

Analytical Determination of Uranium (VI) using 4-hydroxybenzaldehydethiosemicarbazone by Spectrophotometry

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Abstract: The reagent 4-Hydroxy benzaldehyde thiosemicarbazone (4-HBTS) has been synthesized and characterized and its analytical applications were investigated. The complexing reagent 4-HBTS reacts with aqueous solution of U (VI) ion in the pH range of 5.0-5.5 at room temperature and forms a yellow coloured 1:1 [U(VI):4-HBTS] complex with stability constant 3.74×10^5 . The complex has maximum absorption at 350 nm. The molar absorptivity and sandell's sensitivity for the coloured solution are found to be $1.1 \times 10^4 \text{ L mol}^{-1} \text{ cm}^{-1}$ and $0.002164 \mu\text{g cm}^{-2}$ respectively. Beer's law is obeyed in the range of 0.9522-9.552 $\mu\text{g/mL}$. The interference of various diverse ions has been studied.

Keywords: Uranium (VI). 4-Hydroxybenzaldehydethiosemicarbazone, Spectrophotometry, environmental samples,

Date of Submission: 03-10-2017

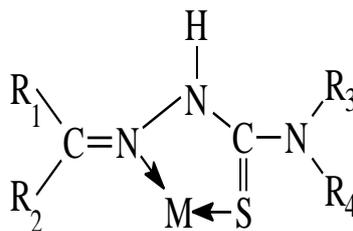
Date of acceptance: 14-10-2017

I. Introduction

Uranium was discovered by Klaproth in 1789 in pitchblende, and received its name from the planet Uranus. Uranium occurs in nature chiefly in the form of pitchblende. This mineral is a compound of uranium(IV) or uranium (VI) oxide. Its formula is U_3O_8 . The deposits of pitchblende were discovered in Portugal, Australia, and United States and in smaller quantities in India. Uranium deposits are found in West Bengal and Nellore (AP) in our country.

Pure uranium is a silver-white, lustrous metal which gradually tarnishes in air. It is not very hard and can be deformed at ordinary temperature by hammering and rolling. The density of pure uranium is 19.05 and it has a relatively low melting point (1130°C) as compared with its homologues like molybdenum and tungsten. Uranium appears to be capable of forming compounds with every valence state from (II) to (VI). With a few exceptions, only uranium(IV) and uranium(VI) compounds are capable of existing in aqueous solution. In general, the uranium(VI) compounds are the most stable in aqueous solution. The uranyl salts correspond to the general formula UO_2X_2 (X = univalent acid radical) and most of them are soluble in water. As a rule they are yellow in colour, with a yellow-green fluorescence. The absorption spectrum and fluorescence spectrum being characteristic of the $(\text{UO}_2)^{+2}$ group. The most common uranium compounds are uranyl nitrate, $\text{UO}_2(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ and uranyl acetate, $\text{UO}_2(\text{C}_2\text{H}_3\text{O}_2)_2 \cdot 2\text{H}_2\text{O}$. There is a need, and has been a growing interest to develop the analytical procedures for the micro gram determination of uranium. Several organic reagents were used for the determination of uranium (VI) ¹⁻¹⁷

Thiosemicarbazones contain nitrogen as well as sulphur. Thiosemicarbazones are good analytical reagents ¹⁸⁻²⁵. Thiosemicarbazones contain azomethine nitrogen atom and thioamide group. These reagents act as good chelating agents and form complexes with various metal ions by bonding through thioketosulphur and hydrazino- nitrogen atom.



Many thiosemicarbazone ligands have been derived by condensation reaction between aliphatic, aromatic or heterocyclic aldehydes or ketones with thiosemicarbazide.

Experimental part:

The absorbance were made on a Shimadzu UV-Visible spectrophotometer (model UV-160A) fitted with 1.0cm quartz cells and pH measurements by Elico digital pH meter (model LI20) respectively.

