

CHAPTER II

SPECTROPHOTOMETRIC DETERMINATION OF OSMIUM (VIII) IN TRACE AMOUNTS USING ETHYLENE THIOUREA (ETU) AS CHROMOGENIC REAGENT

2.1 INTRODUCTION

2.2 EXPERIMENTAL PROCEDURE

2.3 RESULTS AND DISCUSSION

2.4 CONCLUSION

2.5 REFERENCES

This chapter of the thesis is published in Indian Journal of Chemical Technology.

18 (2011) 113-117.

2.1 INTRODUCTION

Osmium is a rare metal that occur in nature in the form of an alloy with platinum. It is mainly used to make very hard alloys. The applications of such alloys vary from ballpoint pen tips to pacemakers and heart valves [1-6]. Osmium tetra oxide has been used in fingerprint detection and in staining fatty tissues for biological studies of materials by transmission electron microscopy [7]. Various osmium complexes have been reported as catalyst for olefin metathesis [8], micro enzyme sensors [9] and electroluminescent materials [10-12]. Also osmium-191 isotope is used in radiopharmaceuticals [13]. Various reagents such as thiobenzhydrazide [14], ethyl isobutrazine hydrochloride [15], 4-(2-pyridylazo) resorcinol [16], pyrocatechol and hydroxyamidine [17], pyrimidinethiols [18], carminic acid peroxide [19], basic dyes [20], diantipyrylphenylmethane derivatives [21], trioctyl-amine [22], phenothiazine derivatives [23], phenanthrenequinone monoxime [24], and 9,10-phenanthrenequinone monoxime [25], have been reported for the spectrophotometric determination of osmium after liquid-liquid extraction [14-23], solid-liquid extraction [24] and co-precipitation on microcrystalline naphthalene [25]. Most of the existing spectrophotometric methods using sulphur containing molecules lack adequate sensitivity and selectivity. Other than direct spectrophotometric methods of determination, certain reagents were employed for the spectrophotometric determination of osmium based on its catalytic activity [16, 26]. Derivative spectrophotometric methods have also been used for the determination of osmium under different experimental conditions [27-29].

In the present work, a reaction of osmium(VIII) with ETU has been examined under various experimental conditions and the most suitable analytical conditions have been ascertained for the quantitative determination of osmium(VIII). The proposed direct spectrophotometric method offers no interference from Ru^{2+} , Fe^{2+} , Fe^{3+} and other platinum group metals.

2.2 EXPERIMENTAL PROCEDURE

2.2.1 Apparatus

The absorption spectra were recorded using a JASCO V-550 UV-VIS spectrophotometer with 1cm matched quartz cells. All reagents used were of analytical reagent grade. Digital pH meter (EUTECH instruments) was used for pH measurements. Derivative spectra were also recorded using the same spectrophotometer with scan speed 1000 nm/min, slit width of 1nm and $\Delta\lambda = 2$ nm for derivative mode in the wavelength range 400-800 nm.

2.2.2 Reagents and chemicals

Stock solution of osmium(VIII) was prepared by dissolving osmium tetroxide (J.M. Chemicals Ltd., London) in 1M H₂SO₄ and standardized [30]. Aliquots for spectrophotometric measurements were obtained by appropriate dilution of the stock solution using double distilled water. Solutions of different metal ions for the interference studies were prepared by dissolving weighed quantities of their salts in double distilled water or 1M H₂SO₄ solution. Solutions of anions were also prepared by dissolving the respective alkali metal salts in double distilled water. Ethylene thiourea (ETU) solution was prepared by dissolving 1g of the reagent (procured from E.Merck) in 100 ml of double distilled water.

2.2.3 Procedure

Aliquots of the stock solution containing 0.03-3 μg of osmium(VIII) were pipetted out into a series of 10 ml standard flasks, mixed with 0.1 ml of 1 % ethylene thiourea solution, and shaken well. It is then made up to the mark with 1M H₂SO₄ (to maintain pH 1). Purple color is developed instantaneously and measured the absorbance at 490 nm against the reagent blank (1% ethylene thiourea in 1M H₂SO₄ solution). The calibration graphs were constructed by plotting the absorbance against the amount of metal ions.

2.3 RESULTS AND DISCUSSION

2.3.1 Spectral studies

Spectral studies clearly show that ethylene thiourea reacts with osmium at room temperature to form a purple colored complex having maximum absorbance at 490 nm (Fig.2.1). Subsequent studies have been therefore carried out at this wavelength. The variation of absorbance with pH for a known concentration of osmium solution was studied and maximum absorbance was found at pH1, and hence this pH has been maintained throughout the study (Fig.2.2). Different amounts of ETU were added to a fixed quantity of osmium(VIII) and the absorbance was measured according to the standard procedure. A volume of 0.14 ml 1% solution of ETU was found to be optimum for the determination of 0.75 μg of osmium (Fig.2.3). It was noticed that an excess of the reagent does not have any adverse effect on the sensitivity and stability of the complex. The complex was found to be stabilized within minutes (Fig.2.4) and produced the same absorption spectra even after 24 hours at room temperature, indicates that the colored complex species is having substantial stability.

