

CHAPTER - IV

SPECTROPHOTOMETRIC DETERMINATION OF RHENIUM(VI) AFTER
EXTRACTION OF ITS 2-FURANTHIOCARBOXYHYDRAZIDE COMPLEX WITH
MOLTEN NAPHTHALENE

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2 - FURANTHIOCARBOXYHYDRAZIDE

(A) SYNTHESIS AND CHARACTERISATION OF

2 - FURANTHIOCARBOXYHYDRAZIDE

INTRODUCTION:

Carboxylic acid hydrazides have a wide variety of applications ranging from biological, pharmaceuticals activity to heavy chemical uses and, therefore the importance of this group of compounds has grown. During an analytical study to develop universal method for carboxylic acid hydrazides, complexation of metal ions by hydrazides¹ appeared likely. The earliest investigations on the use of acid hydrazides as complexing agents were made by Albert and Fallab²⁻³. Since, then a voluminous work on analytical applications of acid hydrazides is reported every year.

The hydrazides, their derivatives and metal complexes have long been known for their pharmacological activities. The substituted benzoic acid hydrazides⁴ were screened in vitro for their antibacterial activity and are found to be most effective. 2,6- dihydroxyisonicotinic acid hydrazide⁵ is reported to be useful as virucides and bactericides. The mechanism of the

anti-tubercular activity of INH⁶ appears to be via complexing copper ions. The acid hydrazides⁷ however find applications as plant growth regulants. P-^aAmino benzoic acid hydrazide terephthaloyl chloride polymer⁸ has been reported to be useful as a fire resistant, whereas sulphohydrazides⁹ are employed as crosslinking agents for carboxyl containing rubber, and certain hydrazides¹⁰ when added to synthetic carboxylic ester lubricants inhibit corrosion. The phosphate esters¹¹ of hydroxy carboxylic acid hydrazides are utilised for fire resistant treatment of fibers and fiber products.

Several reagents have been proposed for the detection and quantitative determination of acid hydrazides. Krishna Rao et al. recommended the use of 2,3,5 - triphenyltetrazolium chloride which permits the detection of hydrazides in presence of hydrazine, semicarbazide, hydroxylamine, urea, aliphatic hydrazides and several anions¹². Potassium ferri- and ferrocyanides¹³ are also employed for spot test detection. Among the reagents reported for quantitative determination of acid hydrazides, photometric methods include the use of isopropenyltrichloroacetate¹⁴, 2,3 - dichloro-1,4 - naphthaquinone¹⁵, while titrimetric methods make use of cerium nitrate¹⁶ and ammonical silver nitrate¹⁷.

The hydrazides form coloured coordination compounds with many metal ions which are found suitable for their photometric determination. Benzoic acid hydrazide was used for the photometric determination of substituted chloroformates¹⁸. It has been also investigated as an analytical reagent for the photometric determination of Au (III) in alkaline medium at 520 ~~nm~~ nm whereas *o*-chlorobenzoic acid hydrazide is used for extractive photometric determination of nickel²⁰. Isonicotinic acid hydrazide was used to determine vanadium²¹ and copper²² photometrically, the method is applicable for determination of vanadium (V) in iron - vanadium alloy and iron ores²³, Sanke Gowda recently reported the use of isonicotinic acid hydrazide for the detection and gravimetric estimation of selenium²⁴. Ethylenediaminetetraacetic acid hydrazide was used for the photometric determination of Fe (III) and Cu (II)²⁵⁻²⁶. Klimovich et al. recommended benzenesulphonyl benzyol - hydrazide as a selective reagent for the determination of Os (VIII)²⁷. Palladium (II) and Co (II) were determined colorimetrically in aqueous medium using thiophene - 2 - carboxylic acid hydrazide and 2 - pyridylcarboxylic acid hydrazide respectively²⁸⁻²⁹. The absorption depended on the pH.

Investigations on solid complexes of hydrazides with metal ions began in 1969 with a view to ascertain the composition

and to throw light on the nature of bonding involved³⁰. The investigations include the synthesis of the adduct, measurements on magnetic, ^{susceptibility} electrical conductance, U.V., I.R. Spectra and chemical analysis.

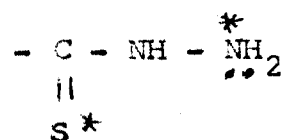
It may be concluded from the findings of the investigations made by several authors³¹⁻³⁶ that, the acid hydrazides behave as bidentate ligand; the probable bonding sites in the chelates are the enolic 'O' arising from enolisation of the keto-group and 'N' of the primary amine³¹.



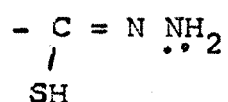
Although the first report on the synthesis of thio- analogue of carboxylic acid hydrazides³⁷ has appeared in year 1961, but the analytical properties are investigated recently by Shome³⁸. Since then many papers are published on the use of organic thiohydrazides as a sensitive photometric reagents for platinum as well as iron group metals³⁹⁻⁴⁵. Thio-organic hydrazides have gained a wide popularity because of greater chemical versatility of the thiono group compared with that of keto group which is responsible for their more varied behaviour.

This class of compound is obtained by the reaction either of dithiocarboxylic acid or the esters of dithio carboxylic acids with hydrazine hydrate in alkaline or neutral medium. They have

active grouping for chelation as given below.



The presence of mobile hydrogen atom adjacent to the thiocarbonyl group permits the formation of acidic mercapto-function in the form shown below.



Like carboxylic acid hydrazides, the complex formation with thiohydrazides is assumed to take place by the metal ring closure via primary amine N (marked with asteric).

Preparation of ammonium polysulphide :

Ammonium sulphide yellow (NH_4)₂ S_x of approximately 6M was prepared by passing hydrogensulphide gas into 150 ml conc - NH₃ solution for about 5 hr followed by addition of 10g. of flower of sulphur and additional 250 ml conc. NH₃ solution. The solution was finally diluted to 1 liter.

