CHAPTER - V

EXTRACTIVE PHOTOMETRIC DETERMINATION

OF RUTHENIUM (III) WITH

4'-CHLORO-2'-TOLYL TPT

C H A P T E R - V

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INTRODUCTION :

Ruthenium is one of the nobel metals and the common oxidation states are II, III and IV. Ruthenium (III) occurs as the volatile oxide, RuO_4, which is formed when an acid solutions of ruthenium species are heated with powerful oxidising agents like OsO_4. Ruthenium tetroxide is extractable by carbontetrachloride and chloroform from acid solution thereby providing a convenient separation of osmium and ruthenium from other platinum metals.   Shaking the extract with reducing agent such as sulphurous acid returns the ruthenium to the aqueous phase. Ruthenium is one of the most effective hardners in high density alloys. It is alloyed with platinum and palladium to make electrical contacts for wear resistance and it is also a versatile catalyst and used in jewellery. Ruthenium alloys with and without added as osmium, are very hard and are used for pintips, nonmagnetic instruments, pivots and similar items. It may be electrodeposited from molten salts bath, for electroplating of brass metals.

Because of its commercial importance numerous reagents have been proposed for its determination. Beamish and van Loon[1] have critically reviewed the use of organic thioligands in photometric determination of Ruthenium(III) but these reagents lack sensitivity. Many of the recent reagents are also deficient in this respect. Hence, very few methods can be recommended for rutine analysis. One of the widely utilized photometric methods for Ru(III) is based upon the formation of blue complex with thiourea92 in an alcoholic acidic medium. However, the intensity of the colour depends markedly upon the acid concentration, time of heating and the temperature. Moreover, in this method Fe(III), Co(II), Cr(III), Os(VIII), Ni(II) Cu(II), Pd(II) interfere and sensitivity is low. Several modified procedures have been developed. Some reagents investigated include

<u>Substituted ureas</u> : N-phenyl-N'-acetylthiourea[3], 1-benzyl-3 -tolyl-2-selenourea[4], monothiourea-3-nitropthalic acid[5], phenyl or diphenyl thiourea[6], N-Benzoyl-N'-methylphenyl selenourea[7].

<u>Substituted azines</u> : 2,4,5-triaminopyrimidine-6-ol[8], phenothi-azine[9], 3-(4-dimethyl-aminophenyl)-3-hydroxy-1-phenyl-triazine[10] mepazine (pecazine) hydrochloride[11], 2,4,6-tri-(2-pyridyl)-1,3, 5-triazine[12], promazine hydrochloride[13], promethazine hydro-chloride[14], trifluoperazine dihydrochloride[15], chloropromazine hydrochloride[16], diethazine hydrochloride[17], ferrozine[18], pro-chloroperazine maleate[19] thioridazine hydrochloride[20], 5-6-di-phenyl-3-(2-pyridyl)-1,2,4-triazine[21].

<u>Thiazole</u> : 2-mercaptobenzothiazole[22], and <u>Azides</u> : 1,5-diben-
zylidene-3-thiocarbohydrazide[23], o-hydroxythiobenzhydrazide[24].

<u>Thiosemicarbazones</u> : Phenanthrenequinone monothiosemicarbazone[25]
<u>Dyes</u> : 5-chloro-2-hydroxy-3-(4-oxo-2-thioxothiazolidine 5-ylazo)
benzene sulphonic acid-I[26], N-(4-aminobenzoamido)-N'-(benzene-
sulphonylbenzamidine)[27] chrome azurols hexadecylpyridinum bro-
mide[28], N-(α-benzenesulphonylhydrazo-bezylidene) benzene-sulpho-
namide[29] 1-(2-pyridylazo) phenanthren-ol[30].

