CHAPTER - V

SPECTROPHOTOMETRIC DETERMINATION OF
RHODIUM (III) WITH 4'-BROMO-PTPT

C H A P T E R - V

SOLVENT EXTRACTION AND SPECTROPHOTOMETRIC DETERMINATION OF RHODIUM(III) WITH 1-(4'BROMOPHENYL)-4,4,6-TRIMETHYL, (1H,4H)-2 PYRIMIDINETHIOL

Rhodium has III positive most stable oxidation state. On heating in air it forms a film of oxide Rh_2O_3. The Rhodium (III) belongs to platinum metals. The six platinum metals resemble each other in many respects to the extent that separations with the group are difficult. All the metals in this group are "noble" i.e. unreactive and found free in the nature.

Rhodium finds its principal use as an alloy with platinum, in the 10% Rh alloy. It is used as a catalyst and in spinnerets. Of the platinum metals it is the one most used in electroplating as a noncorrosive, decorative finish, and for its reflectance in mirrors, and searchlights.

Compact rhodium is practically insoluble in all acids at 100° including aqua regia. When finely divided it dissolves slowly in hot conc sulphuric acid and when alloyed with 90% or more of platinum, it dissolves in aqua regia. It is attacked by fused bisulphates.

Platinum-rhodium alloy gauze is used in the oxidation of ammonia to nitrous gases, with nitric acid as the final

product. In the field of high temperature technology the platinum metals, either singly or alloyed in various proportions, have many uses, such as the platinum resistance thermometer, the platinum/platinum-rhodium and rhodium iridium/iridium thermocouples. Rhodium (III) in most of its compounds is more inert than palladium or platinum, but less so than iridium. Fused potassium hydrogen sulphate reacts to form $Rh_2(SO_4)_3$. Fluorine forms RhF_3 at 500° - 600°, together with some RhF_4 and RhF_5, Chlorine forms $RhCl_3$.

Rhodium forms many complexes with ammonia, amines, cyanide, polynitrogen and polyoxygen chelating agents, and bromide. It also forms several complexes in hydrochloric acid but if the solution is boiled the cherry-red colour of the hexachlororhodate (III) ion is shown. Base metals can be removed after the dissolution of the sample by titration followed by hydrolysis.

A 1 : 1 mixture of 1,4-diphenyl carbazide and 1,4-diphenyl carbazone[1] reacts with rhodium (III) salts to form a purple complex of unknown structure. The optimum range is 0.3 - 1.5 ppm with a 1 cm optical path, and the optimum wavelength for absorbance measurements is 565 nm. The colour is developed in a perchloric acid medium of pH 3.0. Both the acidity and volume of water are critical. Indium, iron, cobalt, nickel lead and copper interfere. Tin (II)[2] remains one of the most useful reagents for ascertaining the presence

of a number of platinum metals including rhodium(III).
Rhodium(III) forms red coloured complex with stannous
chloride in 2 M hydrochloric acid medium, after heating for
one hour in boiling water bath. The absorbance of red complex
is measured at 470 nm in a 5 cm cell against reagent blank.

Berman and Ironside[3] were able to increase materially the
sensitivity of the tin(II) method through the use of tin(II)
bromide. The sensitivity of the method is 0.0035 μg cm^{-2}. The
tin(II) bromide reacts with rhodium(III) in perchloric acid
medium and absorbance of yellow complex is measured at 427 nm
against a reagent blank. Method requires 20 min. waiting for
full colour development and is used for the separation of
rhodium from the platinum metals and associated base metals.
Iridium produces the least interference. Several modified
procedures have been developed. Besides, di-0-tolythiourea[4],
unithiol[5], 1,3-diphenylthiourea[6], N-α-pyridyl-N-benzoyl thiou-
rea[7], 1-phenyl-3-(2-pyridyl) thiourea[8], 1-phenyl-2-thio-
-3-(thiobenzoyl) urea[9]: Di-o-tolylthiourea form yellow
complexes with $RhCl_3$ that is extracted into dichloroethane from
1-6 M HCl medium in the presence of 100 fold molar excess of
reagent. N-α-pyridyl-N'-benzoylthiourea reacts with Rh(III) in
HCl-Na acetate medium of pH 5.24 - 6.3 after heating the
reactants on water bath and the complex is measured after
extracting into chloroform. and absorbs at 360 nm 1-phenyl-3-
-(2-pyridyl) thiourea is a novel reagent for spectrophotometric
determination of rhodium(III). It reacts with rhodium(III) in

