

Extractive Spectrophotometric Determination of Os (VIII) by using bis 1,6 (2 – mercapto 4,4,6, trimethyl pyrimidine) – hexane (MTPH)

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Abstract— A thiol, bis 1,6 (2 – mercapto 4,4,6, trimethyl pyrimidine) – hexane (MTPH), was prepared from 2 – methyl –2-isothiocyanato – 4 – pentanone and 1, 6 diamino hexane. It was characterized by m.p. (1750°C), elemental analysis (C = 60.57%, H = 9.07%, N = 14.22%, S = 16.47%) and IR spectra (2860 cm^{-1} - SH stretching, 1598 cm^{-1} >C = N stretching). MTPH forms a pink colored complex with Os (VIII) which can be extracted into chloroform under optimum conditions. Beer's law was obeyed over the range of 5 to 30 $\mu\text{g ml}^{-1}$ of Os (VIII). The molar absorptivity and Sandells sensitivity of Os (VIII)-MTPH system was found to be $3.1 \times 10^3 \text{ L mol}^{-1}\text{cm}^{-1}$ and 61 ng cm^{-2} respectively at 540 nm. The probable composition of extracted species was found to be 1:2 (metal: ligand) stoichiometry. Interference due to cations and anions has been investigated. The method has been employed for the determination of Os (VIII) from synthetic mixtures.

Index Terms – Osmium, Schiff base, solvent extraction, Spectrophotometric determination.

I. INTRODUCTION

Osmium is one of the minor constituents of the natural platinum group metal deposits. Osmium, the heaviest element of the platinum metals, occurs in the +VIII, +VI, +IV & + II oxidation states. It exhibits +VIII oxidation state in osmium tetra oxide, which is a pale yellow crystalline solid used for hydroxylation of double bonds in the synthesis of certain organic compounds. Another remarkable characteristic of this metal, which affects its solvent extraction behavior, is that the rate of complex formation is sometimes extremely slow. The metal ions are extractable in some systems only when they are treated with the extractant on boiling or when the metal ions and the extractants are contacted for a very long time. Extraction of osmium tetroxide becomes poorer at higher pH, as it tends to ionize with increase in pH.

Various other studies on the extraction of osmium have been reported. It was found that this metal is to some extent extractable from hydrochloric acid into dichloroether and from hydrobromic acid with methyl isobutylketone. The extraction of osmium from hydrochloric and hydrobromic acids with a

number of solvents has been investigated systematically. The extraction is in the order of the extractant as ethers < esters < alcohols < ketones < tributylphosphite < tributyl phosphineoxide. Extraction of osmium from thiocyanate

solution with 2-octyl alcohol and from chloride solutions with amines has also been reported. The extraction of osmium with ephedrine into carbon tetrachloride and with thiocarbanilide into diethylether is a well known classic method. Other reagents have also been used for the extraction of osmium [1].

Numerous organic reagents have been used for the spectrophotometric determination of osmium. Beamish et al has reviewed the methods used for the photometric determination of osmium [2]-[3]. Due to increasing range of applications in industry and research, the development of new procedures for the separation and determination of osmium is rapid.

Thiourea and its derivatives have been used for the spectrophotometric determination of osmium, with Ru(III) and Pd(II) as interfering ions [4]. Os (IV) reacts with thiourea much more rapidly than does Os (VIII), based on this the procedure was developed by Rao et al. in which the Os (VIII) was reduced with As (III) before its complexation in a medium of 10% sulphuric acid [5].

The various substituted thioureas which have been proposed for osmium determination are 1-benzoyl-3-(o-tolyl) thiourea [6]. These osmium complexes, which are extractable in organic solvents from moderately to strongly acidic medium, exhibit λ_{max} around 400 nm.

The methods which requires heating of the aqueous phase for full color development are ferrozine [7] (4h), quinisatin oxime [8] (below b.p. for 1.5 h), 3-nitrosopyridine-2, 6 diol [9] (30 min.), 1- naphthylamine-4, 6,8 tri sulfonic acid [10] (45 min.), and pyrogallol [11] (30 min.)

