

## Analytical Determination of Uranium (VI) by Spectrophotometry

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**Abstract:** A new reagent namely 3,4-Dihydroxybenzaldehyde Thiosemicarbazone (3,4-DHBTSC) synthesized by the authors for the determination of uranium(VI) in monazite sand, pitchblend ore, spiked water, human hair and human blood samples. A brown colored complex was formed between uranium(VI) and 3,4-DHBTSC in a media of pH 7. The developed method can be conveniently applied for the analytical determination of uranium (VI) in the concentration range 0.476 – 4.760 µg/ml. The molar absorptivity and sandell's sensitivity were found to be  $2.0833 \times 10^4$  L/mol/cm and  $0.0114$  µg/cm<sup>2</sup> respectively. The proposed method was found to be linear ( $R > 0.01$ ), selective, accurate (recovery = <99.7%) and precise (RSD < 1.1%) in the reported linear calibration line.

**Keywords:** 3,4-DHBTSC; Spectrophotometry; Uranium(VI); Spiked water sample.

### 1. INTRODUCTION

Uranium and its compounds are highly toxic. Exposure to elemental uranium and all of its inorganic compounds can cause cancer and acute respiratory illness. Though they are toxic, they have been widely used in medicinal, ceramic, glass, electrolytic and electrical appliances industries. Releasing of uranium into the environment is inexorable as the compounds of uranium are highly reactive, volatile and soluble in water. Hence there is a need, and has been a growing interest to develop the analytical procedures for the micro gram determination of uranium.

### 2. EXPERIMENTAL

The buffer solutions were prepared as follows;

**pH 1.0 to 3.0:** By mixing hydrochloric acid and sodium acetate.

**pH 3.5 to 7.0:** Acetic acid and sodium acetate.

**pH 8.0 to 12.0:** Ammonium chloride and ammonium hydroxide.

All solvents and chemicals used were of analytical reagent grade. By appropriate dilutions of the stock solution the working solutions were prepared. For the preparation of solutions double-distilled water was used.

**Table1.** A comparison to show the merits of the reported method

S.NO.	Method	Detection limit	Remark	Ref.No.
1	Spectrophotometric determination of uranium(VI) via complexation with prioxicam	0.094 µg/ml	Though it is sensitive but not selective	1
2	Spectrophotometric determination of uranium(VI) with pyrocatechol violet in surfactant media	0.15 µg/ml	Though it is simple and sensitive but not selective	2
3	Spectrophotometric determination of uranium(VI) by extraction with tropolone	Microgram levels	Involves preconcentration and extraction steps	3
4	A comparative analysis of uranium ore using laser fluorimetric and gamma spectrophotometry techniques	399.4 µg/g	Involves complicated procedure, not sensitive and selective	4

5	Solvent extraction studies of uranium(VI) from aqueous media into Chloroform Solution of <i>N,N'</i> -ethylenebis(4-propionyl-2,4-dihydro-5-methyl-2-phenyl 3H-pyrazol-3-oneimine)	Microgram levels	Involves separation and preconcentration steps	5
6	Accurate determination of uranium in Soils using electroplating and closed vessels microwave digestion methods	Microgram levels/kg	Time consumption method, low yield and recovery	6
7	Determination of depleted uranium using a high-resolution gamma-ray spectrometer and its applications in soil and sediments	15.97 Becquerel/kg	Involves complicated, tedious steps and also preconcentration steps	7
8	Determination of uranium isotopes in soil samples by coprecipitation	5.88 mg/kg	Lack of accuracy and foreign ions may effect in the determination	8
9	Determination of uranium contents in the soils	13 Bq/kg	Proper analytical parameters had not been fixed	9
10	Solvent extraction and spectrophotometric determination of uranium(VI) using phenylene bisphenol as an analytical reagent	10.0 ppm	The stability of the complex compound is low	10
11	Spectrophotometric determination of uranium(VI) using 2-(2-Thiazolylazo)-p-cresol in the presence of surfactants	26 ng/ml		11
12	Speciation and spectrophotometric determination of uranium in seawater	Microgram levels	Involves extraction and preconcentration steps	12
13	Spectrophotometric determination of uranium in bacterial leach liquors using arsenazo-III	6 µg/l	Involves preconcentration steps	13
14	Determination of uranium by fluorescence method	0.05 ppm	Complicated and require skilled analysts	14
15	Determination of uranium in tap water by ICP-MS	2 ng/L		15
16	Determination of uranium in seawater samples by liquid chromatography using mandelic acid as a complexing agent	500 ppb		16