One of the important characteristics of derivative spectrophotometry is the precise determination of the position of absorption maxima. For a single peak spectrum having a broad band, the position of absorption maxima can be only approximately determined. The derivative spectra can be used to accurately locate the peak [32-33]. From the Figures of different order (0, 1, 2 & 3) derivative spectra, it is clear that maximum absorbance was observed at 490 nm {Fig.2.5 (a, b, c & d)}.

2.3.2 Analytical data

The Beer's law was obeyed in the range of 0.03 - 3 $\mu\text{g}/\text{ml}$ with relative standard deviation in the range of 0-8% (Table II.1 & Fig.2.6). The molar absorptivity and Sandell's sensitivity for the colored system were found to be $16.87 \times 10^4 \text{ Lmol}^{-1}\text{cm}^{-1}$ and $1.13 \times 10^{-3} \mu\text{gcm}^{-2}$ respectively, which are comparable with other methods (Table II.2). The detection limit ($D_L = 3.3 \sigma/S$) and quantitation limit ($Q_L = 10\sigma/S$) (where σ is the standard deviation of

reagent blank; $n=5$, and S is the slope of the calibration curve) were found to be $0.0291 \mu\text{g/ml}$ and $0.0883 \mu\text{g/ml}$ respectively. The effect of milligram amounts of several ions on the determination of $0.75 \mu\text{g}$ of osmium was studied. No interference were noticed in the presence of anions like NO_2^- , Br^- , SCN^- , SO_3^{2-} , AsSO_3^{3-} and cations like Li^+ , Mg^{2+} , Ca^{2+} , Ba^{2+} , Cd^{2+} , Hg^{2+} , Al^{3+} , Tl^+ , Pb^{2+} , Sb^{3+} , Zn^{2+} , UO_2^{2+} , Se^{4+} , Cr^{3+} , Mn^{2+} , Fe^{3+} , Ni^{2+} , Pt^{4+} , MoO_4^{2-} , WO_4^{2-} and Co^{2+} . The presence of Fe^{3+} , Ru^{3+} , VO_4^{3-} , CrO_4^{2-} , Pd^{2+} , Cu^{2+} , and Co^{2+} gave high recoveries while Ir^{4+} , Zr^{4+} , Ti^{4+} and Be^{2+} caused low recoveries.(Table II.3).The application of suitable masking agents can sometimes effectively avoid the interference from different cations and anions. The interference due to Zr^{4+} , Ti^{4+} , Be^{2+} and Ir^{4+} were overcome by the addition of a 2 % solution of sodium fluoride and the interference due to Co^{2+} , Cu^{2+} , Pd^{2+} and VO_4^{3-} was eliminated using 0.1 % solution of EDTA. The results of the recovery of osmium from synthetic mixtures clearly show that the method works satisfactorily in the presence of noble and base metals. To overcome the interferences, fluoride and EDTA were added in the sample solution before the addition of reagent (Table II.4).

A plot of absorbance at 490 nm versus the mole fraction of metal indicated the formation of a 1:3 Os-ETU complex (Job's method of continuous variation and mole ratio method; Fig.2.7.(a&b). In order to understand the nature of bonding and the composition of the Osmium-ETU complex, attempts have been made to synthesize the solid complex by refluxing 0.01 mole of Os(VIII) solution and 0.03 mole of ETU. The solid complex obtained was characterized by physicochemical methods including C, H & N analysis[Calculated %:C 21.76; H 19.34; N 16.93; S 3.63; Os 38.32. Found %: C 19.61; H 17.43; N 15.25; S 4.35; Os 34.54], IR and electronic spectra. These results also confirm the composition of metal to ETU is 1:3. The IR data provides information about probable coordination sites of ETU in this complex. The most probable structure of the complex and its optimized geometry is given in Fig.2.8 (a & b). The IR spectra showed bands for a). ETU: ν (N-H) 3170, ν (C=S) 1200, ν (-NCS) 1310,1050,760 b).Complex: ν (O-H/N-H/H₂O) 3450, ν (M-S) 340 {Fig.2.9.(a&b)}.

2.4 CONCLUSION

Ethylene thiourea provides a simple, rapid, sensitive and selective method for the spectrophotometric determination of osmium(VIII). The main advantage of the proposed method is its rapidity, as the colour development is instantaneous at room temperature. It does not require heating, cooling, or long standing to record constant absorbance or extraction with a solvent or addition of a surfactant to intensify the color of the system, which is an inevitable part of quite a number of the reported methods. The metal salt and the reagent are soluble in water and hence the entire experiments can be performed without using any other mixed solvent systems. The stoichiometry of the compound is found to be 1:3. This method offers no interference from Ru^{2+} , Fe^{2+} , Fe^{3+} and other platinum group metals. Quite a large number of cations and anions also offer no interference at pH1, and hence osmium (VIII) can be estimated without using any secondary masking agents.