In some of the methods, formation of the complex is quite slow in aqueous medium and conditions for obtaining reproducible color development are usually critical e.g. quinoxaline-2, 3 dithiol [12] (1.5 h), tetramethyl thiourea disulfide [13] (2 h), pthalamide bis- thiosemicarbazone [14] (30 min.), and o- hydroxy thio-benzhydrazide [15] (10 min.). Few reagents form complex with osmium with either low stability or low sensitivity such as pyrocatechol [16] ($S=48\text{ngcm}^{-2}$), 2-amino- β -naphthol-3, 6—disulfonic acid [17] ($S= 200 \text{ ng cm}^{-2}$). Sanke Gowda et al. have reported a series of organic azine compounds, including thioridizine hydrochloride [18], diethazine hydrochloride [19], for the

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photometric determination of osmium in hydrochloric acid medium having the absorption maximum around 512-530 nm. The sulphur containing reagents such as 2-mercaptobenzothiazole [20], triazine derivatives [21], bismuthol II [22], thiosalicyl amide [23], and rubeanic acid [24], are used for the photometric determination of osmium. Recent techniques used for the separation and determination of Osmium are inductive coupled plasma mass spectrometry[25] and spectrometric method with 1,5 diphenylcarbohydrazide[26], 3-methyl-2,6-dimercapto-1,4-thiopyrone[27] and ethylisobutrazine hydrochloride[28].

The present method for the extractive spectrophotometric determination of trace amount of Os (VIII) is simple, sensitive, and rapid. It is also applicable for determination of osmium from synthetic mixtures.

II. EXPERIMENTAL

A. Materials

Osmium tetroxide (s.d.Fine Chem.Ltd., India), 4-methyl-pent-3-ene-2-one, ammonium thiocyanate, hexamethylene diamine, chloroform and DMF are used after purification. Standard solutions of diverse ions were prepared by dissolving AR grade salts of cations and anions and other chemicals were used as such.

B. Synthesis of bis 1,6-(2-mercapto- 4,4,6-trimethyl pyrimidine) – hexane [MTPH]

The MTPH was synthesized in two steps; in the first step 2-methyl-2-isothiocyanato-4-pentanone (I) was synthesized from 4-methyl-pent-3-ene-2-one and ammonium (Scheme I). In the second step bis -1,6 -(2-mercapto 4,4,6-trimethyl pyrimidine) – hexane was synthesized by reacting (I) with hexamethylene diamine in alcohol (Scheme II) as follows. A mixture of 3.14 g 2-methyl-2-isothiocyanato-4-pentanone (2 mole) and 1.16 g hexamethylene diamine (1 mole) in 50 ml ethanol was taken in 250 ml round bottom flask and 10 drops of H₂SO₄ were added and the mixture was refluxed for 30 min. On cooling solid was separated, it was filtered and dried. Recrystallization was carried out from glacial acetic acid (yield 74%), m.p. 175° C. The purity of compound was checked by thin layer chromatography and elemental analysis.

C. Spectral analysis

IR spectra were taken on Perkin Elmer FTIR spectrum BS spectrophotometer using KBr pellet technique. Absorbance measurements were made on Elico digital spectrophotometer model L-171 with 1 cm quartz cell

D. Standard solution of osmium:

A stock solution of Os (VIII) was prepared by dissolving 1g osmium tetroxide in a glass stoppered conical flask containing 100 ml 0.2 M sodium hydroxide solution. The supernatant liquid is transferred to 1 L volumetric flask, the ampule is washed 2-3 times with 0.2 M sodium hydroxide solution and washings are also taken to the same flask and diluted up to the mark with 0.2 M sodium hydroxide solution and standardized by the iodometric method of Ayres [35]. The working solutions for spectrophotometric measurements are prepared by appropriate dilution of the stock solution with 0.1 M sodium hydroxide solution.

E. Spectral determination of Os(VIII)

To an aliquot of solution containing 300 µg of Os (VIII) was added the required amount of perchloric acid (60%) to get desired acidity of 1 M, and 5 ml of 0.04 M of MTPH solution in DMF into a standard 25 ml volumetric flask. The total contents of the flask are diluted up to the mark with double distilled water. The flask was heated in a boiling water bath for 3 min. and cooled. The pink complex formed is then extracted with 2 x 5 ml portions of chloroform. The combined extract after drying over anhydrous sodium sulphate was made up to 10 ml with chloroform in standard 10 ml volumetric flask. The absorbance of the Os-MTPH complex was measured against solvent blank at 540 nm. A calibration graph was prepared and unknown amount of Os (VIII) was determined.