Preparation and characterization of 4-hydroxy benzaldehydethiosemicarbazone:

The reagent was prepared by simple condensation of 1 mole of 4-hydroxy-benzaldehyde(1.22gm) with 1-mole (0.92gm) of thiosemicarbazide in a clean 250ml round bottomed flask 4-hydroxybenzaldehyde was dissolved in 100ml of methanol and thiosemicarbazide was dissolved in hot water. (Fig-1) The solutions were mixed and refluxed for two hours. On cooling brown colored product was formed which was collected by filtration. It was recrystallized using methanol and dried in vacuum.

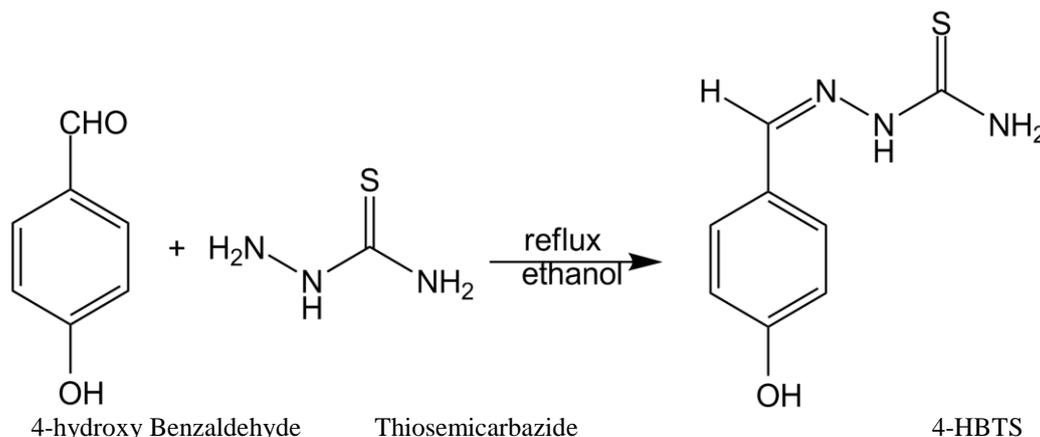


Fig:1 : Preparation of 4- Hydroxy benzaldehydethiosemicarbazone

The yield was 80% by weight. and the M.P. is 207-209⁰C. The structure of the compound was established using IR spectra and NMR spectra,

Characterization:

The IR spectrum of the compound was recorded using Perkin-Elmer 137 IR spectrometer in KBr. The peaks observed at 3458cm⁻¹ and 3342⁻¹ may be assigned to symmetric and asymmetric (-N-H) stretching frequency of primary amino group. The peak observed at 3028cm⁻¹ may be assigned to Ar-H stretching frequency of aromatic proton, and that observed at 1595cm⁻¹ to C=N stretching frequency of azomethine. The peak observed at 3218-3092 for -OH group. A strong peak observed at 1056cm⁻¹ may be assigned to C=S stretching frequency. The peaks observed in the range of 1530-1360cm⁻¹ frequency were characteristic aromatic ring stretching frequency.

The ¹H-NMR spectrum of the compound was recorded with DRX300 NMR spectrometer in DMF solvent. The characteristic peak at δ value 10.74(H) was because of phenolic -OH group. The peak found at δ value 7.86(4H) may be due to aromatic protons, the peak found at δ value 6.8 (2H) may be due to -NH₂ protons attached to thionyl group (C=S) and the peak observed at δ value 9.0 is due to aldehydic proton. The peak at δ value 11.5 may be due to -NH proton (azomethine).

Experimental

1 ml of 1 x 10⁻³ M uranyl acetate solution, 10 ml of buffer solution of required pH, 1 ml of 1 x 10⁻² M 4-hydroxy benzaldehydethiosemicarbazone are taken in a 25 ml standard flask. The contents of the flask are made up to the mark with double distilled water. The solution is shaken well for uniform concentration. The blank solution is prepared in the same way but without adding the metal ion. The spectrum of the experimental solution is recorded in the wavelength range 350 to 700 nm against the respective blank solution.