2.5 REFERENCES

1. Kaner.R.B & Gilman.J.J, *Publication Number: WO/2005/110924* (2005).
2. Kaner.R .B & Gilman.J.J, U S Patent. 20070224100 (2007).
3. Hebbache.M, Stuparevic.L & Zivkovic.D, *Solid State Commun.* 139 (2006) 227.
4. Yoshino.K, Kajiwara.Y, Takaish.N , Inamoto.Y & Tsuji.J, *J Am. Oil Chem. Soc.* 67 (1990) 21.
5. Smotkin.E.S, Ley.K.L, Pu.C & Liu.R, *Publication No.* Wo/1998/040161 (1998).
6. Patrick.C, “*Platinum Group Metals: Canadian Minerals Year Book*”. 41 (2005) 8.
7. Sawant.S.Shakuntala, *Analytical science.s* 25 (2009) 813.
8. Grubbs .R .H, Johnson. L. K & Nguyen. S. T, *U. S. Patent.* 5312940 (1994).
9. Motonaka.J, K.Miyata & Faulkner.L.R, *Anal Lett.* 47 (1994) 1.
10. Tao .Y & Carty .A, *Canadian Patents database.* CA 2448718 (2003).
11. Carlson.B, Phelan.G .D, Benedict.J, Kaminsky.W & Dalton.L, *Inorg Chim Acta.* 357 (2004) 3967.
12. Tao.Y & Carty.A, U.S.Patent, 20070001166,(2007).
13. Srivastava.P. C, *Science and Technology Subcommittee Meeting Report.* CONE-840R21400 (1986).
14. Shome.S.C, Nandy.S, Guhathakurta.A, Ghosh.N.C, Das.H. R & Gangopadhyaya .P .K, *Mikrochim Acta.* 11 (1978) 343.
15. Katyal. M, *Fresenius' J Anal Chem,* 328 (1987) 516.
16. Dadfarnia .S & Shamsipur. Bull. M, *Chem Soc Jpn.* 64 (1991) 3036.
17. Deb.M.K, Mishra .N, Patel.K .S & Mishra.R.K, *Analyst.* 116 (1991) 323.
18. Malik.A K, Atmajyot & Rao.A.L, *J.Chem Environ Res.* 2 (1993) 135.

19. Manzoori.J.L, Sorouraddin.M.H & Amjadi .M, *Talanta*. 53 (2000) 61.
20. Cao.Q.E, Li .Z, Wang .J & Li .C, *Chem Anal* [Warsaw]. 47 (2002) 701.
21. Huang .Z, Hu.Q, Yang.G, Wang .J, Jing .C, Xu .Q & Li. Z, *Chem Anal* [Warsaw]. 50 (2005) 913.
22. Balcerzak.M ,Komar.K,Swiecicka.E & Kasiura .K, *Anal Sci*. 13 (1997) 33.
23. Seetharamappa.J,Motohashi.N & Kovala-Demertzi.D,*Current Drug Targets* .7 (2006) 1107.
24. Wasey.A, Bansal.R. K & Puri.B.K, *Mikrochimica Acta*, 82 (1984) 211.
25. Wasey.A, Puri.B.K, Katyal.M & Mehra.M.C, *Anal Sci*. 2 (1986) 153.
26. Ensati.A. A & Sollari.E.S.E, *Talanta*. 4 (1994) 1651.
27. Balcerzak.M & Marczenko.Z, *Talanta*. 43 (1996) 471.
28. Balcerzak.M & Swiecicka.E, *Analytica Chimica Acta*, 53 (1997) 349.
29. Anna Kosiorek Rupinska, Elzhieta Swiecicka- Fuchsel & Maria Balcerzak., *Analytical letters* .39 (2006) 589.
30. Marczenko Sygmunt, “*Separation and spectrophotometric determination of Elements* ‘Ellis Horwood Ltd, John Wiley and Sons. 429.
31. Battenbury.J.M, Amino Acid Analysis, *Halsed-Wiley Press, Chichester* .92 (1982).
32. Gordana.Popovic.V, Lidija.B Pfendt, Violeta.M .Stefanovic, *J Serb Chem Soc* .65 (2000) 457

Table II.1 Determination of Os(VIII) in pure aliquots.

| Osmium taken(μg) | Osmium found (%) | S.D (%) | R.S.D (%) | Relative error (%) |
|-------------------------------|------------------|---------|-----------|--------------------|
| 0.030 | 0.028 | 0.001 | 0.357 | -0.066 |
| 0.150 | 0.140 | 0.010 | 0.714 | -0.066 |
| 0.750 | 0.740 | 0.020 | 0.270 | -0.013 |
| 1.500 | 1.500 | 0000 | 0000 | 0000 |
| 3.000 | 3.030 | 0.010 | 0.033 | 0.010 |

*Average of five determinations.