III. RESULT AND DISCUSSIONS

A. Spectral Analysis

The IR spectra of MTPH in KBr pellets were recorded on Perkin- Elmer model 883 spectrophotometer in the range of 4000-200 cm⁻¹. The IR spectra reveals the presence of – SH stretching peak at 2860 cm⁻¹, C = N peak at 1598 cm⁻¹ and C=C bending peak at 840 cm⁻¹. Elemental analysis results found are C = 60.57 % (60.91%), H = 9.07% (8.62%), N = 14.22 % (14.21%), S = 16.47 % (16.24 %). The figures in parenthesis indicate the theoretical percentage values of C, H, N and S elements respectively (Figure 1).

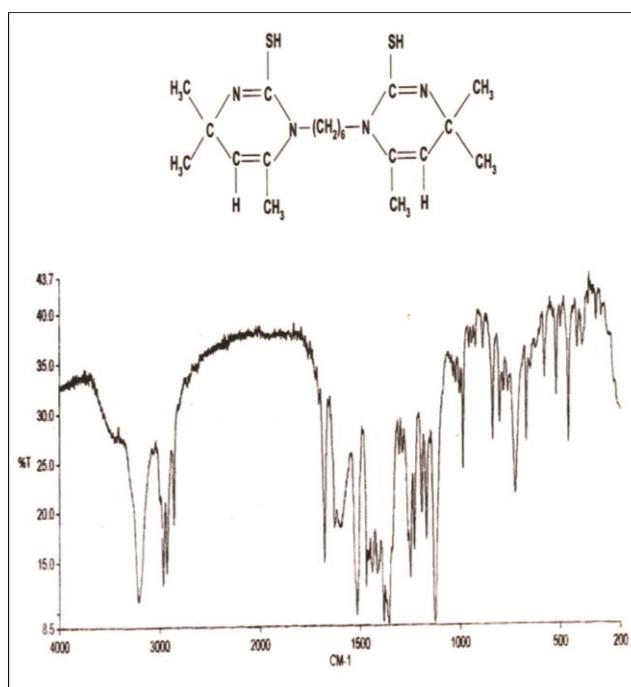


Figure 1: IR spectra of bis 1,6-(2-mercapto- 4,4,6-trimethyl pyrimidine) – hexane (MTPH)

The absorption spectrum of the extracted complex in chloroform was compared with that of solvent blank. It was found that the Os-MTPH complex exhibits a sharp absorption maximum at 540 nm, at which wavelength the absorption due to the reagent is absent (Figure 2).

Table No: I– Effect of solvent on determination of Os(VIII)

Sr. No.	Solvent	Absorbance
01	Chloroform	0.489
02	Benzene	No extraction
03	4- methyl-2-pentanol	0.368
04	Methy iso butyl ketone	0.290
05	Toulene	No extraction
06	Carbon tetrachloride	No extraction

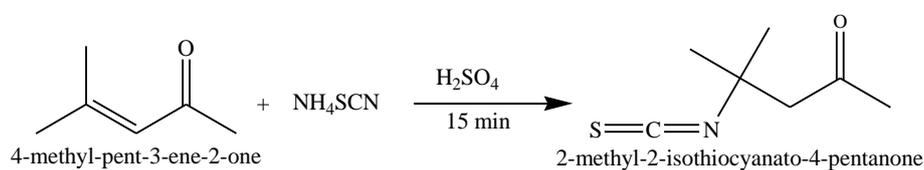
Table No: II- Application of method for the separation of osmium from real mixture

Composition in µg	^a Recovery of Osmium in µg	Relative error in %
Os (VIII) 300,Zn (II) 500, Pb (II) 500, Mn (II) 500	298.2	0.60
Os (VIII) 300,Cu (II) 500, ^b Co (II) 500, Mn (II) 500, ^b Fe (III) 500	299.1	0.30
Os (VIII) 300,Bi(II) 200	297.8	0.73