Purification of furfuraldehyde :

Commercial furfuraldehyde (BDH) product undergoes polymerisation on standing. It was, therefore, purified by carrying out vacuum distillation at 10 mm pressure keeping the temperature of oil-bath at 150°- 160°. The faint yellow liquid was obtained.

Synthesis of 2 - furanthiocarboxyhydrazide :

A freshly distilled 10 ml - furfuraldehyde was mixed with 30 ml of ethanol in 250 ml beaker and was heated to approximately 65⁰- 70⁰. About 40 - 50 ml of ammonium-polysulphide was added to the mixture with vigorous shaking. The solution first appeared red in colour which was deepened with a further addition of polysulphide. It was then boiled on hot plate for 10 min, cooled to room temperature and filtered through ordinary filter paper to remove the tar material. The filtrate was acidified with ice-cold HCl (1:1). The dithiofuroic acid thus formed was extracted 2-3 times with minimum volume of ether till the aqueous phase becomes faintly yellowish. The ether extract was washed 3 times with 20 ml portions of ice cold brine and backextracted with several 10 ml portions of 10 % hydrazinehydrate solution (sp.gr.1.03) in water. The organic layer was discarded. The aqueous phase was kept in ice-cold water for about 1 hr. A beautiful shining crystals separated out were removed by decantation. FTH remaining still in mother liquor was precipitated by acidifying with acetic acid. The yellowish precipitate obtained was filtered and mixed with first crop. The product was recrystallised from hot water to obtain pure colourless crystals with sharp M.P. 124⁰. The purity of the compound was tested by carrying out thin layer chromatography

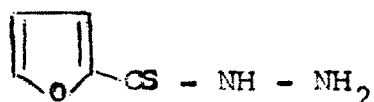
which gave a single spot. The product was analyzed for carbon, hydrogen, nitrogen and sulphur.

	C	H	N	S
Calculated, (%)	42.26	4.23	19.72	11.27
Found, (%)	42.18	4.17	19.62	11.22

Molecular formula : $C_5 H_6 N_2 OS$

Molecular weight : 142

Structural formula :



Properties of the compound :

2 - furanthiocarboxhydrazide (FTH) is a colourless fine crystalline solid with a sharp M. P. (124°). The compound is highly soluble in ethanol, methanol, acetone, benzene, chloroform, carbon - tetrachloride and oxygenated solvents. It is sparingly soluble in water but dissolves in boiling water. The compound is sensitive to heat and light. It is quite stable at room temperature when stored in amber coloured bottle. Its ethanolic solution is also stable for more than a week when bottle containing it is protected from light. It is preferably prepared as and when required.

U.V. Spectrum of FTH :

U.V. spectrum of 0.02 M ethanolic solution of FTH is shown in fig. 4.1. the curve exhibits sharp absorption maximum around 395 nm. with extinction coefficient $2700 \text{ L mole}^{-1} \text{ cm}^{-1}$.