Table II.2. Analytical performance of the proposed method over other reported methods.

| Reagent | Sandell's sensitivity (ppm) | Molar absorptivity ($1 \text{ mol}^{-1} \text{ cm}^{-1}$) | Limitation |
|---|-----------------------------|---|--|
| Thiobenzhydrazide | 0.022 | 8.83×10^3 | Multiple extraction |
| Ethylisobutrazine hydrochloride | 0.009 | 1.80×10^4 | Strongly acidic aqueous phase |
| 4-(2-pyridylazo) resorcinol | 0.007 | 2.50×10^4 | Multiple extraction |
| Pyrocatechol and hydroxyamidine | ---- | 3.95×10^6 | Multiple extraction |
| o-Hydroxy-thiobenzhydrazide | 0.016 | 1.18×10^4 | Limited pH range & many interferences |
| α -Naphthalene-thiocarbonylhydrazide | 0.023 | 8.10×10^3 | Multiple extraction |
| Phenanthrenequinone monosemicarbazone | 0.0009 | 1.80×10^4 | Narrow pH range |
| 5-Chloro-2-hydroxythio benzhydrazide | 0.018 | 1.06×10^4 | Co-precipitation on microcrystalline naphthalene |
| Proposed method | 0.001 | 16.87×10^4 | |

Table II.3 Determination of Os (VIII) in the presence of diverse ions (0.75 µg).

| Diverse ions | Amount of diverse ions (µg) | Osmium* found (µg) | Relative error (%) |
|---------------------------------|-----------------------------|--------------------|--------------------|
| Al ³⁺ | 100 | 0.73 | -0.03 |
| Ba ²⁺ | 80 | 0.74 | -0.01 |
| Be ^{2+a} | 450 | 0.72 | -0.04 |
| Ca ²⁺ | 80 | 0.76 | 0.01 |
| Cd ²⁺ | 130 | 0.74 | -0.01 |
| Co ^{2+b} | 200 | 0.75 | 0.00 |
| Cr ³⁺ | 30 | 0.73 | -0.03 |
| Cu ^{2+b} | 200 | 0.75 | 0.00 |
| Fe ²⁺ | 300 | 0.74 | -0.01 |
| Fe ^{3+b} | 450 | 0.75 | 0.00 |
| Hg ²⁺ | 100 | 0.74 | -0.01 |
| Ir ^{4+a} | 450 | 0.72 | -0.04 |
| Li ⁺ | 150 | 0.74 | -0.01 |
| Mg ²⁺ | 110 | 0.73 | -0.03 |
| Mn ²⁺ | 20 | 0.73 | -0.03 |
| Ni ²⁺ | 100 | 0.73 | -0.03 |
| Pb ²⁺ | 50 | 0.76 | 0.01 |
| Pd ^{2+b} | 200 | 0.75 | 0.00 |
| Pt ⁴⁺ | 50 | 0.72 | -0.04 |
| Rh ³⁺ | 20 | 0.76 | 0.01 |
| Ru ^{3+b} | 200 | 0.75 | 0.00 |
| Sb ³⁺ | 10 | 0.74 | -0.01 |
| Se ⁴⁺ | 70 | 0.76 | 0.01 |
| Tl ⁺ | 130 | 0.74 | -0.01 |
| Ti ^{4+a} | 450 | 0.72 | -0.04 |
| Zn ²⁺ | 400 | 0.73 | -0.03 |
| Zr ^{4+a} | 450 | 0.72 | -0.04 |
| UO ₂ ²⁺ | 70 | 0.73 | -0.03 |
| AsSO ₃ ²⁻ | 25 | 0.74 | -0.01 |
| CrO ₄ ²⁻ | 75 | 0.75 | 0.00 |
| MoO ₄ ²⁻ | 120 | 0.74 | -0.01 |
| VO ₄ ^{3-b} | 200 | 0.75 | 0.00 |
| WO ₄ ⁻ | 20 | 0.73 | -0.03 |
| Br ⁻ | 210 | 0.74 | -0.01 |
| NO ₂ ⁻ | 250 | 0.73 | -0.03 |
| SCN ⁻ | 300 | 0.74 | -0.01 |
| SO ₃ ²⁻ | 120 | 0.73 | -0.03 |

*Average of five determinations; a. Masked by sodium fluoride.; b. Masked by EDTA

Table II.4 Recovery studies (0.75 μg of Osmium).

