

# ECO FRIENDLY ANALYSIS AND SPECTROPHOTOMETRIC STUDIES ON THE REACTION OF DIOXOURANIUM (VI) WITH 2-HYDROXY-4-CHLORO-5- METHYLACETOPHENONE OXIME AND 2-HYDROXY-4-CHLORO-5-METHYLBENZOPHENONE OXIME

Punita S. Bharadwaj

Department of Chemistry , J.P Arts and Science College, Bharuch , Gujarat (INDIA)  
E mail : Punita\_bharadwaj@yahoo.co.in

Received November 10, 2011

Accepted February 25, 2012

## ABSTRACT

Naturally occurring U(VI) forms highly soluble complexes at alkaline pH. This leads to an increase in the mobility and availability of uranium to ground water and soil which leads to health hazards. U(VI) has tendency to form complexes with various organic chelating agents. Orange yellow complexes of U(VI) with HCMAOX and HCMBOX have been studied spectrophotometrically in water ethanol medium at pH 10 and 10.5 respectively. The effects of pH, time, addition of reagents and diverse ions have been studied. The composition of the complexes comes out to be 1:2 (Metal:Ligand) which has been confirmed by continuous variation, the mole ratio and the slope ratio methods. Beer's law is obeyed up to 47.6 ppm of U(VI) with both the reagents. The molar absorptivity of the complexes are  $2.07 \times 10^3$  and  $1.81 \times 10^3$  lit/mole/cm. The stability constants of the complexes are  $3.27 \times 10^5$  and  $7.15 \times 10^5$  respectively. The IR spectral and magnetic studies indicates that both ligands are bidentate and coordination takes place by formation of M-O and M←N bonds through the oxygen of phenolic group and nitrogen of oxime group with metal. New research has been carried out for extracting U(VI) from sea water using different ligands.

**Key Words:** 2-Hydroxy-4-Chloro-5-Methylacetophenone oxime, 2-Hydroxy-4-Chloro-5-Methylbenzophenone oxime, Chelating agents, Absorptivity, Complexes

## INTRODUCTION

2-Hydroxy-4-Chloro-5-Methylacetophenone oxime (HCMAOX) and 2-Hydroxy-4-Chloro-5-Methylbenzophenone oxime (HCMBOX) have been used for analysis of various transition metals and actinides. The present communication deals with the analysis and spectrophotometric studies of dioxouranium (VI) with HCMAOX and HCMBOX. The method is based on chelation of uranyl ions with HCMAOX and HCMBOX to produce orange yellow complexes in water-ethanol medium at room temperature which absorbs maximally at 410 nm and 470 nm respectively. Several reagents/ligands/oximes

have been proposed for the determination of U(VI)<sup>1-4</sup> but HCMAOX and HCMBOX was found to be specific, selective and developing orange yellow water soluble complexes at pH 10.0 and 10.5 respectively. Absence of isobestic point shows that single complex species exist in both cases.

## AIMS AND OBJECTIVES

Uranyl ion (UO<sub>2</sub>)<sup>+2</sup> is the species of interest which is soluble, stable and mobile in aqueous phase. It is found in soil and water near nuclear establishments. Uranium from the environment enters the human body by ingestion with food

and drink and by inhalation.

Daily intake of U in food and water varies approximate 1-5 micrograms u/d in uncontaminated regions to 13-18 micrograms u/d or more in uranium mining areas.<sup>5</sup> Uranium absorbed from the intestine or lungs, enters the blood stream and is rapidly deposited in the tissues, predominately kidney and bones or excreted in urine. Renal toxicity is a major adverse effect of U. The metal has toxic effects on the cardiovascular system, liver, muscle or nervous system as well.

Uranium compounds are carcinogenic and hence there has been interest in development of low cost rapid techniques for measuring uranium in various samples<sup>4, 6</sup>.

Even though there are many techniques for the analysis of U, spectrophotometry is widely used due to its simplicity, low cost and adoptability<sup>7</sup>. Hence this technique can be exploited for the estimation of Uranyl ion in soil<sup>4</sup> and water samples<sup>8,9</sup>. Artificial samples containing different concentrations of Uranyl ions were used for this purpose.