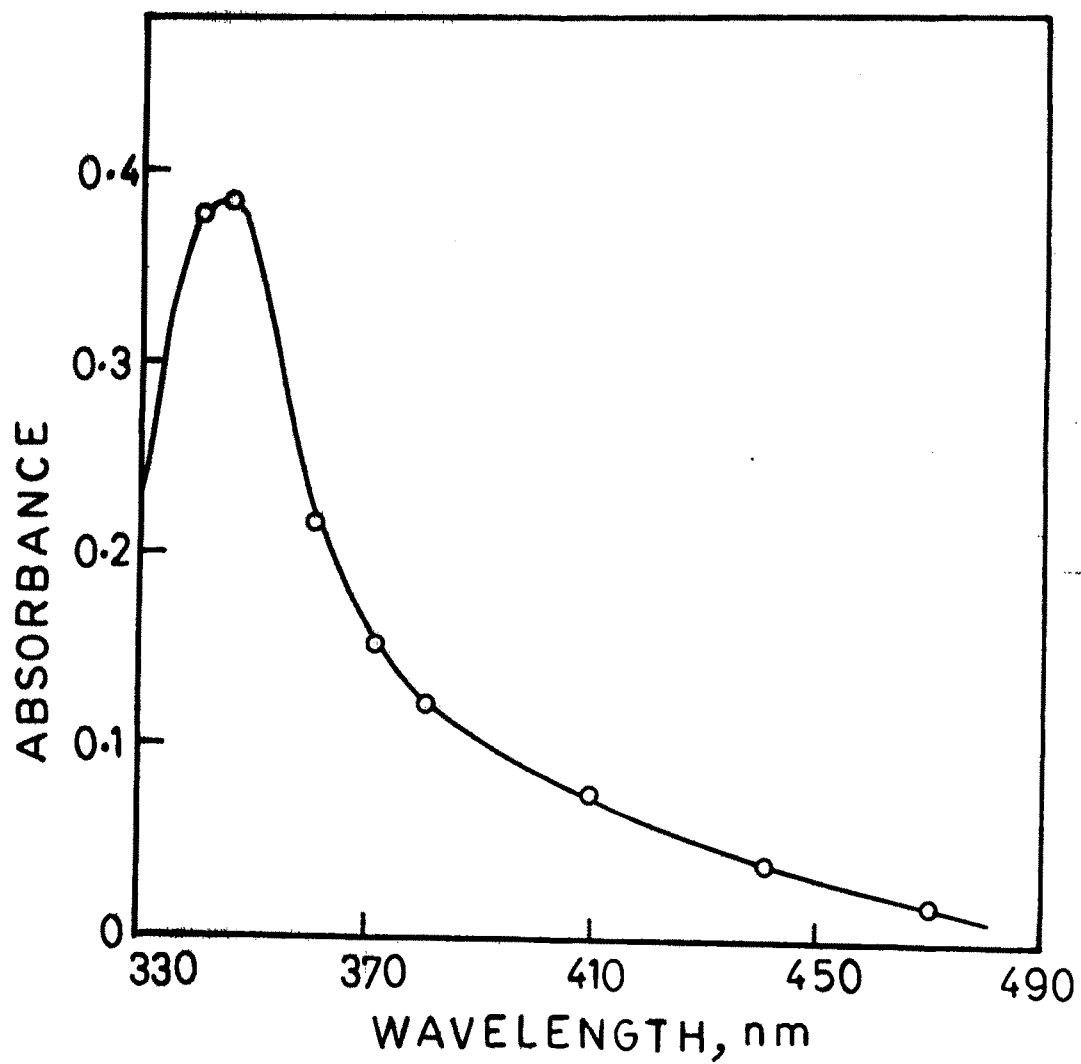


Fig. 41— ABSORPTION SPECTRUM OF FTH
IN ETHANOL.

Spot test detection of FTH with NN - dimethyl - P - aminobenzaldehyde :

An alcoholic solution of the reagent when added to the FTH solution in alcohol containing conc HCl, an intense red colouration was produced. This indicated the presence of hydrazine resulting from hydrolysis of FTH in acidic medium. No colour was formed when the reaction was carried out between FTH and the reagent in the absence of conc HCl

(B) SPECTROPHOTOMETRIC DETERMINATION OF RHENIUM(VI) AFTER EXTRACTION
OF ITS 2-FURANTHIOCARBOXYHYDRAZIDE COMPLEX WITH MOLTEN NAPHTHALENE

INTRODUCTION

Rhenium is a heavier element in a group VIIB of the periodic table. It is very rare element and is present in the earth crust to the extent of only 10^{-9} %.

There are no known minerals or ores of rhenium and the metal does not occur native. It is widely distributed in very small amounts in other minerals and could not economically be mined for its own sake; it is always a by product of the large scale recovery of another metal, generally molybdenum. It is generally associated with molybdenites (MoS_2) which contain from 0.002 to 0.02 % of rhenium, and porphyry copper ores generally chalcocites and chalcopyrites. Now a days applications of rhenium are increasing day by day in industries. It possesses properties useful for catalytic hydrogenation, 75 % of total rhenium production is used in U.S.A. More than 50 % market of rhenium is for catalysis. Either pure Re or Re-Pt alloy is used as catalyst. It is also used in development of ductile high temperature tungsten and molybdenum base alloys. High temperature thermocouples with Magnesium, molybdenum and niobium are manufactured. Rhenium is used in flash bulbs and also it is used for coatings. In petroleum reforming 0.3 % Re and 0.3 % Pt is used as popular catalyst.

A tungsten and 3 % rhenium alloy is used as igniter wire in photoflash bulbs and as filaments in electronic tubes, pure rhenium has replaced tungsten in the small but important use as filament in mass spectrographs and ion gages. Rhenium is Valuable addition to both molybdenum and tungsten and their alloys improving their ductility and other properties, 1-5 %, usually 3 %, **Re** alloys with tungsten are used as heaters in variety of electronic tubes and have minor use as wear resistant coating on air craft parts. Also it is used in electrical contacts in different electronic apparatus and instruments.

Solvent extraction photometric technique for the determination of numerous metal ions using various chelating agents has long been widely used. However, sometimes, there is no clear cut separation of phases or the distribution equilibrium of the metal between the two phases is not quickly attained. The method may even not be applicable when solubility of the complex in organic solvent is less and when the complexes are strongly hydrated.

The use of low melting solids as the organic solvent for liquidliquid extraction of the metals at the elevated temperatures followed by solid-liquid separation at room temperature

with the organic compounds like naphthalene (mp 81°), biphenyl (mp 71°) or naphthalene in acetone, which solidify on cooling has been shown to increase the selectivity and sensitivity of the method. The characteristic of this method is that, the equilibrium distribution in the two phases is attained rapidly owing to high temperature and the metal chelates are dissolved merely by contact with molten naphthalene. Hence, the water insoluble metal complexes are rapidly and quantitatively extracted into molten naphthalene and trace amounts of metals can thus be determined with high degree of accuracy and sensitivity. Here a small amount of organic solvent is required for complete extraction and whole of the organic phase may be taken for analysis. This technique is especially useful for the extraction of those metal ions which forms complexes with the reagents at high temperature and have low solubility in aqueous solutions.

Since 1969 number of papers based on this technique are published. In spite of this the literature is scanty and requires further attention of the researchers to this promising field.

During the past several years Fuginaga et al. have developed useful spectrophotometric methods for the determination of metal complexes into molten naphthalene. Copper (II) was extracted as its oxinate complex into naphthalene, paraffin and diphenyl⁴⁶, Diphenyl was found to possess the advantage of high interfacial

tension against water and of specific gravity greater than one. The method could also be applied to the removal of interfering minor components in trace analysis and to determination of radioactive elements. 8-Hydroxyquinoline has been used as a reagent for photometric determination of Zn(II)⁴⁷, Cd(II)⁴⁸, Ni(II), Co(II), Mo(VI)⁴⁹. The polarographic determination of Mo(VI)⁵⁰, In(III)⁵¹ and Cd(II)⁵² after extraction with oxime into molten naphthalene has also been worked out. The use of diethyldithionate, substituted 8-hydroxy quinoline, benzoin- α -oxime and BPHA for determination of trace amounts of metals after the extraction of their complexes with various metal ions using molten naphthalene has been recommended⁵³. Among the η complexes of oximes with various metals, the DMG⁵⁴⁻⁵⁷, benzyl- α -oxime⁵⁴, Salicyldioxime⁵³, complexes have been thoroughly investigated by this technique. A procedure has also been developed in which a solution of naphthalene in acetone has been recommended instead of naphthalene in order to achieve extraction rather quickly^{56,58}. Tervalent bismuth reacts with 2-mercapto benzothiozole to form water insoluble complex which is extractable at pH^{4.6} to 6.5 in molten naphthalene⁵⁹. The naphthalene containing complex was dissolved in DMF and then measured at 394 nm. Iron(III)-TTA complex formed at pH 4 was

extracted in molten naphthalene⁶⁰. The complex was measured at 480 nm after the dissolution in DMF. This technique is also used for spectrophotometric determination of Bi(III), Co(II) and Ni(II) after extraction of their xanthates with molten naphthalene⁶¹.