aqueous acetate buffer medium of pH 3-6 with 40 min heating at 100° to form the complex and extracted into butanol (ε=28600). Benzil-α-monoxime[10] rhodium(III) complex resulted after heating the mixture at 95° for 10 min, the complex is extracted into chloroform and extinction is measured at 435 nm. Rhodium(III) solution, buffered at pH 6, is warmed on a water bath for 40 min with 2 ml of ethanolic 10% benzoin-α-oxime[11]. The coloured complex is extracted into chloroform and measured at 390 nm (ε=2900). Interference is caused by Th, Zr and W(VI) which prevent colour development, while Os(VIII), Ce(III) and Ru(III) gave intense colours. Copper(II) is extracted in the process. Rhodium(III) solution was mixed with thiocamphor oxime[12] in ethanol and solution was adjusted at pH 3, mixture was then heated on waterbath for 10 min, cooled and equilibrated with chloroform for 1 min and absorbance was measured at 345 nm against reagent blank. Numerous azodyes have been investigated as the sensitive reagents for rhodium(III). In 5-chloro-3-hydroxy-2-(4-azo-2-thioxothiazolidin-5-ylazo) benzene sulphonic acid[13] (ε=65000), 1-(2-pyridylazo)-2-naph-thol[14], eriochrome cyaine R[15], nitroso R salt[16], (2-hydroxy-phenylazo)-2-naphthol[17], 1-(2-pyridylazo)phenanthren 2-ol[18], 5-(2-pyridylazo)-p-cresol[19] (ε=85000), melachite green[20], 5--diethyl amino-2-(2-thiazolylazo) phenol[21], chrome Azurol S[22], 2-(5-bromo-2-pyridylazo)-5-diethyl aminophenol[23] (ε=90,000), pyrazolone (4-azo-2)-1-naphthol-4- sulphonic acid[24] (ε=48800), 4-(2-pyridylazo) resdorcinol[25], rhodamine 6 G[26] (ε=120,000),

2-(2-thiazolylazo)-5-diethylamino benzoic acid[27], 2-(2-benzo-thiazolylazo)-5-diethylamino benzoic acid[28] (ε=144000), many ions interfere. Phthalimide bis (thiosemicarbazone)[29] in dimethyl DMF formamide, forms complex with rhodium(III) in acetate buffer solution. It absorbs at 420 nm. Rhodium(III) forms complex with phenanthrene quinone monosemicarbazone[30] at pH 7.2 to 8.8 by heating on a water bath for 2 h and is dissolved by adding dimethylformamide to final conc of 70% (v/v). The absorbance of the 1:3 (metal : ligand) complex is measured at 480 nm. Thiotropolone[31] forms a brown complex on heating on water bath with maximum absorption at 500 nm. 2-Octylaminopyridine[32] and n-octylaniline[33] are used for extraction and separation of platinum metals. The methods can be used for analysis of platinum bearing materials. A 1% solution of 1-phenyltetrazoline-5-thione[34] in 0.2 M NaOH was heated with a solution of rhodium(III) in 1-3 M HCl and the precipitated yellow complex was extracted into chloroform. The extinction of the extract was measured at 340 nm. Ruthenium(IV) interfers. Rhodium(III) reacts with ethyl-α-(hydroxyimino)-acetoacetate[35] in sodium acetate-acetic acid buffer medium (pH 5.5) and mixture is heated for 30 min;10 M LiCl (5 ml) was added and complex was extracted into ethylmethylketone. The absorbance of the extract is measured at 390 nm versus a reagent blank. The di-2-pyridylglyoxa-2-quinolylhydrazone[36] mixed with rhodium (III) solution and pH is adjusted to 3.0 - 5.5 and the mixture is heated for 30 min on a water bath, then cooled and diluted

with ethanol (50%). The absorbance of the complex is measured at 540 nm.