## MATERIAL AND METHODS

Bausch and Laumb spectrophotometer was used for the absorbance measurements. The pH measurements were carried out on Elico pH meter and IR spectra was recorded on PERKIN EIMER model no. 783 using KBr pellet technique. 2-Hydroxy-4-chloro-5-methylacetophenone and 2-Hydroxy-4-chloro-5-methyl-benzophenone was synthesized quantitatively by Fries migration of m-Cl-p cresyl acetate and m-Cl-p cresyl benzoate respectively by acetylation and benzylation of m-Cl-p cresol. The oximes were prepared by usual method with  $\text{NH}_2\text{OH}\cdot\text{HCl}$  and crystallized from ethanol (M.P. HCMAOX 85°C, HCMBOX 169°C). Ethanolic solution of the reagent was used in all experiments. Standard solution of Uranium was prepared by dissolving requisite amount of uranyl nitrate  $\text{UO}_2(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$  in double distilled water and standardized by standard measures<sup>10</sup>.

### Spectrophotometric Study

Vosburg and Cooper's method<sup>11</sup> employed to 1:1

,1:2, 1:3 and 2:1 mole ratio of U(VI) to HCMAOX and HCMBOX showed that the reagent forms only one complex with these metal ions which exhibit maximum absorbance at 360nm and 380 nm respectively but band occurs at 410 nm and 470 nm respectively.

### Effect of pH, Time and Addition of Reagent

The uranium complexes with both the reagents HCMAOX and HCMBOX were found to be stable in pH range 9.5 to 11.0 and 10.0 to 11.0 respectively. Hence subsequent studies were carried out at 10.0 and 10.5 pH respectively. It was observed that color development is quite rapid and remains unchanged for at least three hours. It was also observed that sequence of reagent addition got no significant effect on absorbance. It was found that about 10-15 fold excess of the reagent was necessary to attain the constant and maximum color intensity.

### Composition and Constitution of Complex

In all the measurements requisite amount of ethanol were added to maintain 50-60% proportion of ethanol in final dilution. The compositions of both the complexes were determined by Job's method of continuous variation<sup>12</sup>, the mole ratio method<sup>13</sup> and the slope ratio method<sup>14</sup>. Molar absorptivity and stability constants of the complexes were calculated from Beer's law and mole ratio method respectively. Magnetic susceptibility measurements and absorption spectra in infra red region were also carried out.

### Procedure For Estimation

The solution containing varying concentration of U(VI) ions were added to 25 ml volumetric flasks containing 10-15 fold excess of reagents and 5 ml of buffer solution at pH 10.0 and 10.5 respectively for HCMAOX and HCMBOX. Requisite amount of alcohol was added to maintain its 50-60% proportion in final dilution. The absorbencies were measured at 410 nm and 470 nm with HCMAOX and HCMBOX respectively using reagent solution as blank. The absorbance values were plotted against U(VI) ion concentration. A straight line passing through the origin was obtained up to 47.6 ppm of U with both the reagents. Molar absorptivi-

ties were found to be  $2.07 \times 10^3$  and  $1.81 \times 10^3$   $\text{lit mol}^{-1}\text{cm}^{-1}$  respectively for HCMAOX and HCMBOX. Sandell's sensitivity for both the complexes are  $0.01513 \mu\text{g}/\text{cm}^2$  and  $0.02174 \mu\text{g}/\text{cm}^2$  for HCMAOX and HCMBOX respectively.

## RESULTS AND DISCUSSION

Beer's law obeyed up to 47.6 ppm for both complexes. From the absorbance value, concentration of U(VI) ions in unknown samples can be evaluated with the help of calibration curve drawn under identical conditions. (Fig. 1 and Fig 2) From the job's method of continuous variations from the graph it has been found that maximum