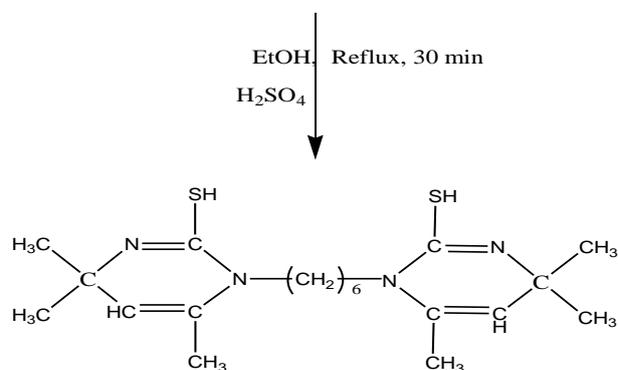
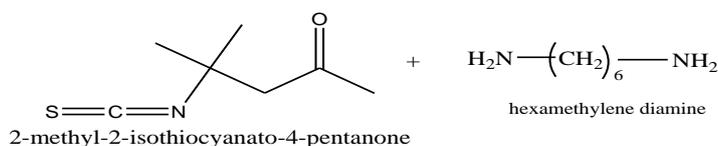
a - Average of five determinations

b- Masking with 100 mg of EDTA

SCHEME I



SCHEME II



Bis- 1,6- (2-mercapto- 4,4,6-trimethyl pyrimidine)-hexane

A. *Effect of reagent concentration:*

Complexation between osmium and MTPH was also studied by taking different volumes of 0.04 M MTPH solution in DMF. The color was developed as per the recommended procedure and absorbance was measured at 540 nm against solvent blank. For full color development at least 200 fold molar excess of the reagent was required. There was no effect on complexation with excess of reagent (Figure 3).

B. *Effect of heating and stability of complex:*

As Os (VIII) forms pink colored complex with MTPH on heating of aqueous phase, for complete complexation the effect of time of heating on the development of color was studied over a period of 0.5 min. to 10 min. The data showed that full color development requires heating of aqueous phase for 3 min. before extraction (Figure 4). Stability of complex was also studied and found that the intensity of the extracted complex remained constant for more than 24 h.

C. *Effect of solvent:*

The extraction of pink colored complex was investigated by using various solvents such as chloroform, benzene, carbon tetrachloride, 4-methyl-2-pentanol, toluene, methyl iso butyl ketone etc. The data obtained show that maximum extraction is possible only in chloroform because the highest absorbance of the complex was obtained in this solvent (table 1).

D. *Validity of Beer's range:*

Validity of Beer's law was studied by taking varying amounts of Os (VIII) in 1 M perchloric acid. The complexation was carried out as per recommended procedure using 5 ml of 0.04 M MTPH solution in DMF. The pink complex of Os- MTPH was extracted with chloroform and absorbance was recorded at 540 nm against solvent blank. The data obtained show that Beer's law is valid up to 30 ppm (Figure 5). According to Sandell's expression, the sensitivity of the reaction is 61 ng/cm² and extinction coefficient is 3.1 X 10³ L mole⁻¹ cm⁻¹.

E. *Composition of the complex:*

The composition of the Os- MTPH complex was determined by the mole ratio method (Figure 6), Jobs method (Figure 7) and slope ratio method (Figure 8). The data obtained show that the metal to ligand ratio is 1:2.

F. *Effect of diverse ions:*

The tolerance of various interfering ions with Os (VIII) was studied by measuring the absorbance of 30 ppm Os (VIII) with different amounts of foreign ions. The tolerance limit of an ion was fixed as the maximum amount causing an error not greater than + 2 % in the absorbance of the extracted complex. The results obtained show that strong interfering ions are SCN⁻, S₂O₃⁻, and I⁻.

G. *Applications:*

In order to confirm the usefulness of the proposed method, it was applied for the determination of osmium from synthetic mixtures. The results listed in table 2 show that the amount

obtained of osmium by the proposed method is in good agreement with the taken values (table 2).