However, the present method is free from the disadvantages mentioned for the above methods. The method is highly selective, simple and reproducible. The pyrimidinethiol(II) reacts with rhodium(III) in hot aqueous acidic medium to form yellow coloured complex which is extractable into methylisobutylketone (MIBK). The complex is measured at 355 nm against reagent blank.

EXPERIMENTAL

Standard Rh(III) solution :

Standard solution of Rhodium(III) (0.3906 mg/ml) was prepared by dissolving 1 g of pure Rhodium trichloride (Johnson, Matthey, London) in 25 ml conc HCl and diluting to 1000 ml with distilled water. Working solution of lower concentration was made from it by diluting the stock solution with distilled water as required.

Dioxan solution :

Dioxan needs purification to remove acetaldehyde. The cold solution of dioxan 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 dioxan 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 (dioxan) was distilled from sodium, it should be stored out of contact of air. The pure compound has b.p. 101.5^O at 760 mm and m.p. 12°.

Reagent solution

Stock solution of the reagent (0.02 M) was prepared by dissolving 0.156 g pyrimidinethiol II in 25 ml 1,4 dioxan.

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

An Elico digital spectrophotometer model CL-27 with a set of 1 cm quartz cells was used for absorbance measurements.

Recommended Procedure

To a suitable aliquot of Rh(III) solution (8-40 ppm) taken in a 25 ml volumetric flask, concentrated hydrochloric acid was added to give the desired 2 to 2.5 M acid concentration in a volume of 25 ml. Then 2.5 ml of 0.02 M pyrimidinethiol II in 1,4 dioxan was added. The solution was then heated on water bath for 10 min and cooled. The yellow complex of Rh(III) with

pyrimidinethiol II was extracted for one min with 7 ml MIBK. The layers were allowed to separate. The organic layer was removed, dried over anhydrous sodium sulphate and diluted to 10 ml volume with MIBK. The absorbance of the complex was measured at 355 nm against reagent blank. The Rh(III) content was computed from the calibration graph.

RESULTS AND DISCUSSION

Spectral Characteristics

The absorbance spectra of the complex of Rh(III) with pyrimidinethiol II in MIBK is shown in Fig.1. The solution of pyrimidinethiol II in MIBK is colourless and does not absorb significantly in the visible region. The absorbance measurments were made in the region 350-430 nm against the reagent blank. The complex has sharp absorption maximum at 355 nm. Beer's law was valid over the concentration range 2 to 32 ppm of rhodium(III). The Sandell's sensitivity of the reaction is $0.039 \ \mu g \ cm^{-2}$ and the molar absorptivity is $2637 \ L \ mol^{-1} cm^{-1}$ at 355 nm. The characteristics of Rh(III) complex with pyrimidinethiol II is shown in Table 1.

Effect of Acidity

In order to establish the optimum concentration range of acid required for full colour development of 24 ppm of Rh(III), the HCl concentration was varied in the range 0.25-10 M and the

Table - 1 : Characteristics of Rh(III) complex of

Pyrimidinethiol II. Rh(III) = 24 ppm.