| Sample | Composition | Osmium found(μg) |
|--------|--|-------------------------------|
| 1 | Fe^{3+} (6 mg) + Zn^{2+} (3 mg) + Cu^{2+} (2 mg) | 0.73 |
| 2 | Zn^{2+} (3 mg) + Pb^{2+} (1 mg) + Mn^{2+} (4 mg) + Ni^{2+} (2mg) | 0.73 |
| 3 | Cu^{2+} (2mg) + Zn^{2+} (1mg) + Ni^{2+} (3mg) + Fe^{3+} (2mg) | 0.74 |
| 4 | Cu^{2+} (3mg) + Zn^{2+} (1mg) + Ni^{2+} (1mg) + Co^{2+} (2mg) | 0.74 |
| 5 | Pt^{4+} (0.152mg) + Pd^{2+} (0.30mg) + Rh^{3+} (1.5mg) + Ru^{3+} (0.150mg) | 0.74 |
| 6 | Pt^{4+} (2mg) + Pd^{2+} (3mg)+ Rh^{3+} (1mg)+ Ru^{3+} (0.20mg) | 0.72 |
| 7 | Ru^{3+} (1.0 μg) + Ir^{4+} (2 μg) + Pt^{4+} (1 μg) | 0.73 |
| 8 | Pt^{4+} (8 μg) + Ru^{3+} (2 μg) + Ir^{4+} (30 μg) + Rh^{3+} (1 μg) | 0.73 |

*Average of 3 determinations.

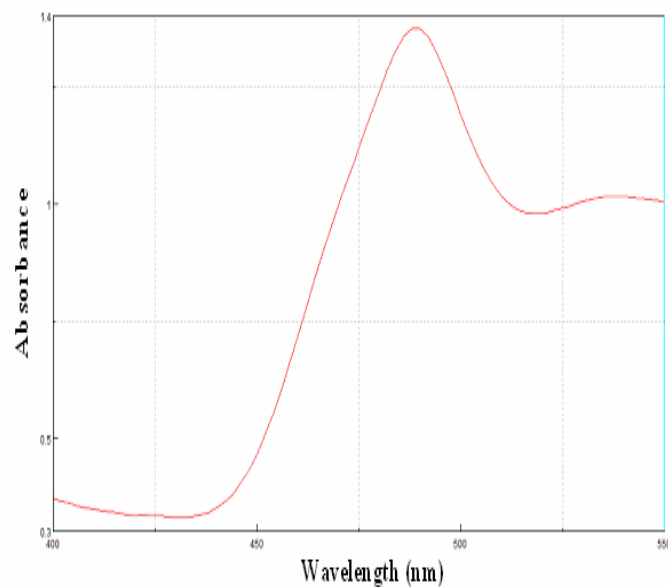


Fig.2.1 Absorption spectrum of Os- ETU Complex.

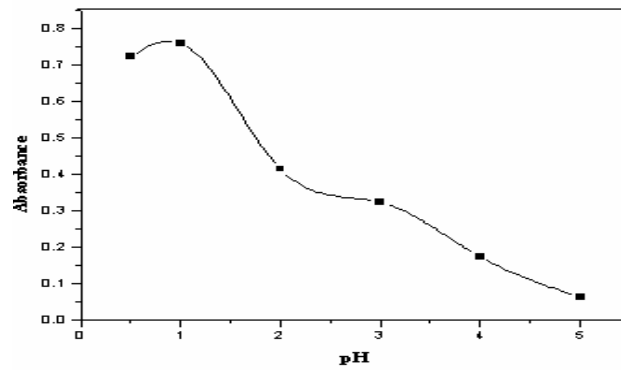


Fig.2.2 Variation of absorbance with pH.

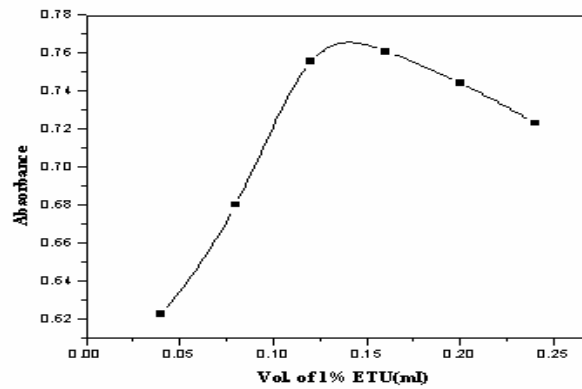


Fig.2.3 Variation of absorbance with vol of 1% ETU.

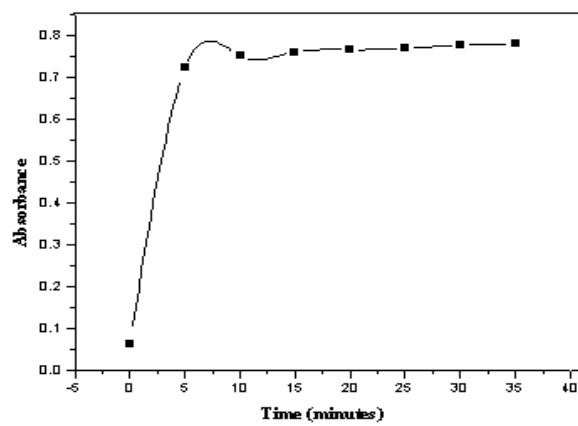


Fig.2.4 Variation of absorbance with time.