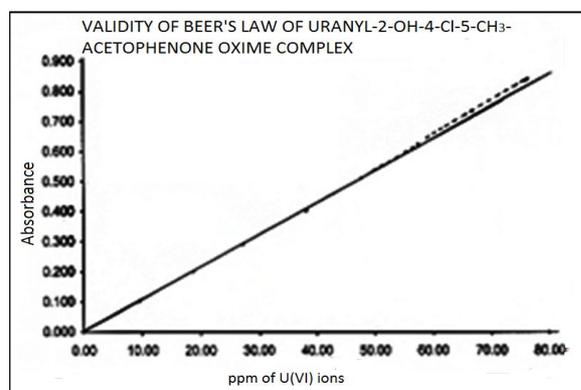


Fig. 1 : Beer's law for uranyl HCMAOX

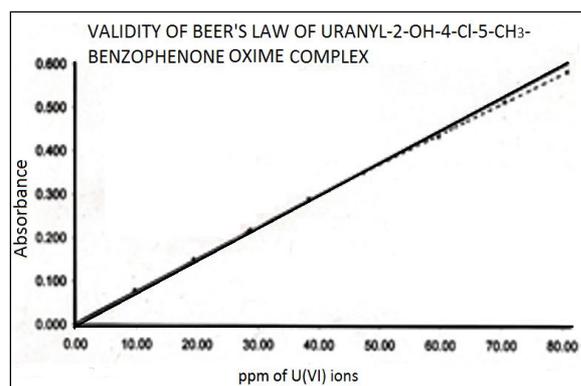


Fig. 2 : Beer's law for uranyl HCMBOX

occurs at 0.333 concentration of metal to concentration of metal and reagent for both the complexes indicating the formation of 1:2 (Metal : Ligand) complex. (Fig. 3 and Fig. 4) From the mole ratio method it has been observed that the absorbance gradually increases till

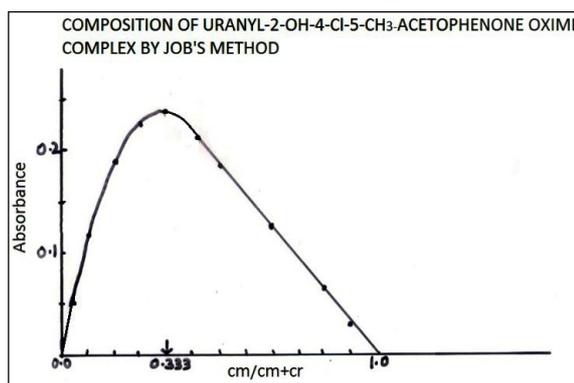


Fig. 3 : Job's method for uranyl HCMAOX

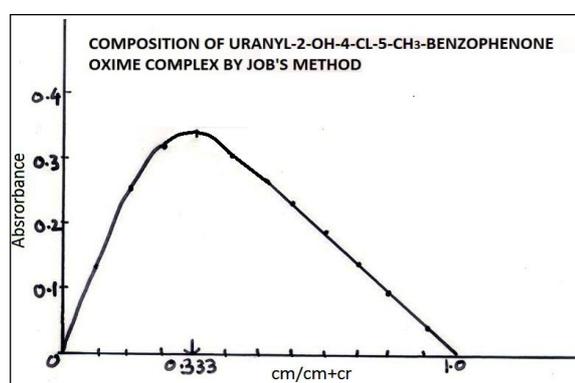


Fig. 4 : Job's method for uranyl HCMBOX

double of the equimolar reagent solution is added. After this quantity, if reagent is added the absorbance curve bends sharply indicating the formation of 1:2 (metal : ligand) complexes. Stability constants of the complexes are  $3.27 \times 10^5$  and  $7.15 \times 10^5$  for HCMAOX and HCMBOX respectively. (Fig. 5 and Fig. 6)