For determination of rhenium photometrically thiocyanate method⁶² is most popular and widely used for the routine analysis. The various modifications⁶³⁻⁶⁸ of this method have been reported recently. Amongst the chelating agents Acetyl acetone^{69,70} 2-thioneyltrifluoroacetone⁷¹, quinoline⁷², 8-mercaptoquinoline⁷³⁻⁷⁴, Feron⁷⁵, Furlil - α -dioxime⁷⁶⁻⁷⁸, 4-amino - α -phenyl-1,2,4-triazole 5-thiol⁷⁹, Diphenyl carbazide⁸⁰⁻⁸³ are reported to be very good reagents for extraction photometric determination of rhenium(VI).

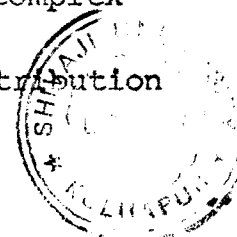
Several synthetic dyes have been investigated for the extractive spectrophotometric determination of rhenium(VI), these includes methyl violet⁸⁴, methyl green^{85,86} Brilliant green⁸⁷ ethyl violet⁸⁸, methylene blue⁸⁹, safranine T⁹⁰, Astraphloxine G⁹¹. The extractions are generally carried out from acidic media with λ max in the range between 382-635 nm.

At present, the sulphur containing ligands are widely applied in analytical chemistry. Some of the sensitive and selective colour ~~forming~~^{forming} thioligands used for the photometric

determination of rhenium are ammonium pyrrolidine thiocarbamate⁹² ($\epsilon = 5.6 \times 10^{-4}$ at λ_{\max} 243 nm), 1-phenyl thiosemicarbazide⁹³ ($\epsilon = 1.54 \times 10^4$ at λ_{\max} 365 nm), thiosalicylic acid⁹⁴ ($\epsilon = 6.1 \times 10^3$ at λ_{\max} 380-420 nm), Sodium thiocyanate⁹⁵ ($\epsilon = 6.2 \times 10^3$ at λ_{\max} 420-430 nm), 4-phenyl thiosemicarbazide⁹⁶ ($\epsilon = 9.1 \times 10^3$ at λ_{\max} 395 nm), O-hydroxythiobenzhydrazide⁴⁰ (HTH), ($\epsilon = 9.62 \times 10^3$ at λ_{\max} 560 nm), thiobenzhydrazide⁴¹ (TBH) ($\epsilon = 7.39 \times 10^3$ at 360 nm in 50% ethanol and 1.15×10^4 at λ_{\max} 650 nm in CCl_4).

2-Thiophene-Thiosemicarbazide (TTH)⁴⁴ and 2-furathiocarbox hydrazide (FTH)⁴⁴ (TTH 8.98×10^3 at λ_{\max} 600 in CHCl_3 , FTH = 6.64×10^3 at λ_{\max} 570 nm in 50% ethanol) are recently reported to be versatile reagents, for Re(VI) determination. But these methods suffer from poor sensitivity. Of these, ammonium pyrrolidine dithiocarbamate and 1-phenyl thio-semicarbazide methods require 40 min^{waiting} for the development of the colour and permit determination in u.v. region only. Whereas with thiosalicylic acid method, the sensitivity of extractive method is poor.

In order to eliminate the draw backs shown for the above methods, it was thought worthwhile to develop the method of determining rhenium (VI) with FTH by extraction of its complex into molten naphthalene. In the proposed method the distribution



equilibrium is attained very rapidly as the distribution coefficient is high enough at the temperature used. Besides there is enhancement in the sensitivity of the method. The tolerance limit for diverse ions is also considerably high as compared to FTH method of Shome⁴⁴.

EXPERIMENTALReagents Solutions:

A stock solution of rhenium was prepared by dissolving KReO_4 (JM 99.9 % pure) in distilled water, and was standardised gravimetrically⁹⁷. A freshly prepared 0.02 M solution of 2-furan-thiocarboxydrazide (0.141 g of reagent in 50 ml ethanol) was used. The reagent solution is protected from light by wrapping the flask with black paper. It was prepared daily when required.

Standard solutions of diverse ions were prepared by dissolving AR grade reagent in distilled water or dil hydrochloric acid. All the organic solvents were used after double distillation. A fresh 10 % solution of tin (II) chloride in 2 M HCl was used.

Apparatus :

A Carl-Zeiss (JENA) spectrophotometer with 1 cm quartz or glass cells are used for the absorbance measurements.

General procedure :

An aliquot of test solution containing 50-400 μg of Re(VI) (VII) and 1 ml solution of tin (II) chloride was taken in 25 ml volumetric flask and to this was added 2-3 ml solution of the reagent ^(0.02M) ~~(0.02M)~~. The acidity of the solution was adjusted to 0.4-0.8 M in respect of hydrochloric acid. The solution was heated on a steam-bath for 15-20 min followed by addition of 2 gm of solid naphthalene.

The heating was continued to melt the naphthalene completely. The flask was stoppered, shaken vigorously and cooled. The solidified naphthalene containing the blueviolet complex was filtered, washed with water, dried at room temperature by blotting the surplus water in the folds of dry filter and dissolved in chloroform containing 2-drops of pyridine. The solution was diluted to 25 ml with chloroform. The absorbance of the extract was measured at 610 nm and 680 nm against the solvent blank.