<u>Oximes</u> : Furil-α-dioxime[31], 3-hydroxy-2-methyl-1,1,4-naphtha-
quinone monoxime[32], benzoyl-α-monoxime[33], thiophene-2-carboxa-
ldoxime[34], 1,2-diphenylpropane-trione-2-oxime[35], 2-methyl-1,4-
butanolnaphthaquinone monoxime[36], Furil-α-monoxime[37] phenyl 4,
6-dihydroxy-5-nitroso-nicotinate[38] 2-hydroxylimino acetophe-
none[39,40], pyridine-2-aldoxime[41], ethyl-α-isonitrosoacetoaceta-
te[42], p-chloro and p-bromo-benzoyl acetone oxime[43], isonitroso-
ethylbenzoylacetate[44]. These reagents suffer from either low
sensitivity or interference of platinum metal and base metals,
prolong heating time for the development of colour or low
stability of the complex.

In the determination of Ru(III) with triophene-2-carboxal-
doxime[34], many metal ions interfere in addition to the observed
low tolerance limit for platinum metals. In the method using
isonitrosobenzylacetone[45], Ru(III) is extracted with MIBK at pH
3.5-4.5 and is measured at 470 nm. But Pt(IV), Pd(II) and
Fe(III) interfere. In the method using selenourea[46], 35 min

waiting for full colour development is required and moreover complex has low stability (45 min).

Shome[47-49], has reported various organic thiohydrazides as analytical reagents for ruthenium. Although the method is sensitive, it lacks selectivity and needs longer time of heating for full colour development. The extraction of Ru(III) with isonitrosoacetophenone[40] requires strict control of acidity. Recently some important reagents are reported for extractive spectrophotometric determination of ruthenium. These include o-mercaptoacetoacetanilide[50] rhodamine 6 G[51], cyclohexylthioglycolate[52], cinnamoyl hydroxionic acid (CHA)[53], 4-methoxy-benzene dithiocarboxylic acid[54], 5-benzyldithiocarbazate (BDTC)[55] etc. Strict control of pH is needed in case of some of these reagents in the determination of Ru(III). However, these possess the disadvantages e.g. dithiocarboxylic acid requires the presence of EDTA as masking agent and BDTC requires heating for long time about 1 hr for full colour development. Also they suffer from either low sensitivity or interference of platinum metals and base metals.

However, the present method for determination of Ru(III) is free from disadvantages mentioned above. This method is simple, reproducible and highly selective. Quantitative separation and determination of Ru(III) in presence of other platinum metals as well as noble metals is possible in this method. The proposed reagent pyrimidinethiol reacts with

Ru(III) is hot acidic medium to form blue coloured complex which is easily extractable into chloroform. The complex is measured at 620 nm against solvent blank.

EXPERIMENTAL

Standard Ru(III) Solution :

A stock solution of Ru(III) was prepared by dissolving 1 g Ru(III) chloride hydrate (Johnson Matthey, London) in dilute analar hydrochloric acid (1M) and diluting to 1000 ml with distilled water and standardised[56]. Working solutions of lower concentration were made from it by diluting the stock solution with distilled water as described.

Dioxan :

The cold solution of dioxon was treated with KOH pellets with shaking until some remains undissolved, and the aqueous layer was run off. Most of the residual water was removed by keeping the dioxon over a fresh KOH pellets for 24 h. This was followed by refluxing over excess of sodium for 6-12 h i.e. until reaction ceased and the sodium remained bright, finally the diethylene dioxide (dioxon) was distilled from sodium, it should be stored out of contact of air. The pure compound has b.p. 101.5°, 760 mm and M.P. 12°C.

Reagent Solution :

Stock solution of the reagents (0.02 M) was prepared by dissolving pyrimidinethiol in 25 ml dioxon (0.140 g).

Standard solution of diverse ions were prepared by dissolving AR grade reagents in distilled water or dilute hydrochloric acid. All the organic solvents were used after double distillation. The mineral acids, used to adjust the acidity of the medium were of AR grade.

Apparatus :

All absorbance measurements were carried out with a Elico spectrophotometer model Cl-27 equipped with 1 cm quartz cells.

Recommended Procedure :

To a suitable aliquot of Ru(III) solution (5 ppm) taken in a 25 ml volumetric flask, concentrated. Hydrochloric acid was added to give the desired acid concentration in a volume of 25 (4 M HCl) then followed by addition of 3 ml reagent solution respectively. The solution was then heated on boiling water bath for 10 min. The blue complex of Ru(III) with pyrimidine-thiol was extracted for two min with 7 ml portion of chloroform The layer was allowed to separate. The organic layer was removed, dried over anhydrous sodium sulphate and was diluted upto 10 ml in volumetric flask with chloroform. The absorbance of the blue complex was measured at 620 nm against the solvent blank. The Ru(III) content was computed from the calibration graph.