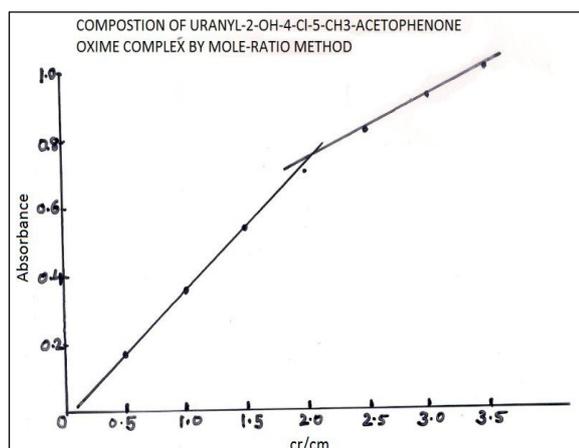


Fig. 5 : Mole-ratio method for uranyl HCMAOX

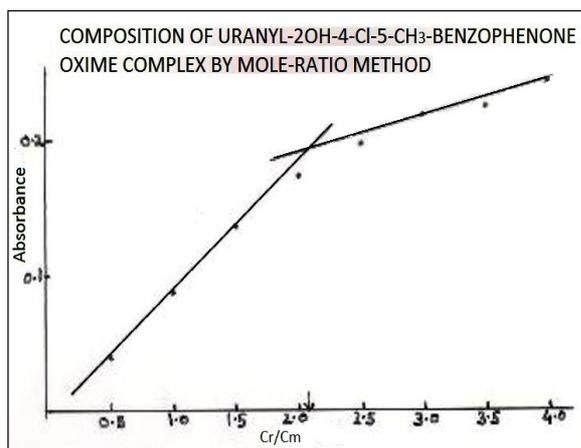


Fig. 6 : Mole ratio method for uranyl HCMBOX

Slope ratio method also indicates the formation of 1:2 ( metal : ligand ) complexes. The influence of foreign ions on the estimation of U(VI) ions using HCMAOX and HCMBOX was studied in the usual manner. A limit of 5% change in absorbance was taken as limiting concentration. It was observed that Ba<sup>+2</sup>, Be<sup>+2</sup>, Ca<sup>+2</sup>, Sr<sup>+2</sup>, K<sup>+</sup>, Na<sup>+</sup>, NH<sub>4</sub><sup>+</sup>, Cl<sup>-</sup>, Br<sup>-</sup>, I<sup>-</sup>, NO<sub>3</sub><sup>-</sup>, SO<sub>4</sub><sup>-2</sup>, CO<sub>3</sub><sup>-2</sup>, OAc<sup>-</sup>, and CrO<sub>4</sub><sup>-2</sup> did not interfere in the estimation of uranium but Fe<sup>+3</sup>, Cr<sup>+3</sup>, Al<sup>+3</sup>, Ti<sup>+4</sup>, Mn<sup>+2</sup>, Cu<sup>+2</sup>, Co<sup>+2</sup> and Ni<sup>+2</sup> interfere even when present in traces.

Magnetic study of these complexes claims octahedral diamagnetic character. (Fig. 7 and Fig. 10)

