitivity were calculated to be is 2896.43 L $mol^{-1}cm^{-1}$ and 0.0823 µg cm^{-2} respectively.

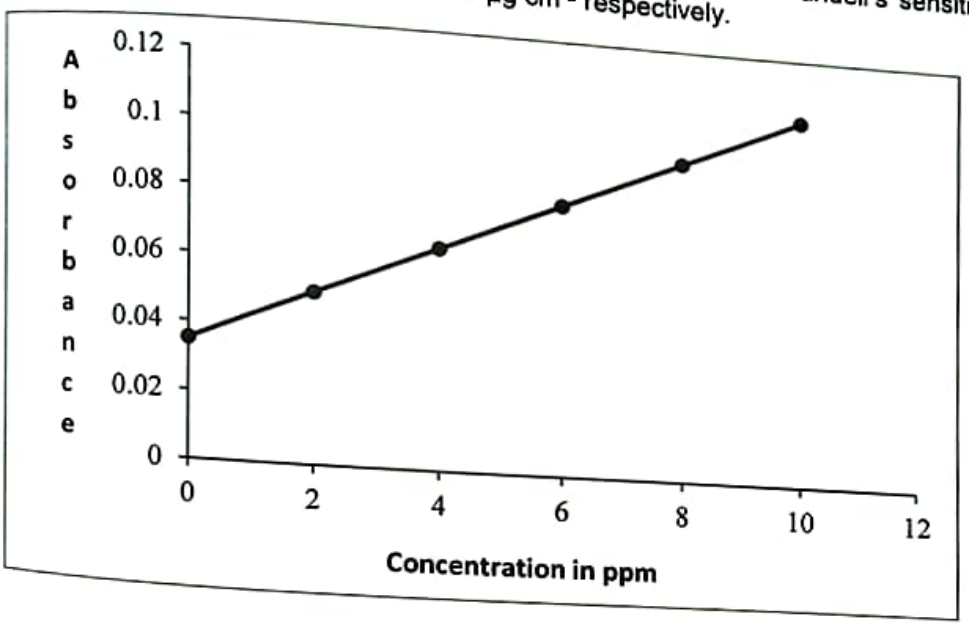


Fig. 4. Calibration plot

4.7 Limit of Detection (LOD)

LOD of the present method was calculate at 98.3 % confidence level, it was 0.442 µg/mL.

4.8 Effect of Divalent Ions and Foreign Ions

The effect of other ions presents (Table 4, 5) in various amount indicated no interference in the spectrophotometric determination of 5ppm of Uranium. The ions which show interference in the spectrophotometric determination of Uranium were overcome by using appropriate masking agents (Table 6).

4.9 Precision and Accuracy

The precision and accuracy of the developed spectrophotometric method have been studied by analyzing ten solutions each containing 3 µg of Uranium in the aqueous phase. The average of ten determinations was 3.005 and variation from mean at 95% confidence limit was ± 0.00888.

Table 4. Interference of some anions

Sr. No.	Anion	Tolerated ratio	Interference
1	Cl^{-1}	1:48	0.165
2	Br^{-1}	1:28	0.165
3	I^{-1}	1:38	0.165
4	F^{-1}	1:29	0.165
5	ClO_3^{-1}	1:27	0.165
6	BrO_3^{-1}	1:25	0.165
7	IO_3^{-1}	1:29	0.165
8	NO_2^{-1}	1:24	0.165
9	NO_3^{-1}	1:23	0.165
10	ClO_4^{-1}	1:21	0.165
11	PO_4^{-3}	1:26	0.165
12	$P_2O_7^{-2}$	1:12	0.165
13	Oxalate	1:18	0.165
14	SO_3^{-2}	1:24	0.165
15	$S_2O_3^{-2}$	1:31	0.165
16	EDTA	Masked	0.165
17	Tartarate	1:23	0.165
18	CN^{-1}	Masked	0.165

Table 5. Interference of some cations

Sr. No.	Cation	Tolerated ratio	Interference
1	Li^{+1}	1:35	0.164
2	Na^{+1}	1:38	0.164
3	K^{+1}	1:34	0.164
4	Mg^{+2}	1:17	0.164
5	Ca^{+2}	1:25	0.164
6	Ba^{+2}	1:34	0.164
7	V^{+5}	Masked	0.164
8	Al^{+3}	1:18	0.164
9	Pb^{+2}	1:28	0.164
10	Bi^{+2}	1:26	0.164
11	As^{+3}	1:26	0.164
12	W^{+2}	1:34	0.164
13	Th^{+4}	1:37	0.164
14	Zn^{+2}	1:24	0.164
15	Ag^{+1}	1:27	0.164
16	Ni^{2+}	1:34	0.164
17	Co^{2+}	1:32	0.164
18	Mn^{2+}	1:20	0.164
19	Fe^{3+}	Masked	0.164
20	Mo^{6+}	Masked	0.164
21	Ti^{4+}	Masked	0.164
22	Cu^{+2}	Masked	0.164

Table 6. Effect of divalent ions and foreign ions

Sr. No.	Interfering Ion	Masking agent
1	V(V)	Thiourea
2	Fe (III)	Thiocyante
3	Mo (VI)	Citrate
4	Cu (II)	Thiosulphate
5	Ti (IV)	Ascorbic acid

4.10 Nature of Extracted Species

The composition of extracted U (IV): A24DHS complex has been determined by Job's continuous variation method, Slope ratio method and Mole ratio method. It shows that the composition of U (IV): A24DHS complex is 1:2. (Fig. 5).