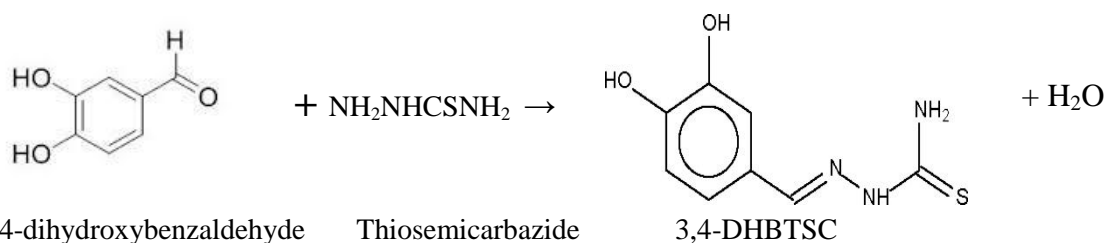
In order to develop a new method for the determination of uranium(VI) as very few methods are available which do not require expensive instrumentation and do not involve extraction and preconcentration steps [17]. The authors have reported a simple, sensitive and selective method for the determination of uranium(VI). The reported method is based on the chromogenic reaction between U(VI) and 3,4-DHBTSC to give a brown colored complex which has absorption maximum at 370 nm.

Required amount of uranium trioxide was taken in 100 ml standard flask. The salt was dissolved in distilled water and was diluted to 100 ml. This serves as a stock solution of uranium(VI).

A Shimadzu UV-visible spectrophotometer (Model UV-160A) equipped with 1 cm matched quartz cells was used for the measurement of absorbance. An Elico digital pH meter was used for pH measurements.

### 2.1. Synthesis of 3,4-dihydroxybenzaldehyde Thiosemicarbazone

3,4-dihydroxybenzaldehyde and thiosemicarbazide dissolved in methanol medium were refluxed for 3 hours. The contents were cooled to room temperature. The pale yellow colored product obtained was separated by filtration. The product obtained was washed with hot water and 50 percent methanol. The product was recrystallised twice from boiling methanol and dried in vacuum. 3,4-DHBTSC solution of concentration 0.01M prepared in dimethyl formamide serves as a stock solution.



**Fig.1** Synthesis of 3, 4-dihydroxybenzaldehyde thiosemicarbazone

The melting point of 3,4-DHBTSC is 221-223<sup>0</sup>C, Yield = 9.85 gm, % of yield = 84.9%.

The structure of the reagent has been established based on IR, Mass and NMR spectra.

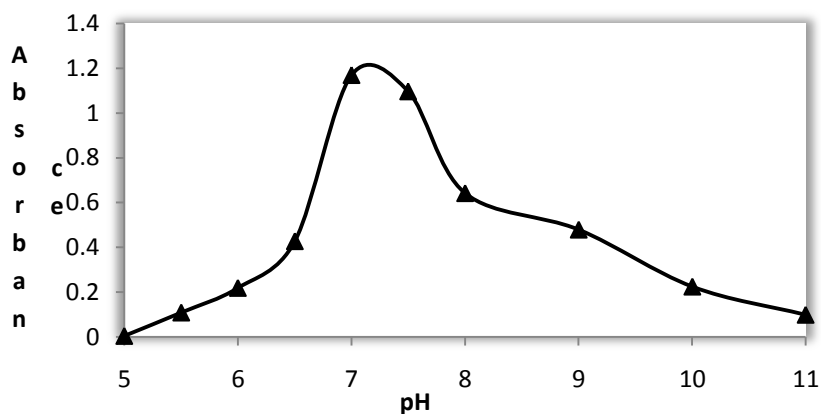
## 2.2. General Experimental Procedure

In a 10 ml volumetric flask, 5 ml of buffer solution of required pH, 1 ml of uranium trioxide of required concentration and 1 ml 3,4-DHBTSC of required concentration were taken. The contents of the flask were made up to the mark, shaken well and absorption spectrum was recorded against reagent blank.