II. Results And Discussions

U (VI) reacts with 4-HBTS in weak acidic pH to give a yellow coloured water soluble species. The colour reaction between U (VI) and 4-HBTS is instantaneous even at room temperature. The maximum absorbance (λ_{max}) of the yellow coloured complex was observed at 350 nm which remains constant for more than 24 hours. The effect of pH on the absorbance revealed that the intense colour was formed in a solution of pH 5. A tenfold excess of the reagent is adequate for complete colour development. Addition of excess of reagent has no adverse effect on absorbance.

The studies relating to the effect of U (VI) revealed that a linear relationship (Fig-2) exists between metal ion concentration and the absorbance in the range of 0.9522 to 9.522 $\mu\text{g/mL}$. The linear plot is fitted into the equation $A_{352} = 0.0105C + 0.0079$. The molar absorptivity and Sandell's sensitivity are $1.1 \times 10^4 \text{ L mol}^{-1} \text{ cm}^{-1}$ and $0.002164 \mu\text{g/cm}^2$ respectively.

The effect of the reagent on absorbance is also studied, no linear relationship is found between the reagent and the absorbance. As the metal ion U (VI) forms a coloured complex with reagent, an attempt is made to determine the composition and the stability of the complex. Job's method (Fig-3) and mole ratio method are conducted to make these determinations. The stability constant of 1:1 . Uranium(VI) - 4-HBTS complex is calculated and is found to be 3.74×10^5 .

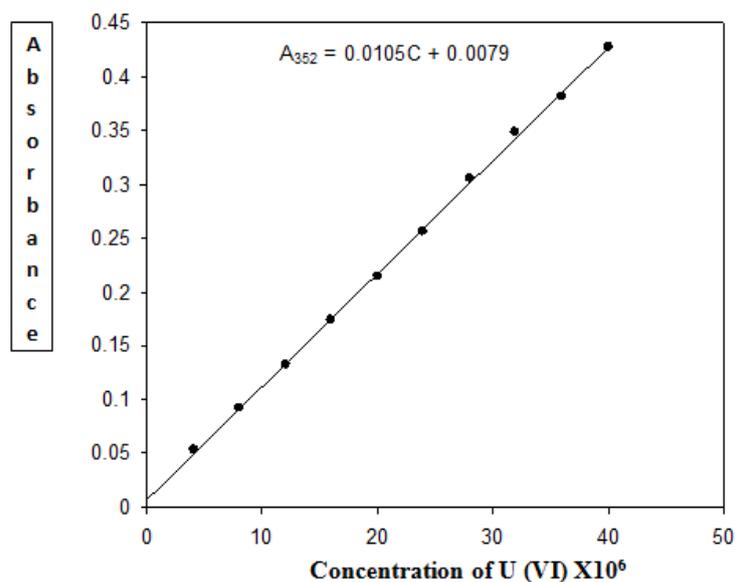


Fig.2. Effect of metal ion concentration (Beer's law)

[4-HBTS] = $8 \times 10^{-4} \text{ M}$
 pH = 5
 λ_{max} = 350 nm

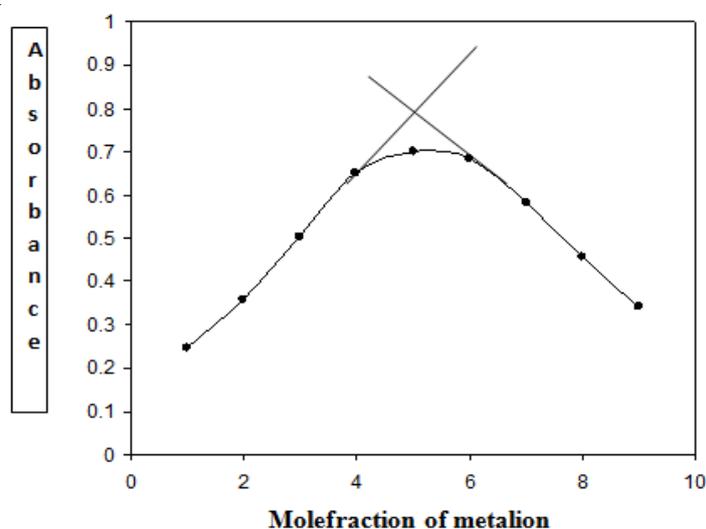


Fig. 3. Job's continuous variation method

[U(VI)] = $4 \times 10^{-5} \text{ M}$
 [4-HBTS] = $4 \times 10^{-5} \text{ M}$
 pH = 5
 λ_{max} = 348.5 nm