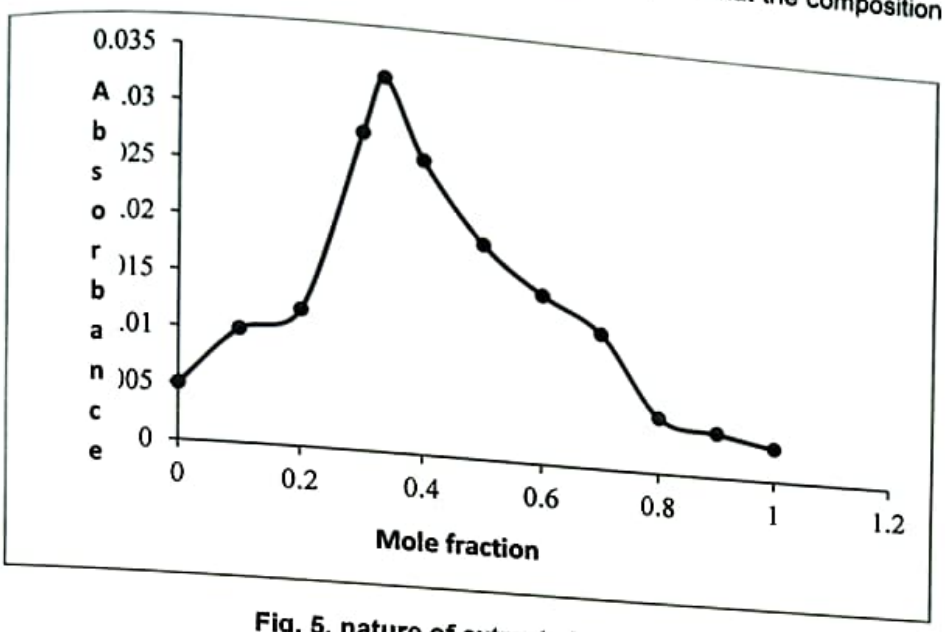


Fig. 5. nature of extracted species

4.11 Applications of the Method

The proposed method was successfully applied for the determination of Uranium from various alloys and pharmaceutical samples. The results found to be in good agreement with those obtained by the standard known method9,10.

4.12 Determination of U (IV) in Ore

An accurately weighed amount of 1 gm of monazite sand (Ita lab, Mumbai) was taken in an round bottom flask fitted with standard joint. 10 ml of 3:1 HCl-HNO_3 mixture was added to it and refluxed for 4 hour. This mixture is then evaporated almost to dryness. 5 ml of 5 M HCl was added and the mixture was further heated for two minutes, allowed to cool and settle. The clear solution was then transferred to 50 ml standard flask. The residue was washed and washing were also collected. A definite volume of this solution was used for the estimation of Uranium following the recommended procedure.

Table 7. Applications of the method

Sr. No.	Sample	Certified value	Present method
1	Monazite sample	0.08 µg	0.079 µg
Synthetic Mixture	**Sample**	**By present method**	**By known method**
1	U (100) + Zn (50)	99.971 ppm	99.980 ppm
2	U (5) + Ce (3) + Th (5)	4.490 ppm	4.485 ppm
3	U (10) + Cu (5) + Mg (10)	9.97 ppm	9.99 ppm

4.13 Commercial Samples

Synthetic mixtures were prepared by taking 100 µg of Uranium in 100 µg of Zinc (II) or 5 µg Uranium in 3 µg Ce (IV) and 5 µg Th (II) or 10 µg Uranium in 5 µg Cu (II) and 10 µg Mg (II) separately. The

mixture was made to 10 ml volume. A definite aliquot of this solution was taken and after adjustment of pH and addition of 2 ml of A24DHS solution, the Uranium complex was extracted into 10 ml 1-Butanol. The amount of Uranium present was computed from the calibration curve. The result obtained was compared with those obtained by using oxine method (Table 7).

5. CONCLUSION

The results obtained show that the newly developed method can be effectively used for estimation of U (IV) from aqueous media. The proposed method is quick and requires less volume of organic solvent. The developed method is compared with result obtained with the thiocyanate method for the estimation Uranium (III) and observed to be comparable. The method is very precise, faster and simpler than other methods. The method is precise, accurate, less time consuming and easily employed anywhere, even in small laboratories as it requires only uv – visible spectrophotometer and not much costly measurement devices or instruments.

COMPETING INTERESTS

Authors have declared that no competing interests exist.

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