Results and Discussion :

Spectral characteristics :

The absorption spectra of Re(VI)-FTH complex in naphthalene chloroform pyridine solution resulting from taking 4.0, 6.0, 8.0 and 10.0 ppm of rhenium (VI) through the recommended procedure are shown in Fig. 4.2. The absorption spectrum of rhenium (VI)-FTH complex has two absorption maxima one at 610 nm and other at 680 nm. The absorption due to the reagent is negligible at these wavelengths.

The physical characteristics of complexes of rhenium(VI)-FTH, relative mean error and the relative standard deviation obtained from 6-variates are indicated in table No.4-1.

Effect of Acidity:

The formation of the coloured rhenium (VI)-FTH complex and its extraction depends upon the acidity of the solution. For the

Table 4.1 : Physical Characteristics of the Re(VI) - FTH Complex

Medium	Wavelength (nm)	Molar absorp- tivity L.Mole ⁻¹ cm ⁻¹	Sensitivity g cm ⁻²	Optional concentration range(ppm)	Relative mean error %	Relative standard deviation Sr %
Naphthalene	610	1.166x 10 ⁴	0.02	3 to 8	0.48	0.65
Chloroform pyridine	680	1.582x 10 ⁴	0.012	3 to 8	0.31	0.67

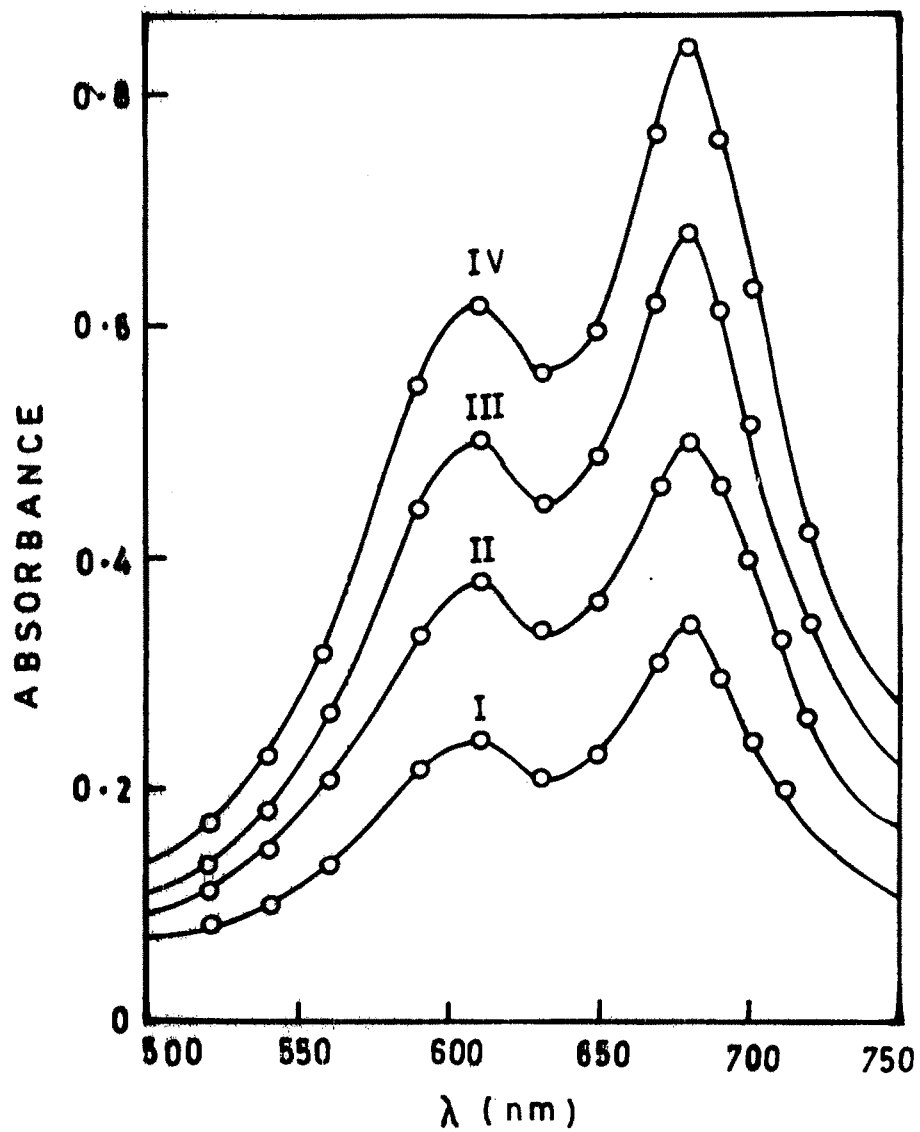


Fig.4.2 – ABSORBANCE CURVES OF Re-TFH COMPLEX.

[Re] : (I) 4 ppm (II) 6 ppm
 (III) 8 ppm (IV) 10 ppm .

study of variation of colour intensity with acidity, standard rhenium (VI) solutions, each containing 200 μg of the metal, were mixed separately with 1 ml of tin(II) chloride solution followed by addition of an excess of reagent and mixture were adjusted to different acidities with diluted hydrochloric acid. Each solution was heated on a steam-bath for 20 min followed by addition of 2 g of solid naphthalene and cooled. The solidified naphthalene containing the Re(VI)-FTH complex was dissolved in chloroform as described in the procedure, Absorbances of the solutions were then measured at 600 nm and 680 nm. against solvent blank. It was observed that the absorbance was maximum and constant over the range 0.4-0.8 M in respect of HCl for 8 ppm of metal at 680 nm (Fig.4.3).

Effect of Reagent concentration :

The effect of reagent concentration on the colour intensity of Re (VI)-FTH complex at 0.6 M hydrochloric acid was studied by using different volumes of 0.01 M reagent solution in the range 0.1 to 8 ml while rhenium(VI) concentration was kept constant at 8 ppm. The colour of the complex was developed as described in the procedure. It was observed from fig. 4.4 that the maximal development of the colour was attained when the FTH concentration was approximately 19 times the molar concentration of the rhenium. However, to ensure complete complexation, 40-60 fold molar excess of the reagent was recommended for further studies. The excess of reagent is not detrimental.