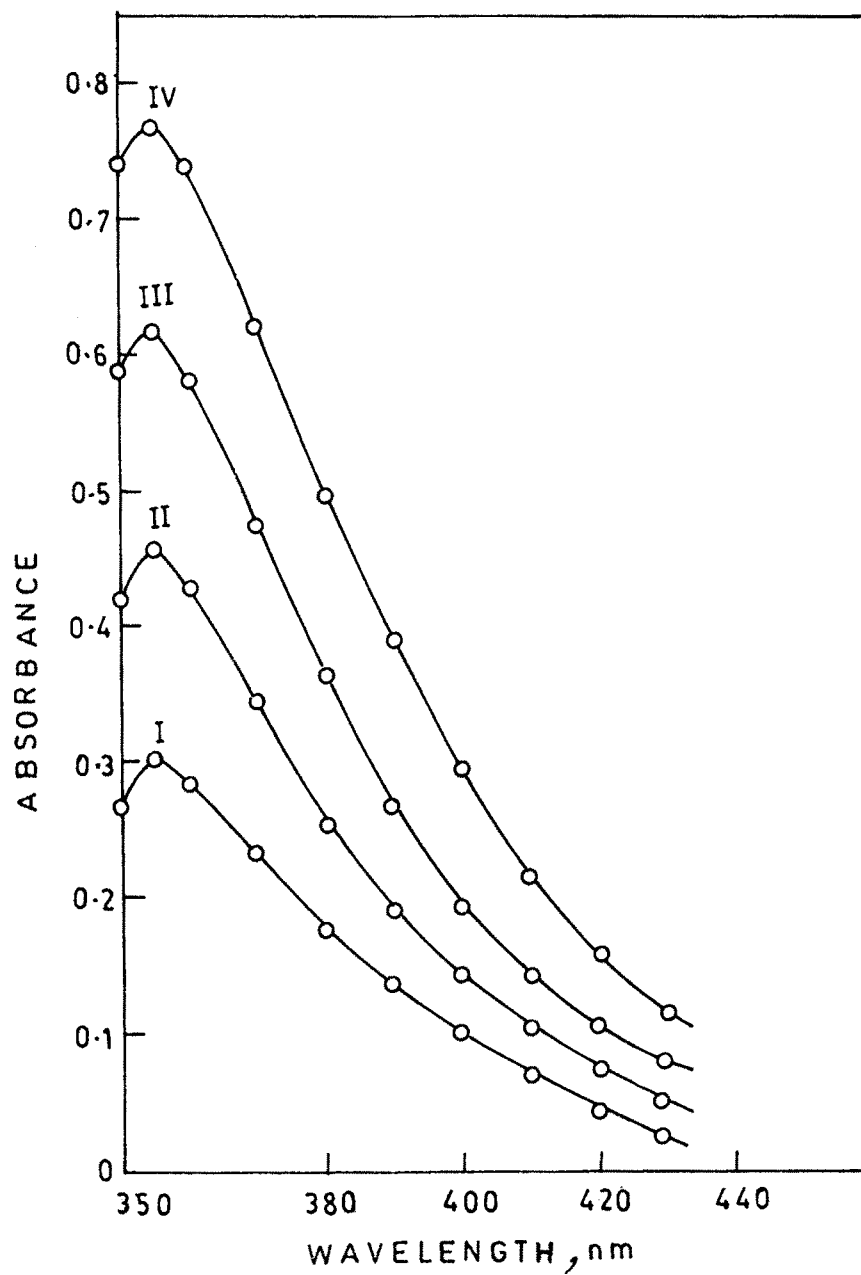| Characteristics	Pyrimidinethiol II
Solvent	MIBK
λ max, nm	355
ε max, L mol^{-1}cm^{-1}	2637
Acidic medium for full colour development	2 to 2.5 M HCl
Stability in hr	$>$ 24
Beer's law range, ppm	2 to 32
Sandell's sensitivity, μg cm^{-2}	0.039

FIG.1 — ABSORBANCE CURVES OF Rh(III)—PYRIMIDINETHIOL
— II COMPLEX.

Rh(II) : I, 12 ppm ; II, 18 ppm ; III, 24 ppm; IV, 30 ppm.

colour of the complex was developed as outlined in the recomm-ended procedure. The curve (Fig.2) of absorbance versus HCl molarity showed the optimum concentration range to be 2-3 M HCl of the various acids, tested as the extracting media. No colour development was observed with nitric acid media while the colour intensity of the complex 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 Reagent Concentration

In order to find the amount of reagent necessary for full colour development of Rh(III), varying volumes of reagent (0.01 M) from 0.125 to 8 ml was used. The colour of the Rh(III) pyrimidinethiol II complex was developed as per the recommended procedure. It was observed that the colour intensity was maximum and constant with 2.0 ml of 0.02 M solution of reagent. It was found that 2.5 ml of 0.02 M solution of reagent was sufficient to extract 20 to 400 μg of rhodium(III) in single extraction, the higher reagent concen- tration had no adverse effect but was avoided because of the higher absorbance of the blank (Fig.3).