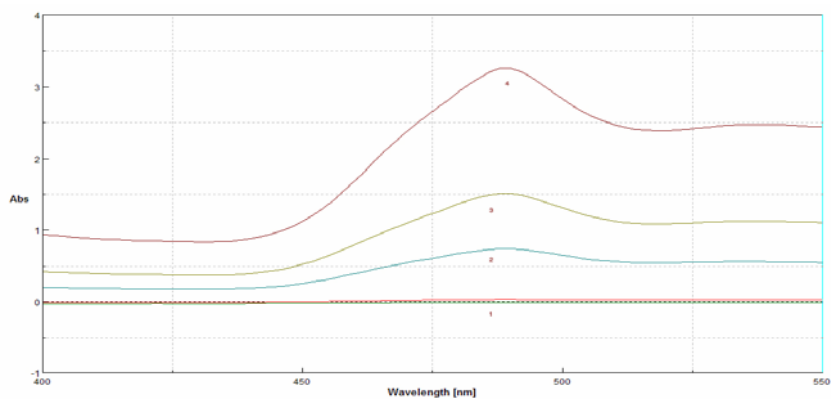


Fig.2.5 (a): Zero order spectra

1:0.03 $\mu\text{g/ml}$; 2:0.75 $\mu\text{g/ml}$; 3:1.5 $\mu\text{g/ml}$; 4:3.0 $\mu\text{g/ml}$.

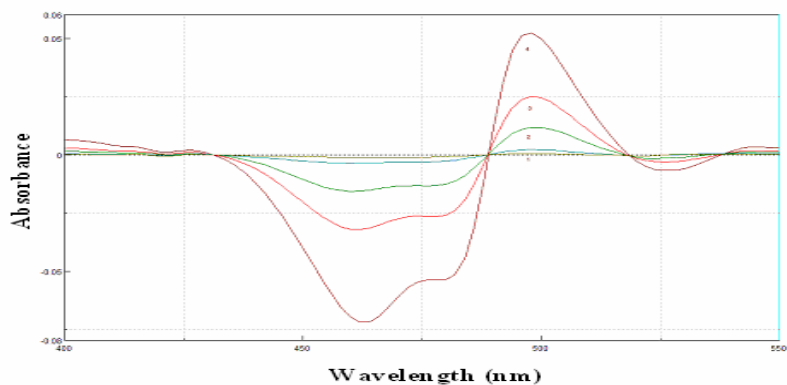


Fig.2.5 (b) First order derivative spectra 1:0.03 $\mu\text{g/ml}$;
2:0.75 $\mu\text{g/ml}$; 3:1.5 $\mu\text{g/ml}$; 4:3.0 $\mu\text{g/ml}$.

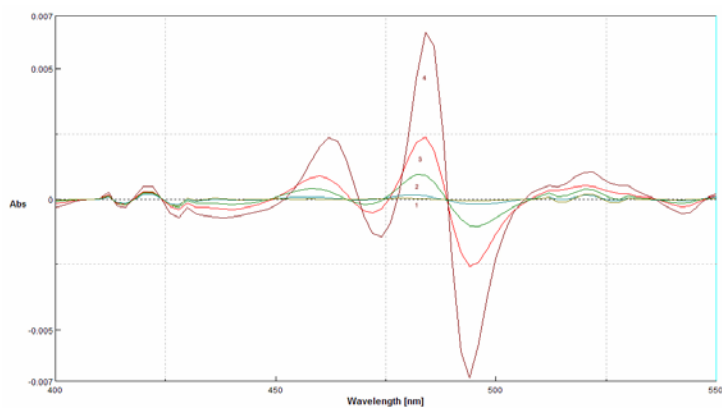


Fig.2.5(c) Second order derivative spectra 1:0.03 $\mu\text{g/ml}$;
2:0.75 $\mu\text{g/ml}$; 3:1.5 $\mu\text{g/ml}$; 4:3.0 $\mu\text{g/ml}$.