## 3. RESULTS AND DISCUSSION

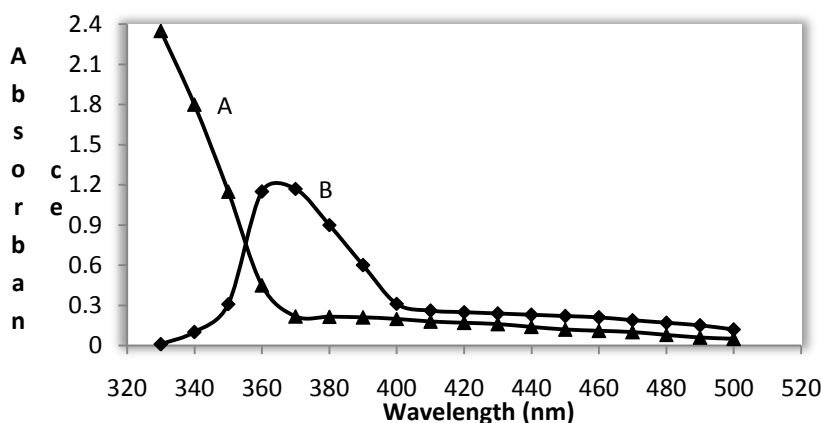
### 3.1. Effect of pH on Absorbance

The effect of pH on the absorbance of the complexation reaction is studied and shown in the Fig.2. The figure gives the information that there is no complex formation between the U(VI) and 3,4-DHBTSC in the acidic media (pH 1 to 4), the absorbance increases and gives a maximum at pH 7 and there is a decrease in the absorbance with the further increase in pH. Keeping in view the reproducibility of the complexation between metal & reagent and stability of the spectrum, a pH of 7 was considered optimum for further detailed investigation. The absorption spectra showed the maximum absorbance at 370 nm and this fact was further depicted by the Fig. 3 which showed that complex formed between metal and reagent was responsible for the absorption spectra.



**Fig.2** Effect of pH on Absorbance

$[U(VI)] = 8 \times 10^{-5} M$ ,  $[3,4-DHBTSC] = 8 \times 10^{-4} M$ ,  $\lambda_{max} = 370 \text{ nm}$ ;



**Fig.3** Absorption Spectrum of

A) 3,4-DHBTSC against the buffer blank.  $[3,4\text{-DHBTSC}] = 8 \times 10^{-3} \text{ M}$ ,  $\text{pH} = 7$ ;

B) U(VI)-3,4-DHBTSC complex against the reagent blank.  $[U(\text{VI})] = 8 \times 10^{-5} \text{ M}$ ,  
 $[3,4\text{-DHBTSC}] = 8 \times 10^{-3} \text{ M}$ ,  $\text{pH} = 7$ ;

### 3.2. Effect of Reagent (3,4-DHBTSC) on Absorbance

The absorbance of the solutions containing fixed concentration of metal ion and varying concentration of 3,4-DHBTSC was recorded in a media of  $\text{pH} 7$ , in order to fix the concentration of 3,4-DHBTSC. It was found that an optimum reagent concentration of 15 fold was sufficient for the formation of complex. The addition of excess of the reagent to the metal ion solution does not alter the absorbance of the complexation reaction.

### 3.3. Effect of Time on the Complexation Reaction

Effect of time on the color reaction was studied by measuring the absorbance values of the solution containing fixed amount of U(VI) at regular intervals of 10 minutes. It was found that the color formation of the complex was instantaneous and absorbance remained constant for more than an hour. This reveals that the complexation between the metal and reagent was stable for a reasonable period of time.

### 3.4. Stoichiometric Determination of the Complex

In order to fix the composition between U(VI) and 3,4-DHBTSC, Job's method continuous variation and molar ratio methods were employed. In Job's continuous variation method [18], a series of solutions containing required concentration of 3,4-DHBTSC and varying concentration of the metal ion were taken in a 10 ml volumetric flask. The absorbance values of these solutions were measured in each case against the suitable reagent blank and the data is represented in the Fig. 4. The figure reveals that uranium forms 1:1 complex with the reagent. The stability constant of the complex was found to be  $3.29 \times 10^7$ . The stoichiometry of the complex was further confirmed by mole ratio method. In mole ratio method, absorbance of the solutions containing fixed concentration of metal and varying concentration of the reagent was recorded at 370 nm. Both the methods showed that there was 1:1 complex between the metal and reagent.