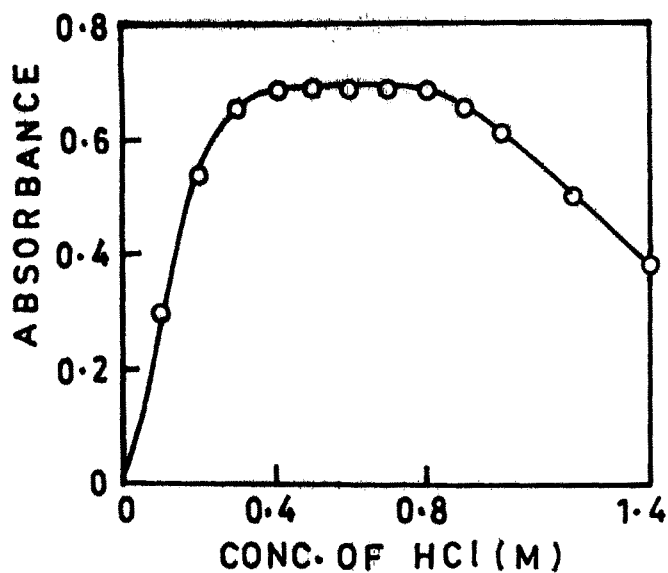


Fig. 4.3 - EFFECT OF ACIDITY.

Re (VI) 8 ppm
 λ_{max} - 680 nm

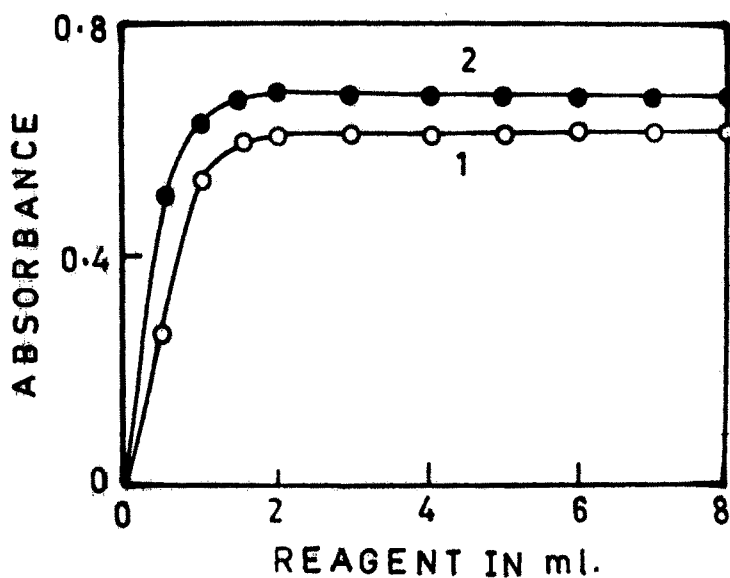
Fig. 4.4 -
 EFFECT OF REAGENT CONCENTRATION.

(-○-) $\lambda_1 = 610$ nm

(-●-) $\lambda_2 = 680$ nm

$[Re(VI)] = 8$ ppm

$[FTH] = 0.01$ M



Effect of Solvent :

The Re(VI)-FTH complex is soluble in ethanol, and ethanolic solution has an absorption peak at 570-580 nm. The Beer's law is obeyed over the concentration range 2-16 $\mu\text{g ml}^{-1}$ with molar absorptivity $8.37 \times 10^3 \text{ L mole}^{-1} \text{ cm}^{-1}$ at 580 nm.

The Re(VI)-FTH complex is also extractable in carbon tetrachloride, chloroform, TBP, isoamyl alcohol, MIBK and mesityl oxide. Of these chloroform and MIBK extracts showed two peaks one at 610 nm and other at 680 nm. However, the colour intensity was found to decrease with time incase of MIBK. Naphthalene-carbon tetrachloride extract of the complex showed single broad peak at 610 nm. TBP and mesityl oxide-extracts of the complex were green coloured with absorption peak at 580 nm. Isoamyl extract of the complex was bluish but its colour decreased on standing. However, the chloroform was recommended because of its high distribution coefficient and the stability of the complex. In addition it affords easy and clear cut separation of phases. The presence of traces of pyridine helps to stabilise the colour intensity.

Effect of Time of Heating and Stability of the complex:

Heating of the aqueous phase on a steam bath necessary for full colour development was studied by varying the time of heating in the intervals 5,7,10,15,20,30 and 60 min. The results plotted in fig. 4.5 indicated that, the heating of the aqueous phase for

Fig. 4.5 — EFFECT OF HEATING PERIOD .

$\lambda = 680 \text{ nm}$ $\text{Re(VI)} \text{ } 8 \text{ ppm}$ $\text{FTH} = 2.4 \times 10^{-3} \text{ M}$