### Spectral Studies

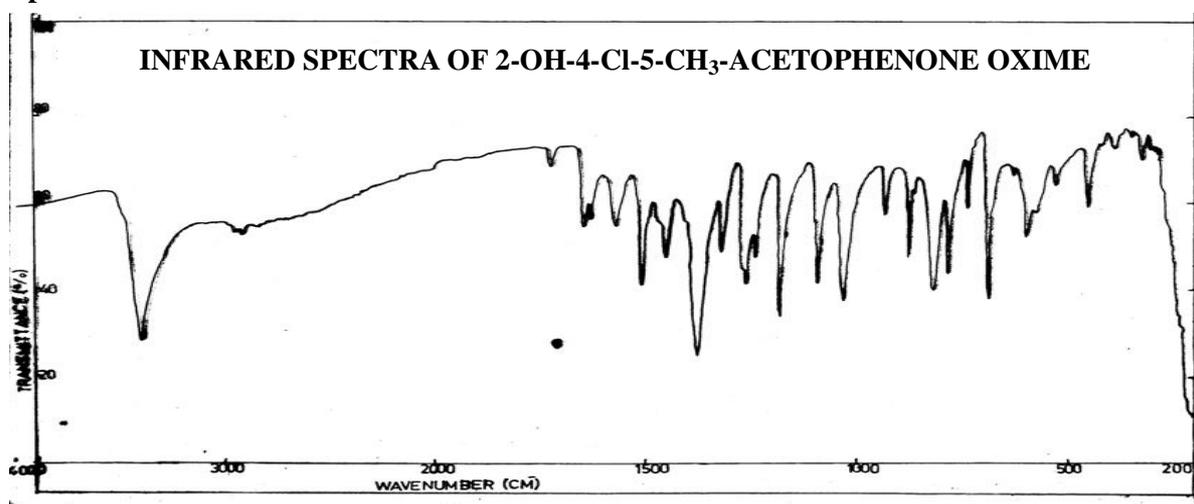


Fig. 7 : Infra Red Spectra of HCMAOX

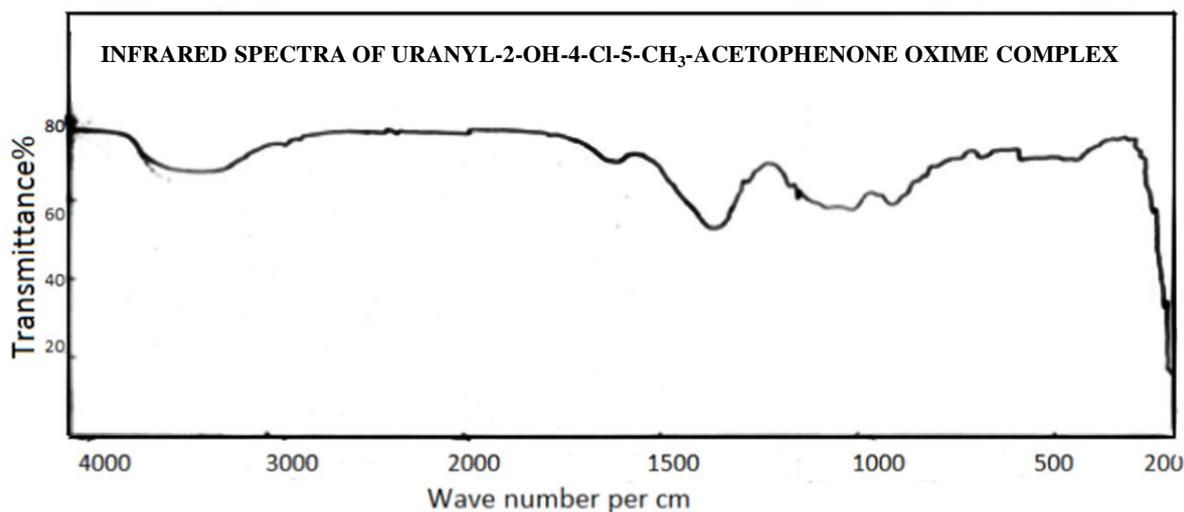


Fig. 8 Infra Red Spectra of Uranyl HCMAOX

### Spectral Studies

IR spectrum of the reagents shows strong absorption bands at  $3400\text{ cm}^{-1}$  and  $2985\text{ cm}^{-1}$  and  $3360\text{ cm}^{-1}$  and  $2950\text{ cm}^{-1}$  assigned to two different types of hydroxyl groups present in HCMAOX and HCMBOX respectively. Only the bands at  $3400\text{ cm}^{-1}$  and  $3360\text{ cm}^{-1}$  disappear, showing the replacement of phenolic hydrogen by the metal in uranyl HCMAOX and HCMBOX respectively. The coordination of the oximino group through nitrogen and not hydroxyl group is indicated by the lowering of C=N frequen-

cies from  $1650\text{ cm}^{-1}$  to  $1620\text{ cm}^{-1}$  and  $1640\text{ cm}^{-1}$  to  $1600\text{ cm}^{-1}$  for uranyl HCMAOX and HCMBOX respectively. The lowering in C=N frequencies and replacement of phenolic hydrogen atoms clearly indicates that chelation takes place through oxygen of -OH group and nitrogen of =N.OH group in both the complexes. Presence of characteristic frequencies in the region  $950\text{--}890\text{ cm}^{-1}$  (i.e.  $920$  and  $910\text{ cm}^{-1}$ ) is clear indication of the development of  $\text{UO}_2^{+2}$  in bonding<sup>3,7,9,11-15</sup>