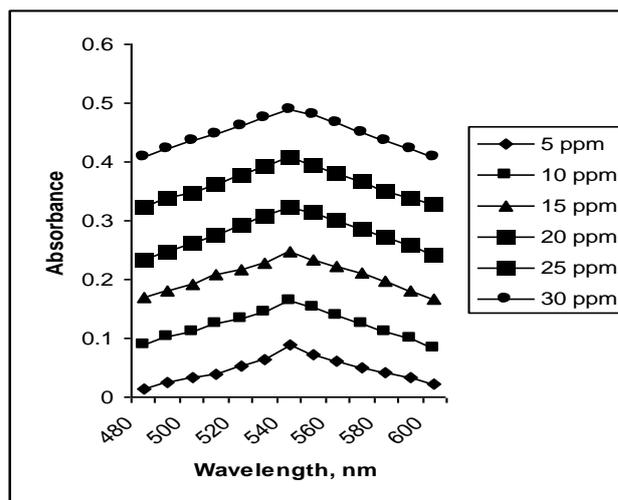


Figure 2 Absorption spectra of Os (VIII) & MTPH

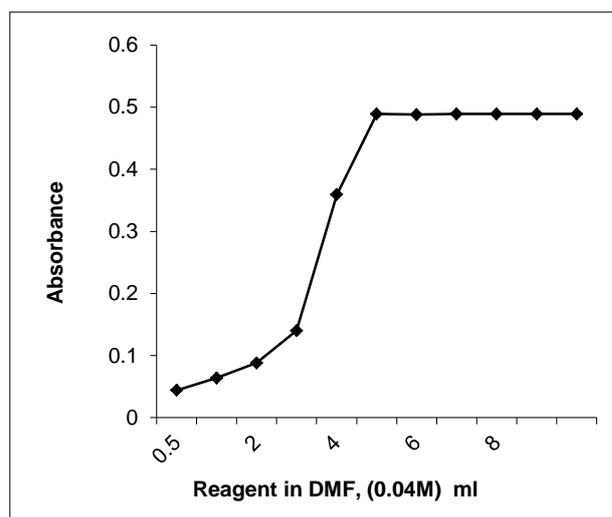


Figure 3 Effect of Reagent concentration

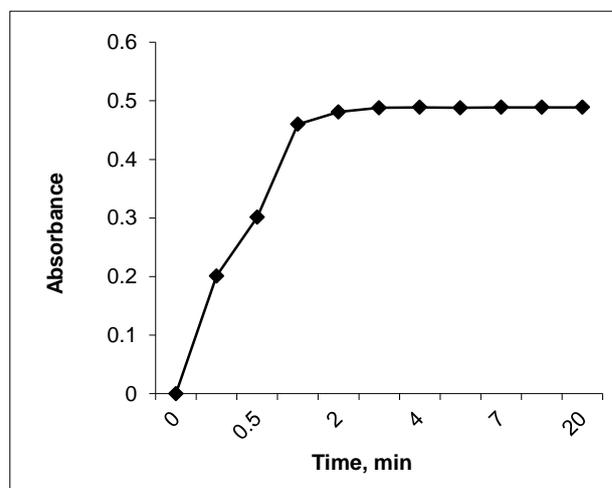


Figure 4 Effect of heating

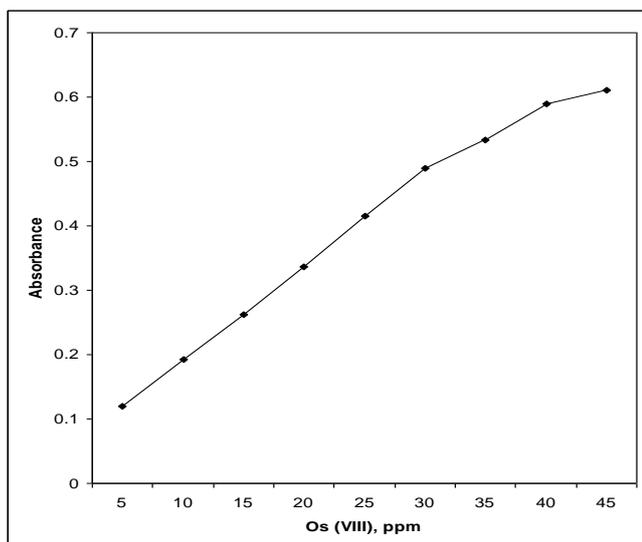


Figure 5 Calibration Curve of Os (VIII)-MTPH Complex. (Beers range)