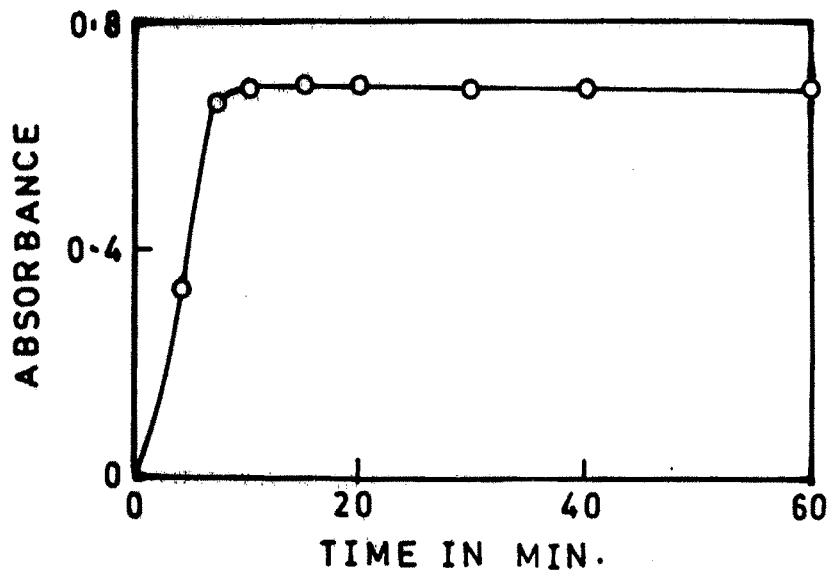
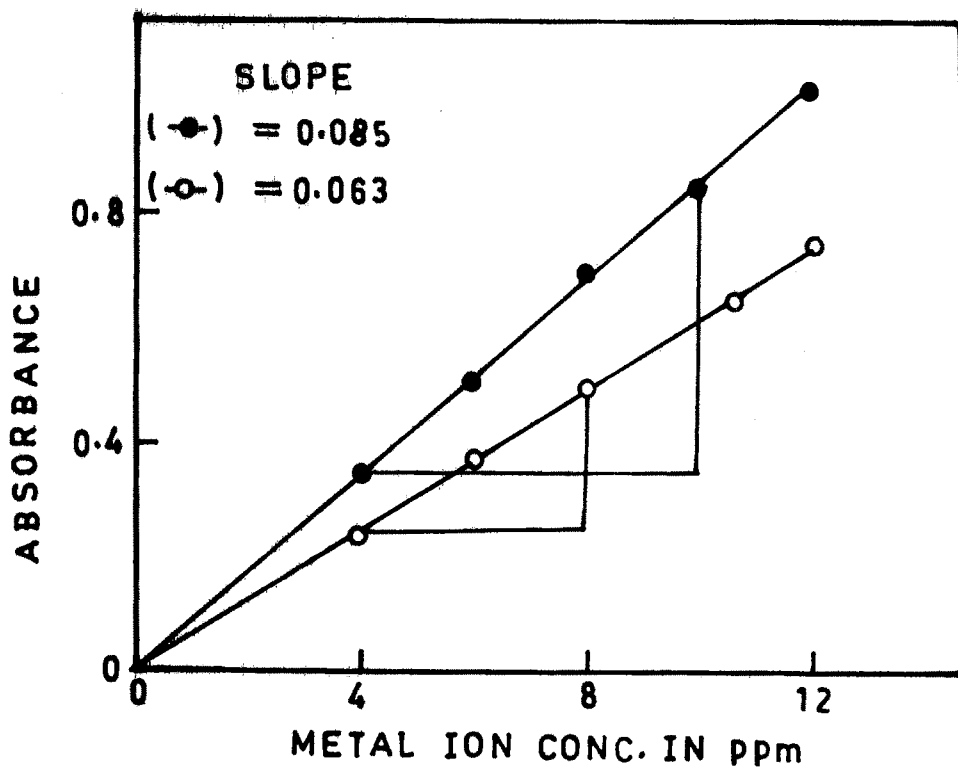


Fig. 4.6 — VALIDITY OF BEER'S LAW .

(●) $\lambda = 680 \text{ nm}$, (○) $\lambda = 610 \text{ nm}$ $\text{FTH} = 2.4 \times 10^{-3} \text{ M}$



10 min was enough ^{for} complete complexation. The blue-violet complex extracted into naphthalene-chloroform when measured at regular intervals of time was found to remain constant for 8 hours. The heating of aqueous phase for ¹⁵⁻²⁰~~25-30~~ min was recommended for further studies.

Validity of Beer's law :

In order to study the validity of Beer's law, the solutions containing rhenium in the concentration range upto 16 ppm were used. The colour of the complex was developed as described in the general procedure using 3 ml of 0.02 M reagent solution, extracted into molten naphthalene and dissolved in chloroform containing few drops of pyridine. The complex was measured at 610 nm and 680 nm, against solvent blank. The absorbances were plotted against the ppm of rhenium (VI) taken. The curves indicate (fig. 4.6) that there is rectilinear relationship between absorbance and concentration of rhenium in the range 2 to 12 ppm both at 610 nm and 680 nm. However, optimum concentration range from the Ring-Bom plot was found to be 3-10 ppm of rhenium (VI) [Figs 4.7 and Fig 4.8].

Composition of the Complex :

An attempts to ascertain the composition of the complex by the Job's continuous variation and molar ratio methods were unsuccessful which might be due to the formation of weak Re (VI) - FTH complex under the experimental conditions.

Fig. 4.7 — RING BOM PLOT .

$\lambda_{\max.} = 610 \text{ nm}$, Re(VI) — FTH COMPLEX .