RESULTS AND DISCUSSION

Spectral Characteristics :

The absorbance spectra of complexes of Ru(III) with pyrimidinethiol in chloroform are shown in fig.-1. The solutions of pyrimidinethiol in chloroform are colourless and do not absorb significantly in the visible region. The absorbance measurement were made in the region 400 to 700 nm against the solvent blank. The complex of Ru(III) with pyrimidinethiol exhibit sharp absorption maximum at 620 nm. The molar extinction coefficient as determined from Beer's law plot are 6102 L mole^{-1} cm^{-1}, Sandell sensitivity is 16.6 ng cm^{-2}. The spectral characteristics of Ru(III) complexes with pyrimidinethiol are shown in Table-1.

Effect of Acidity :

In order to establish the optimum concentration range of acid required for full colour development of 5 ppm of Ru(III), the HCl concentration was varied in the range 1 M to 10 M and the colour of the complexes were developed as outlined in the recommended procedure. The curves (Fig.2) of absorbance versus HCl molarity showed the optimum range 3 to 6 M HCl for pyrimidinethiol. Of the various acids, tested as the extracting media, no colour developed was observed with nitric acid and phosphoric acid media while the colour intensity of the complex

TABLE - 1 : Characteristics of Ru(III) Complexes of
Pyrimidinethiol

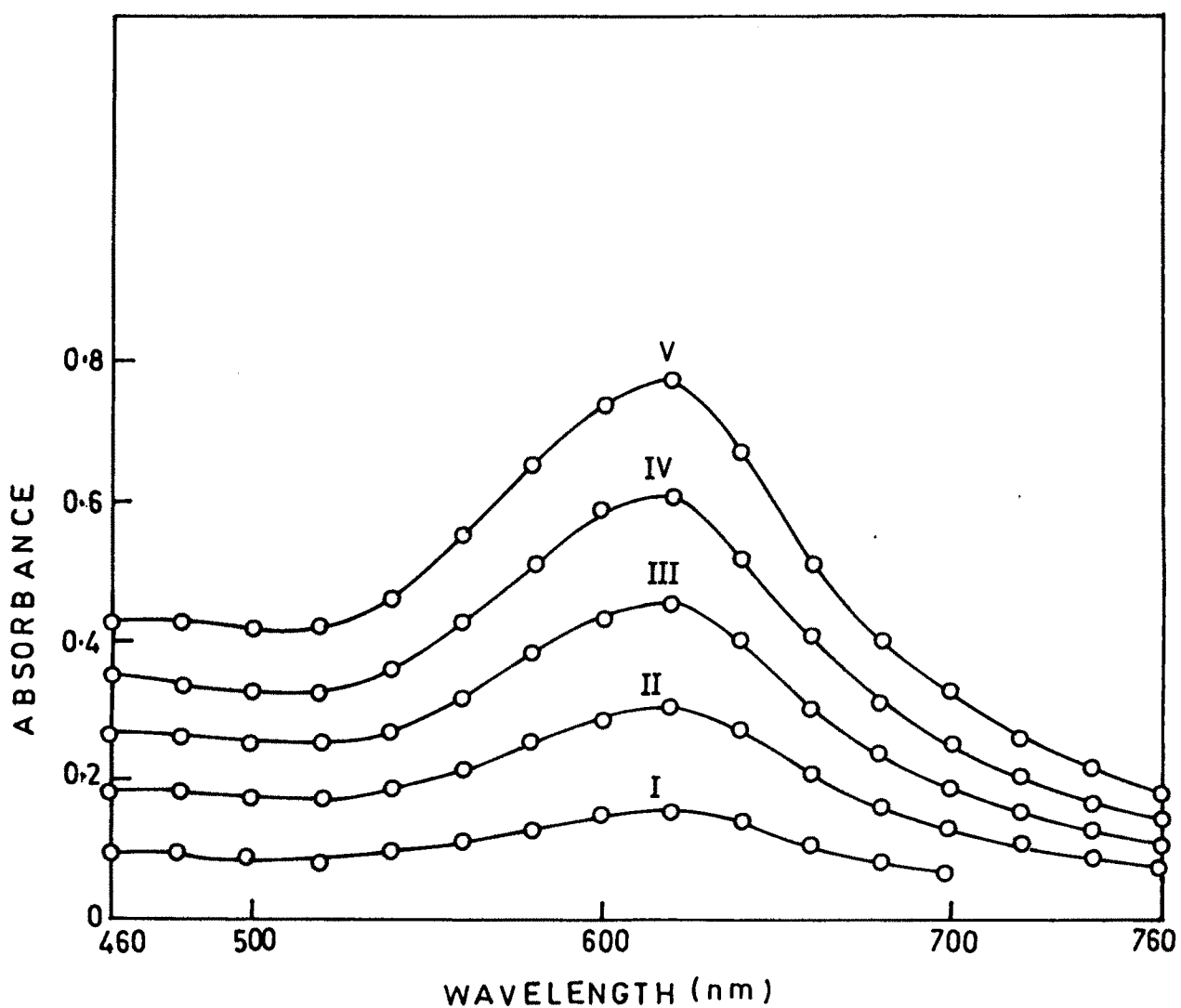| Sr.No.	Characteristics	Pyrimidinethiol
1	Solvent	Chloroform
2	λ max, nm	620
3	ε max, nm	6102
4	Acidic medium for max colour development	3 - 5 M HCl
5	Stability in hr	> 48
6	Beer's range ppm	1 - 12.5 ppm
7	Sandell's sensitivity	16.6 ng cm^{-2}
8	Molar ratio of pyrimidinethiol needed for complete complexation	61.02