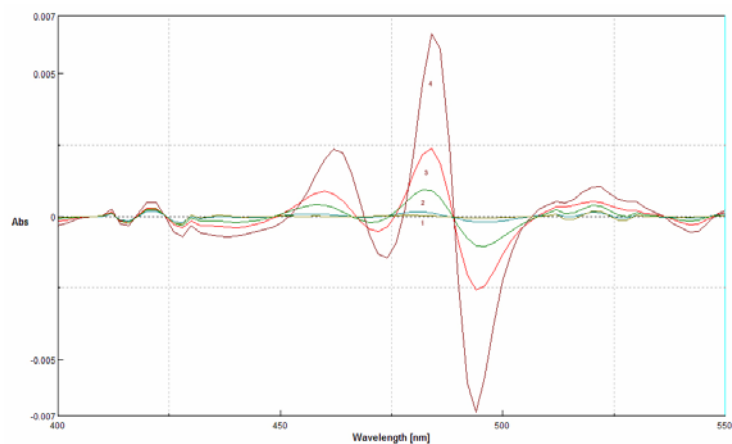


Fig. 2.5(d) Third order derivative spectra

1:0.03 $\mu\text{g/ml}$; 2:0.75 $\mu\text{g/ml}$; 3:1.5 $\mu\text{g/ml}$; 4:3.0 $\mu\text{g/ml}$.

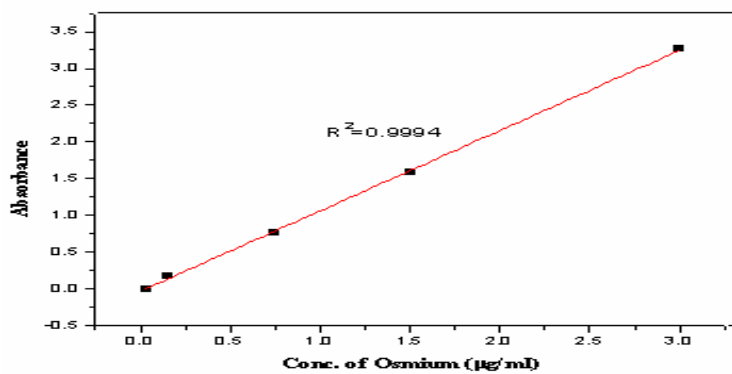


Fig.2.6 Variation of Absorbance with Con. of Osmium.

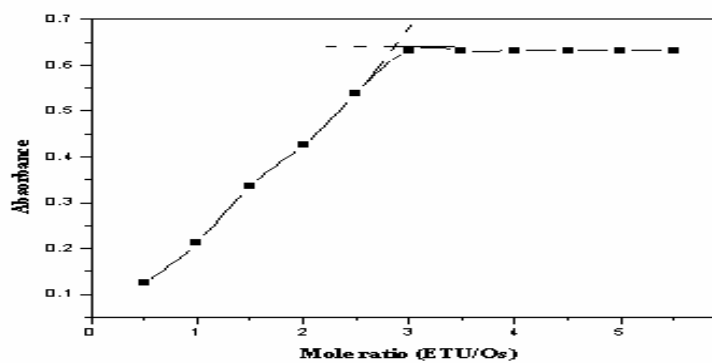


Fig.2.7(a) Mole ratio plot for Os-ETU complex.

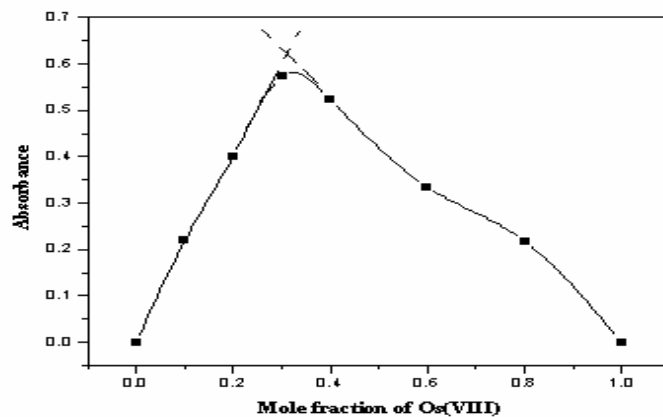


Fig.2.7(b) Job's method of continuous variation.

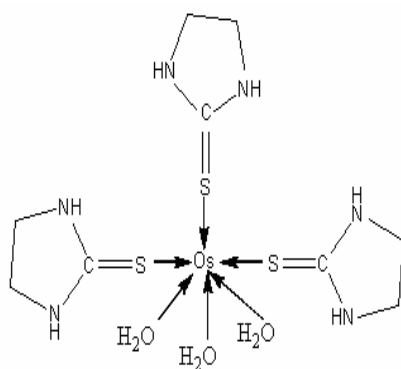


Fig.2.8(a) The most probable structure of Os-ETU complex.

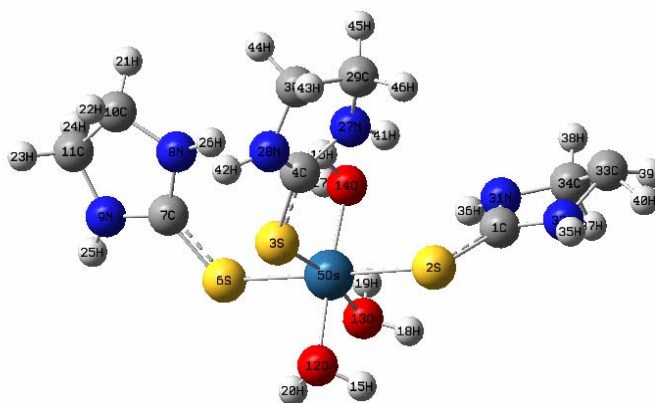


Fig.2.8(b) The optimized structure of the Os-ETU complex.