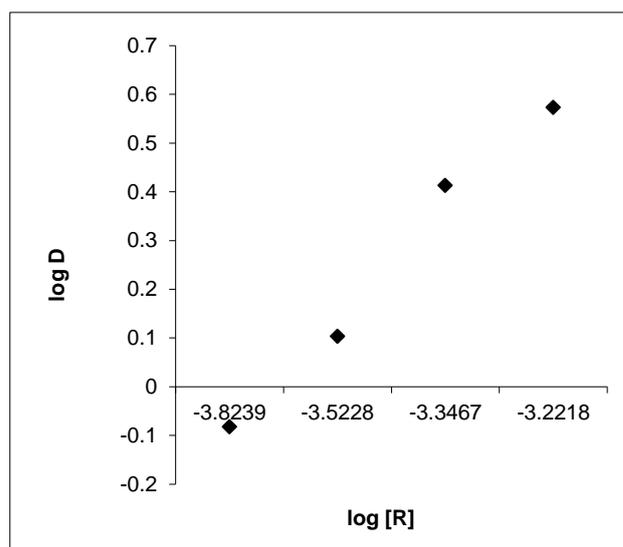


Figure 8 Slope ratio method

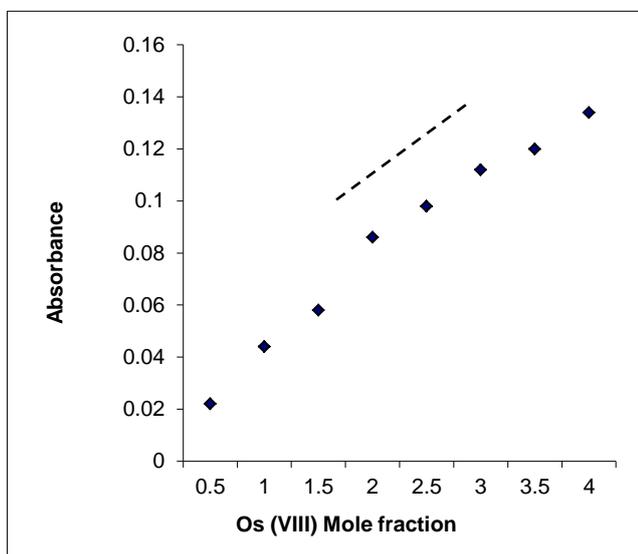


Figure 6 Mole ratio method

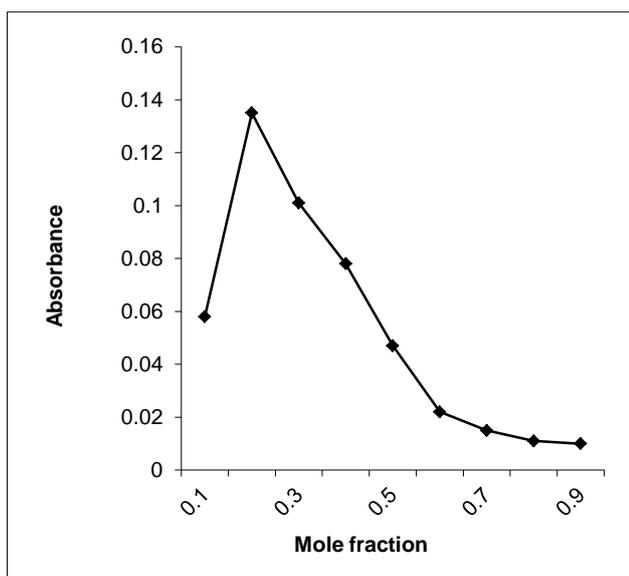


Figure 7 Jobs plot

IV. CONCLUSION

The newly synthesized pyrimidine thiol, bis 1,6 (2- mercapto 4,4,6 trimethyl pyrimidine)-hexane (MTPH), is a bidentate ligand which is highly sensitive and selective reagent used for photometric determination of Os (VIII) –MTPH complex in chloroform. It is also applicable for the determination of Os from number of synthetic mixtures. The photometric determination of Os (VIII) by this method requires overall 15 – 20 min.

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