FIG. 1 — ABSORBANCE CURVES OF Ru(III) − PYRIMIDINETHIOL COMPLEX.

Ru(III) − I, 2·5 ppm ; II, 5 ppm ; III, 7·5 ppm ;

IV, 10 ppm ; V, 12·5 ppm .

was low when the complexation reaction was carried out from sulphuric acid and perchloric acid media. Hence HCl was used in further studies.

Effect of Time of Heating and Stability of the Complex :

Heating of the aqueous phase on a boiling water-bath necessary for full colour development was studied by varying the time of heating in the intervals of 3,4,5,6,7,9,10,15,20 min. The results plotted in the fig.3 indicated that the heating of the aqueous phase in the range 8 to 12 min was necessary for full complexation. The chloroform extract of Ru(III)-pyrimidinethiol complexes when measured at regular interval of time was found to remain constant for more than 48 hr.

Effect of Dioxan Concentration :

The plots of absorbancesd versus the ml of dioxan used in aqueous medium to keep the complex in solution (fig.4) indicated that, for full complexation, the amount of dioxan in aqueous phase should be in the range 3 to 5 ml for pyrimidine-thiol. The excess of dioxan decreases the intensity of Ru(III) complexes.

Effect of Reagent Concentration :

In order to find amount of reagent necessary for full colour development of Ru(III), varying volumes of reagents