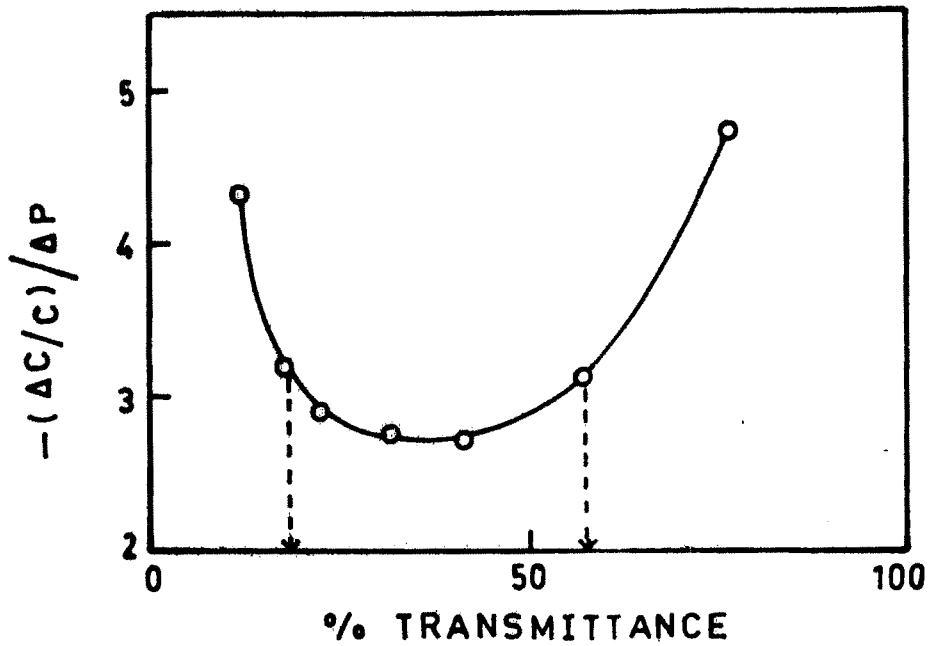
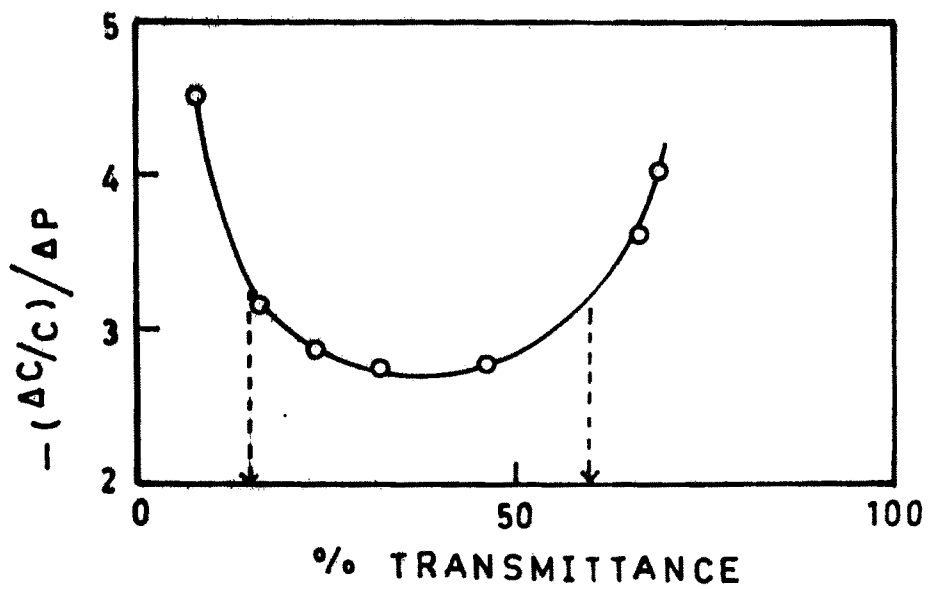


Fig. 4.8 — RING BOM PLOT .

$\lambda_{\max.} = 680 \text{ nm}$, Re(VI) — FTH COMPLEX .



Effect of Diverse ion :

The effect of diverse ion was studied by mixing 8 ppm of metal and the desired amount of foreign ion with 3 ml of 0.02 M reagent solution. The acidity of the solution was adjusted 0.6 M in respect of HCl and the general procedure was applied. An error of less than 2 % was considered to be tolerable. Tolerance limit for the foreign ions tested is shown in table 4.2.

Separation of molybdenum from rhenium :

An aliquot of the test solution containing 200 μ g of rhenium was mixed with 2 mg of molybdenum as ammonium molybdate and the pH of the solution was adjusted to 2.75. 100 mg of Thiobenzoylphenylhydroxylamine⁹⁸ (TBPFA) in iso-amyl alcohol was then added and the mixture was shaken vigorously with four times 10 ml portions of chloroform for quantitative separation. The aqueous phase containing rhenium was reduced to a small volume by evaporation and the colour was developed as per the procedure and measured.

Separation of Osmium from rhenium :

A solution containing 200 μ g of rhenium was mixed with 200 μ g of Osmium. To this solution, a mixture of 2 ml ethanol, few ml water, 1 ml Mg-EDTA complex (5%), and 2 ml of 0.02 M TFH was added. The solution was kept for 10 min and it was adjusted to pH = 3 and then was extracted with 3 x 5 ml portions of carbon tetrachloride for quantitative extraction of osmium. The rhenium in aqueous phase was determined after reducing the aqueous solution to about 5 ml by the general procedure.

Table No.4.2 Effect of diverse ions on the determination of Re(VI)with FTH

Re(VI) = 200 μ g, Acidity 0.4 - 0.8 M HCl
 λ max = 680 nm 3 ml of 0.02 M reagent

Foreign ion added	Amount tolerated (mg)	Foreign ion added	Amount tolerated mg.
V (V)	3.00	U (VI)	2.0
Cr(III)	5.00	Ti(IV)	3.0
Mn(II)	5.00	Sn(II)	4.0
Fe(III)	5.00	Se(IV)	0.5
Co(II)	1.5	Te ^b (IV)	1.0
Ni(II)	1.0	Mg(II)	2.0
Cu(II)	1.0	Ti(IV)	3.0
Zn(II)	4.0	Tartarate	12.0
Ru(III)	0.1	Acetate	15.0
Rh(III)	1.5	Phosphate	12.0
Pd(II)	2.0	Thiocyanate	12.0
Cd(II)	5.0	Citrate	15.0
W(VI)	1.0	EDTA	15.0
Ir (IV)	1.5	Thiourea	10.0
Pt (IV)	2.0	Fluoride ion	12.0
Au ^a (III)	2.0		
Hg(II)	2.0		
Pb(II)	2.0		
Tl(I)	3.0		

a = masking with NaF

b = Centrifuge

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