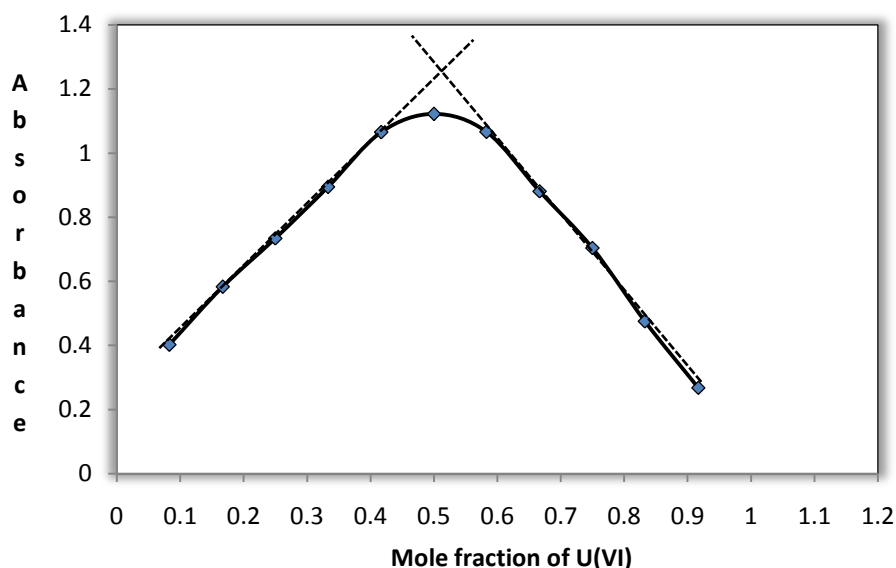
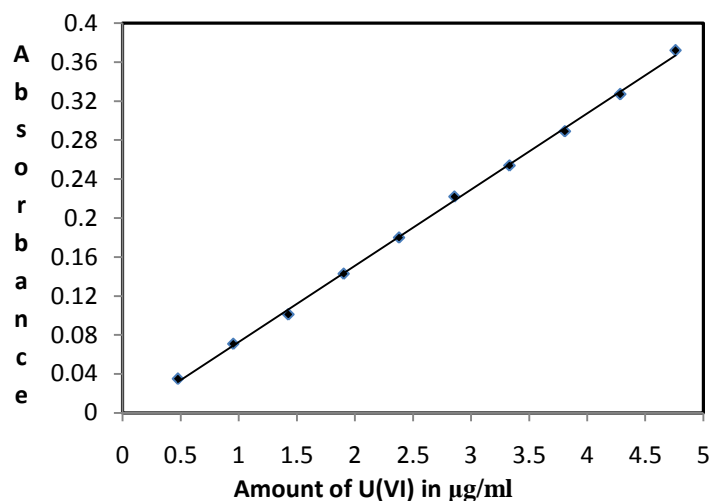


Fig.4 Stoichiometry of the complex by Job's method continuous variation

$[3,4\text{-DHBTSC}] = [U(\text{VI})] = 2 \times 10^{-4} \text{ M}$ ,  $\text{pH} = 7$ ,  $\lambda_{\text{max}} = 370 \text{ nm}$ ;

### 3.5. Analytical determination of U(VI)

In order to estimate the micro gram levels of U(VI), a series of solutions containing varying concentration of metal ion and fixed concentration of the reagent in the appropriate  $\text{pH}$  media was prepared, the absorbance values were measured in each case at 370 nm against the respective reagent blank solution. Linear calibration graph shown in the Fig. 5 reveals that uranium(VI) can be determined in the linear concentration range 0.476-4.760  $\mu\text{g/ml}$ .