FIG. 2

EFFECT OF

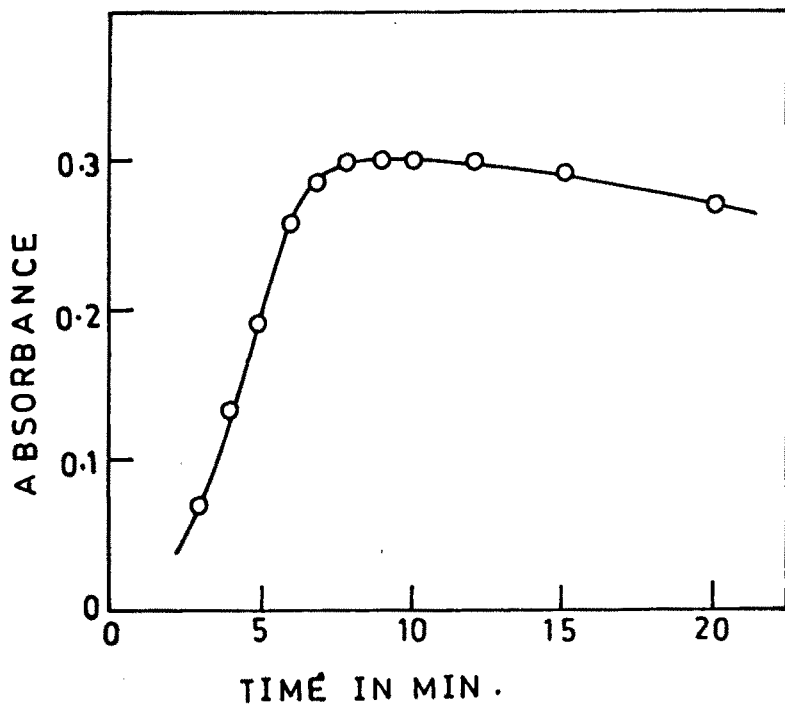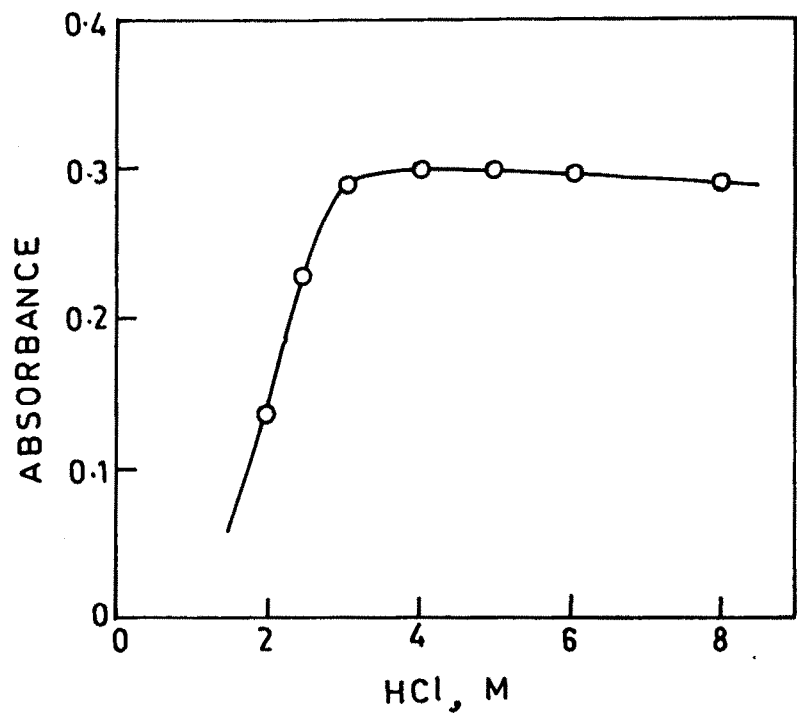ACIDITY (HCl).

Ru(III) —

PYRIMIDINETHIOL

Ru(III) = 5 ppm

FIG. 3

EFFECT OF TIME

OF HEATING.

Ru(III)-PYRIMIDINETHIOL

Ru(III) = 5 ppm

(0.01 M) from 0.5 to 6 ml were used. The colour of the Ru(III)-pyrimidinethiol complexes were developed as per the recommended procedure. It was observed that the colour intensity was maximum and constant with 3.5 ml (70 fold molar excess) of pyrimidinethiol (fig.5).

However, approximately 160 fold molar excess of each of the reagents were recommended in order to ensure complete complexation.

Effect of Solvent :

Various solvents were examined as extractants for Ru(III)-pyrimidinethiol complexes developed as per the recommended procedure. The 100% extraction of Ru(III)-pyrimidinethiol in chloroform while the extraction of the complexes were found to be incomplete in benzene, toluene, isobutyl methyl ketone, amyl alcohol, carbontetrachloride 4 methyl-2-pentanal. Hence chloroform was preferred as an extractant for Ru(III)-pyrimidinethiol complex.