The structure of dioxouranyl complexes with the

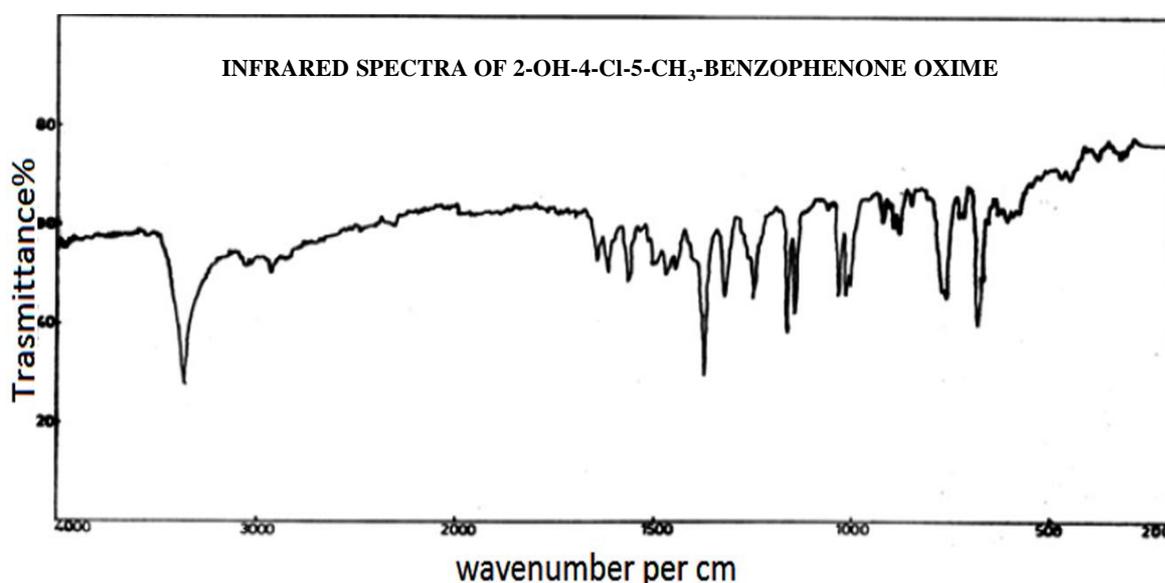


Fig 9 : Infra Red Spectra of HCMBOX

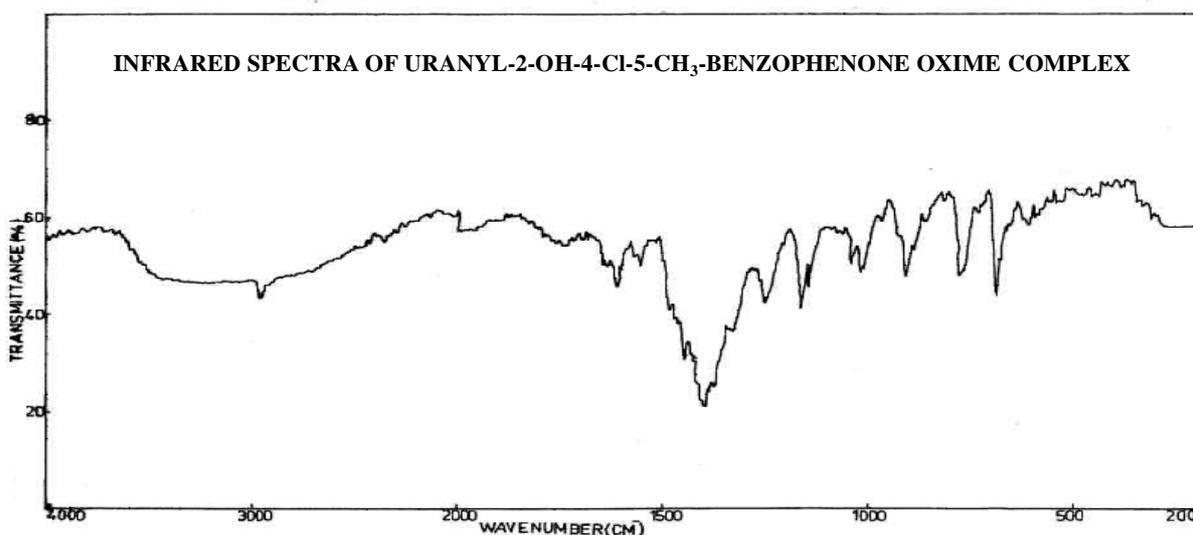


Fig. 10 : Infra Red Spectra of Uranyl HCMBOX

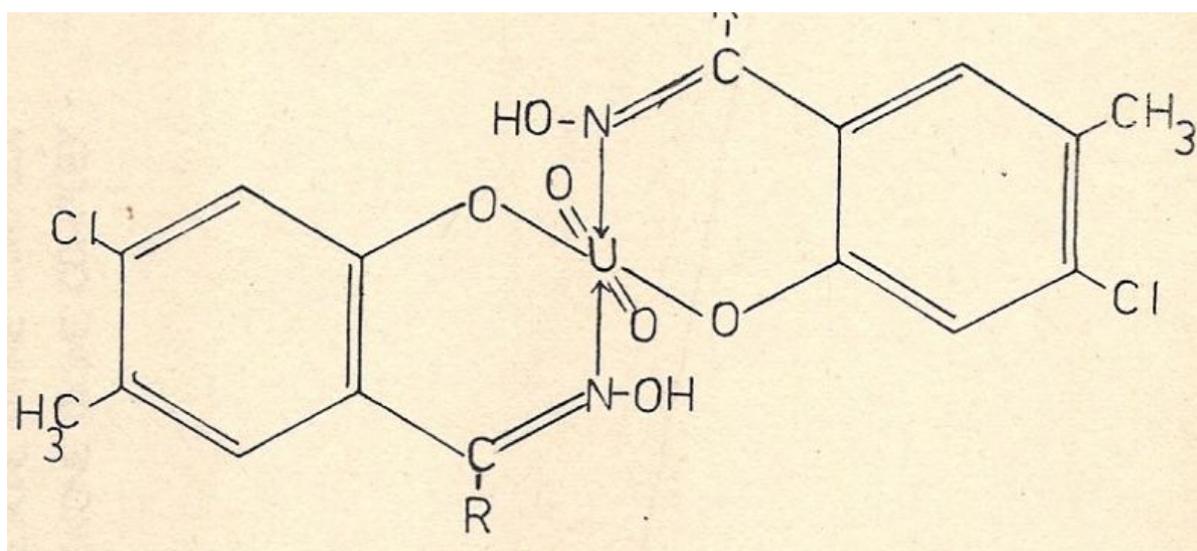


Fig. 11 : Dioxouranyl complex

selected reagents can be depicted as follows:

R =  $-\text{CH}_3$  for acetophenone oxime complex  
 $-\text{C}_6\text{H}_5$  for benzophenone oxime complex

### CONCLUSION

Both the reagents have a different group on carbon adjacent to the nitrogen. On comparison it is found that HCMAOX and HCMBOX are of same potentiality which indicate that the replacement of  $-\text{CH}_3$  by  $-\text{C}_6\text{H}_5$  has a negligible effect. Their solubility and precipitation ranges are close and stability and sensitivity of the chelates do not have much difference. The proposed method has the advantage of having high molar absorptivity  $2.07 \times 10^3$  and  $1.81 \times 10^3$  l/mol/cm with low limit of detection. The method is simple, quick, sensitive, accurate and useful due to high tolerance limits from cations and anions. Therefore, the proposed method is an effective method for the quantitative as well as qualitative analysis of uranyl ions.

### REFERENCES

- Rathnam P., Ramesh A. and Naidu R. R., *Ind. J. Chem.*, **19** (A), 385, (1980)
- Ojha A. C., Singh C. P. and Gupta D. R., *Acta.Ciencia Indica*, **VIC**(4), 234, (1980)
- Singh H. and Rathi U. K., Spectrophotometric study of U(VI) with 2-hydroxy-5-halo chalcone chelate, *J. Indian chem. soc.*, **LVI**, 1028, (1979)