Table-1 Analytical characteristics of U (VI)- 4-HBTS

Chareacteristics	Results
λ_{\max} (nm)	350nm
p ^H range (optimum)	5-5.5
Number of Moles of the reagent required per mole of metal ion for complete colour development	10 folds
Molar absorptivity (Lmole ⁻¹ cm ⁻¹)	1.1 x 10 ⁴ L mol ⁻¹ cm ⁻¹
Sandell's sensitivity(µg/cm ²)	0.002164 µg/cm ²
Beer's law validity	0.9522 to 9.522 µg/mL.
Composition of the complex	1:1
stability constant of the complex	3.74 x 10 ⁵ .
Standard deviation	0.0009254
RSD	0.0097

Interference studies

Interference of various cations and anions on the absorbance values is studied and the data is presented in the **Table 2**. The metalions were chosen in such a way so that they either belong to the same group (or) same period

Table 2: Interference of foreign ions in the determination of uranium

$$\begin{aligned}
 [\text{U(VI)}] &= 4 \times 10^{-5} \text{ M} \\
 [4\text{-HBTS}] &= 4 \times 10^{-4} \text{ M} \\
 \text{pH} &= 5 \\
 \lambda_{\max} &= 350 \text{ nm}
 \end{aligned}$$

Ion (Anions) added	Tolerance limit (µg/ml)	Ion added (Cations)	Tolerance limit (µg/ml)
Chloride	170.17	Thromium(IV)	55.68
Bromide	319.62	Copper(II)	2.54
Iodide	761.45	Nickel(II)	5.86
Nitrate	496.00	Cadmium(II)	11.24
Acetate	424.84	Lead(II)	24.86
Urea	480.00	Silver(I)	3.45
Tartarate	736.00	Vanadium(V)	12.27

Application:

The present method is applied for the determination of U (VI) in environmental samples. The analytical determination of uranium was done as mentioned in the experimental part. The results are presented in table.3.

Table: 3

S.NO	Sample	ICPAES/AAS/ICP-MS U(VI) value in µg/ml	Amount of U(VI) found* in µg/ml by present method	Relative error (%)
1	Monazite sand	4.02	3.94	-1.99
3	Spiked tapwater	52	51.5	-0.96
4	Spiked waste water	102	103	+0.98
5	Spiked well water	210	208	+0.95

- Average of five determinations

III. Conclusions

A new spectrophotometric method is reported for the determination of micro gram levels of U (VI) forms a 1:1 stable Yellow coloured complex with 4-Hydroxy benzaldehydethiosemicarbazone. The Stability constant of the complex is 3.74x10⁵. The molar absorptivity and Sandell's sensitivity are 1.1 x 10⁴ L mol⁻¹ cm⁻¹ and 0.002164 µg/cm² respectively. In comparison with many expensive instrumental techniques and the procedures which usually require prior separation and pre concentration process and time sensitive procedures, the present method is a new, rapid, simple, sensitive and selective method for the micro determination of uranium (VI) in the range of 0.9522 to 9.522 µg/mL. The method has been applied for the analysis of U (VI) in environmental samples.

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IOSR Journal of Applied Chemistry (IOSR-JAC) is UGC approved Journal with Sl. No. 4031, Journal no. 44190.

K. P. Satheesh. "Analytical Determination of Uranium (VI) using 4-Hydroxybenzaldehydethiosemicarbazone by Spectrophotometry." IOSR Journal of Applied Chemistry (IOSR-JAC) , vol. 10, no. 10, 2017, pp. 24-28.