Validity of Beer's Law :

The solution containing Ru(III) in the concentration range upto 12.5 ppm were used for the study of the validity of Beer's law. The colour of the complexes were developed as described in general procedure. The extracted complexes were measured at 620 nm against solvent blank. The absorbance was plotted against the ppm of Ru(III) taken (fig.6). The curves indicate that
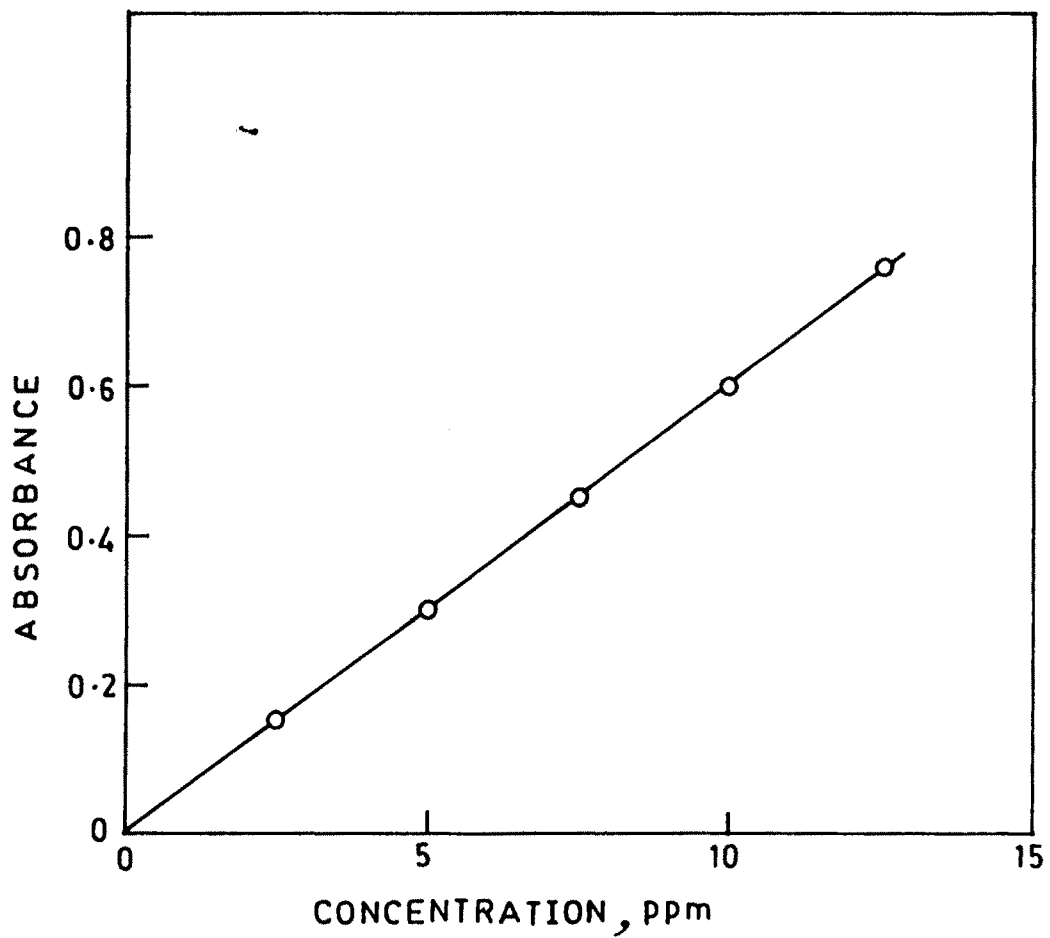
FIG. 6 — BEER'S LAW
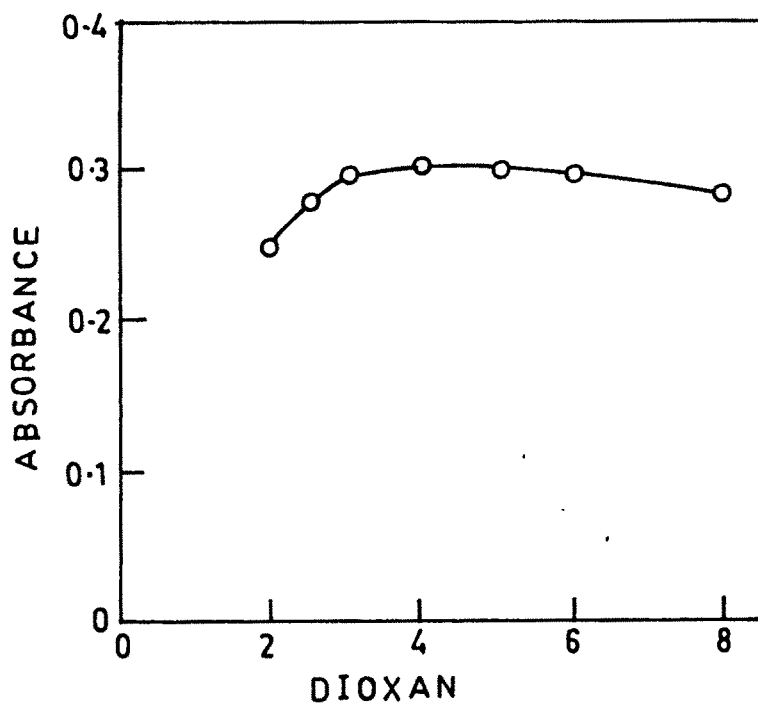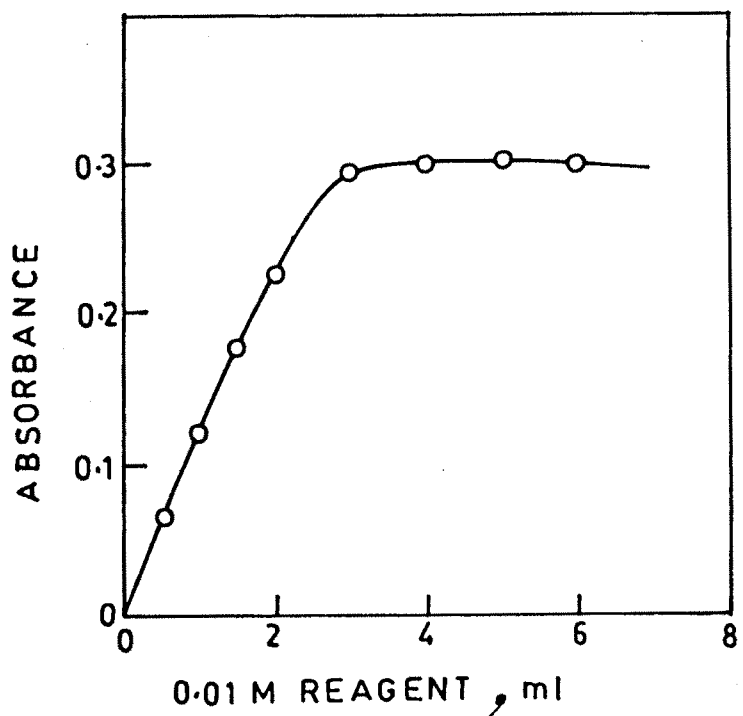
Ru(III) — PYRIMIDINETHIOL COMPLEX .