- Lutfullah Khan F., Rahman N. and Azmi S.N.H., Spectrophotometric determination of U(VI) via complexation with piroxicam, *Ind. J. Chem. Technol.*, **16**, (5) 437-441, (2009)
- Taylor D. M. and Taylor S. K., Environmental uranium and human health, *Rev Environ Health*, **12** (3), 147-157, (1997)
- Beer S., Berryman O.B., Ajami D. and Rebek J., Encapsulation of uranyl dication, *chem. sci.*, **1**, 43-47, (2010)
- Kalinich J. F. and McClain D. E., Development of a colorimetric test for uranium. Paper presented at NATO Human factors and medicine panel research task group 099 Radiation bio effects and counter measures meeting, Held in Bethesda, USA, June 21-23, (2005)
- Djogic R., Sipos L. and Branica M., Characterization of U(VI) in sea water, *limnology and oceanography*, **13** (5), 1122-1131 (1986)
- Nanotechnology net book technology news, New research on extracting U from sea water using self assembled ligands, June 07, (2010)
- Vogel A. I., A textbook of quantitative inorganic analysis, **4th edition**, 487 (1978)
- Vosburg W. C. and Copper G. R., *J. Am. Chem. Soc.*, **63**, 437, (1941)

12. Job P., *Ann. Chim.*, **9** (2), 113, (1928)

13. Yoe J. H. and Jonea A. L., *Ind. Engg. Chem. Anal. Edn.*, **16** (2) 111, (1944)

14. Harvey A. E. and Manning D. L., *J. Am. Chem. Soc.*, **72** (2) 4888, (1950)

15. Parveen nahid and Rohan Y Studies on sepc-trophotometric detamination of some Invironmental samples. *J. Environ. Res. Develop.* **6**(1) 57-62 (2011).