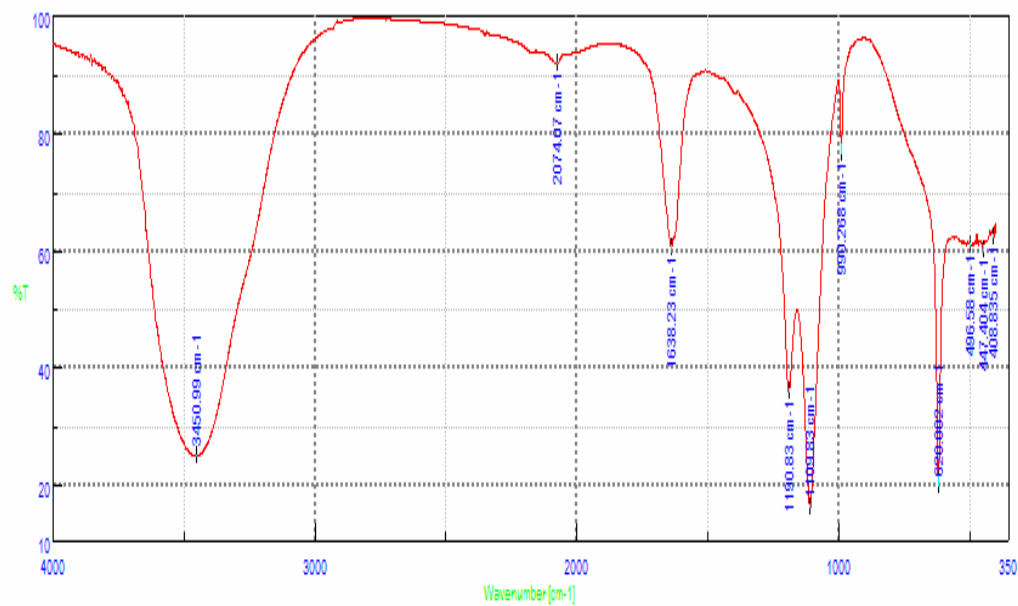


Fig.2.9(a) IR spectrum of Os-ETU Complex.

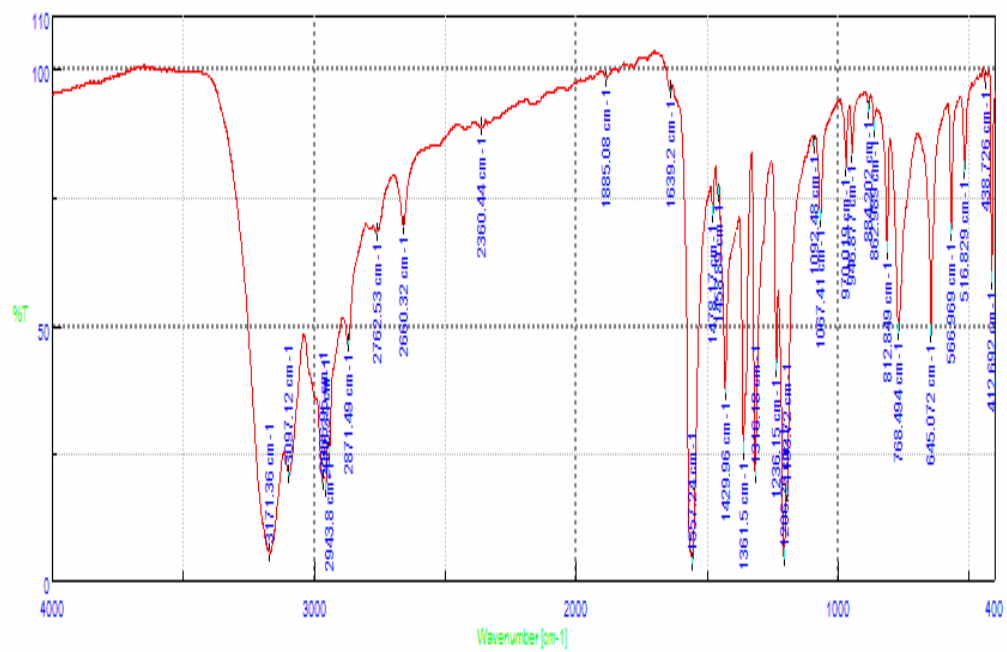


Fig.2.9 (b) IR Spectrum of ETU.