FIG · 4
EFFECT OF DIOXAN
CONC ·
Ru (III) —
    PYRIMIDINETHIOL
Ru (III) = 5 ppm

FIG · 5
EFFECT OF
REAGENT CONC ·
Ru (III) —
    PYRIMIDINETHIOL
Ru (III) = 5 ppm

there is rectilinear relationship between the absorbance and the concentration of Ruthenium(III) in the range 0 to 12.5. However, the optimum concentration range were found to be 2.5 to 10.5 ppm.

Composition of Complex :

The composition of the complex could not be determined as the complex is weak and dissociated rapdly when the ligand concentration is less than 70 fold molar excess.

Effect of Foreign Ions :

The effect of a large number of diverse ions on the determination of 0.050 mg of Ru(III) with pyrimidinethiol was investigated following the recommended procedure. Initially, the foreign ion was added to the Ru(III) solution in large excess. 100 fold for cations and 500 fold for anions when the interference was intensive, the tests were repeated with successively smaller amount of foreign ion. The tolerance for the foreign ion was taken as the largest amount that could be present to give an error less than 2% in the absorbance at 620 nm. The tolerance limits for the ions tested are shown in table no.2.

The anions are tolerable in fairly large amount except thiourea, $S_2O_3^{-2}$, I^-.

TABLE 2 : Effect of foreign ions on the Determination
of Ru(III) with Pyrimidinethiol

Ru(III) = 0.050 mg λ max = 620 nm

Foreign ions added	Tolerance level, mg
Salicylate citrate, oxalate, Fluoride, Phosphate, Borate EDTA, Acetate Tartarate	150
Ir(III)	25
U(VI), Co(II), Sn(II), Cu(II), Zn(II), Hg(II), Mg(II) Ba(II), SCN$^-$	10
Rh(III), V(V), Cr(VI)	5
Fe(III), Mn(II), Mo(VI)	4
Pb(II), Cd(II)	2
Pd(II), W(VI), Au(III), Ni(II), Pt(IV)	1
Os(VIII), Ga(III)	0.2
Thiourea, Iodide, Thiosulphate	Nil

Reproducibility Accuracy and Precision :

For study of reproducibility and accuracy of the method, absorbance measurements with 10 different identical solutions containing 5 ppm ruthenium(III) each, were performed as per recommended procedure and concentration was determined by using calibration curve. The results are shown in Table-3.

Average of these ten readings are calculated and deviation from the average reading was found out in each case and then standard deviation was calculated from the standard deviation reproducibility of the results with 95% confidence limit. Also the Sandell's sensitivity was calculated from Beer's law graph.

TABLE - 3   Precision and accuracy of the method
                  Amount taken of Ru(III) = 5.0 ppm

Sr. No.	Absorbance observed	PPm of Ru found (x)	$x-\bar{x}$	$(x-\bar{x})^2$
1	0.295	4.91	− 0.084	0.007056
2	0.300	5.0	0.006	0.000036
3	0.304	5.06	0.066	0.004356
4	0.307	5.1	0.106	0.011236
5	0.297	4.95	− 0.044	0.001936
6	0.304	5.06	0.066	0.004356
7	0.300	5.0	0.006	0.000036
8	0.295	4.91	− 0.084	0.007056
9	0.300	5.0	0.044	0.001936
10	0.297	4.95	− 0.044	0.001936
	Total	49.94		0.03804

Average value

$$\bar{x} = \frac{49.94}{10} = 4.994$$

Standard deviation $(\delta) = \sqrt{\dfrac{(x_1-\bar{x})^2+(x_2-\bar{x})^2+\ldots(x_n-\bar{x})^2}{n-1}}$

$$= \sqrt{\frac{0.0384}{10-1}}$$

$$\delta = 0.065$$

Error (E) = Observed reading − Actual Reading

$$= 4.994 - 5.0$$

$$= 0.006$$

Relative error = $\frac{0.006 \times 100}{5}$
Percent (accuracy)

$$= 0.12$$

coefficient of
variation $= \frac{\delta \times 100}{\overline{x}}$

C.V. $= \frac{0.065 \times 100}{4.994}$

$$= 1.30$$

Molar Extinction coeff.

$$\varepsilon = \frac{Absorbance}{ppm} \times 1000 \times At.wt.$$

$$= slope \times 1000 \times Atomic \ weight$$

$$= 0.06 \times 1000 \times 101.7$$

$$= 6102 \ L \ mole9-1 \ cm^{-1}$$

Sandell sensitivity

$$= 10^3 \times A \times C_{min}$$

where

$$C_{min} = \frac{D_{min}}{\varepsilon \times b}$$

A = Atomic weight

$$S = 1000 \times 101.7 \times \frac{0.001}{6102}$$

$$= 0.016 \ \mu g \ cm^{-2}$$

$$= 16.6 \ ng \ cm^{-2}$$

Reproducibility with 95% confidence

$$= \bar{x} \pm 2.26 * \frac{\delta}{\sqrt{n}}$$

$$= 4.994 \pm 2.26 \times \frac{0.065}{\sqrt{10}}$$

$$= 4.994 \pm 0.046 \ .$$

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