**Fig.5** Analytical determination of U(VI)  
 $[3,4\text{-DHBTS}] = 1.5 \times 10^{-4} \text{ M}$ ,  $\text{pH} = 7$ ,  $\lambda_{\text{max}} = 370 \text{ nm}$ ;

### 3.6. Fixation of Analytical Parameters and Sensitivity

The linear calibration graph for the analytical estimation of uranium(VI) can be fitted into the formulae  $A_{370 \text{ nm}} = 0.0781C - 0.005$  ( $A$  is absorbance and  $C$  is concentration in  $\mu\text{g/ml}$ ). The correlation coefficient was found to be 0.9995. The molar absorptivity and Sandell's sensitivity were  $2.0833 \times 10^4 \text{ L mol}^{-1} \text{ cm}^{-1}$  and  $0.0114 \mu\text{g cm}^{-2}$  respectively. The relative standard deviation (RSD) was found to be around 8.276%. The corresponding method limit of detection (LOD) and limit of quantification (LOQ) were found to be 0.1528 and 0.4632  $\mu\text{g/ml}$  respectively.

### 3.7. Effect of Foreign Ions in the Determination

The effect of diverse ions in the determination of uranium(VI) was carried out by adding a known concentration of foreign ion to a solution containing 4.76  $\mu\text{g/ml}$  of U(VI) and determining the absorbance latter by the procedure mentioned in 2.2. The tolerance limit of each ion was taken as the concentration of foreign ion which caused less than  $\pm 4\%$  error in absorbance value. It is evident from Table 2 that most of anions and cations did not interfere in the determination. Tolerance limit of Mo(VI) could be increased up to 175  $\mu\text{g/ml}$  in presence of phosphate as masking agent, while the interference of Cr(VI) and Cu(II) can be avoided by masking with 200 ppm of tartrate and 400 ppm of oxalate respectively.

**Table 2.** Effect of foreign ions in presence of U(VI).  $[U(VI)] = 4.76 \mu\text{g/ml}$

Anion	Tolerance limit ( $\mu\text{g/ml}$ )	Cation	Tolerance limit ( $\mu\text{g/ml}$ )
Iodide	1392	K(I)	557
Phosphate	1212	Th((IV)	464
Bromide	800	W(VI)	185
Nitrate	620	Al(III)	135
Sulphate	384	Cd(II)	112
Thiourea	380	Ba(II)	55
Carbonate	300	Co(II)	35
Farmate	270	Ni(II)	29
Oxalate	250	Cu(II)	36 <sup>a</sup>
Thiosulphate	235	Mo(VI)	175 <sup>b</sup>
Fluoride	177	Cr(VI)	120 <sup>c</sup>
Chloride	175	Mn(II)	11
Tartrate	150	V(V)	9
Acetate	120	Zn(II)	5
EDTA	Interferes	Zr(IV)	5
		Hg(II)	precipitate

<sup>a</sup> Avoided by masking with 400 ppm of oxalate

<sup>b</sup> In presence of 400 ppm of phosphate

<sup>c</sup> Avoided by masking with 200 ppm of tartrate

### 3.8. Application

The present method is applied for the determination of U(VI) in biological and environmental samples. The analytical determination of uranium was carried out by the general experimental procedure mentioned in 2.2. The results presented in Table 3 indicate the applicability of the reported method.

**Table3.** Determination of uranium(VI) present in monazite sand, synthetic pitchblend ore, spiked water, human hair and human blood samples.  $[3,4\text{-DHBTC}] = 8 \times 10^{-3} \text{ M}$ ,  $\text{pH} = 7$ ,  $\lambda_{\text{max}} = 370 \text{ nm}$ ;

Sample	ICPAES/AAS/ICP-MS U(VI) value in $\mu\text{g/ml}$	Amount of U(VI) found* in $\mu\text{g/ml}$ By present method	Relative error (%)
Monazite sand	3.03	2.95	-2.71
Synthetic pitchblend ore	12.5	12.4	-0.80
Spiked tap water	50	49.5	-1.01
Spiked waste water	100	99.4	-0.60
Spiked well water	200	202	+0.99
Human hair of cancer patient	0.36	0.35	-2.85
Human blood of leukemia patient	2.89	2.90	+0.34

\*Average of three determinations.

\*The value of  $t$  at 95% confidence level is 50.60

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