Effect of Dioxan Concentration

The plot of absorbance versus ml of dioxan used in aqueous medium to keep the complex in the solution (Fig.4) indicated that, for full complexation, the amount of dioxan in aqueous
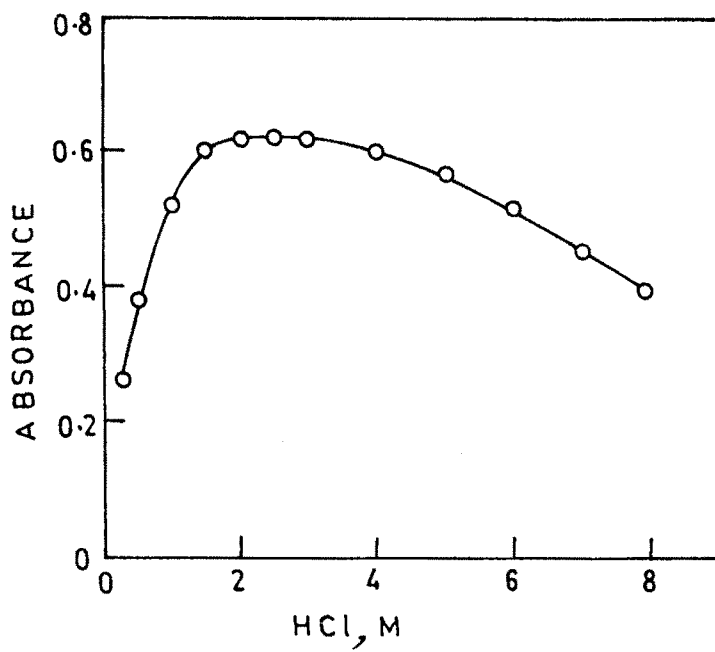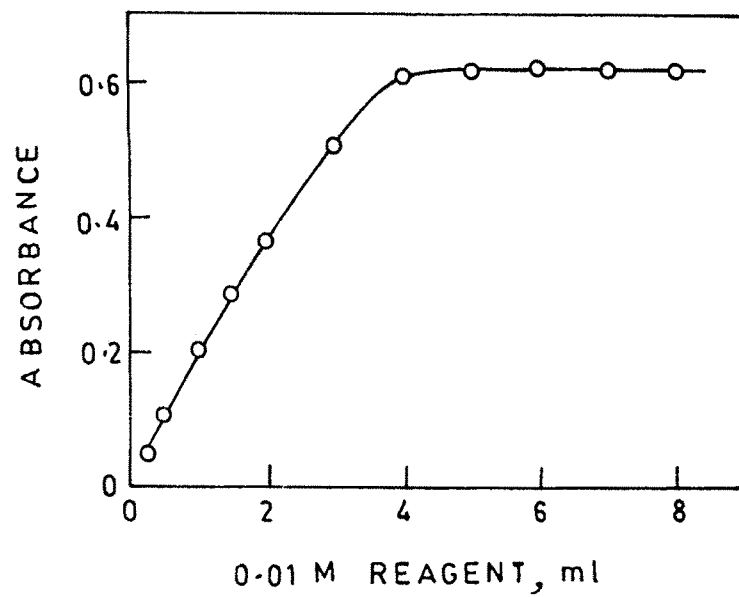
FIG. 2 —

EFFECT OF ACIDITY(HCl)

Rh(III) = 24 ppm

FIG. 3 —

EFFECT OF

REAGENT CONC.

Rh(III) = 24 ppm

phase should be in the range of 10 to 14 percent for the pyrimidinethiol II. The excess of dioxan decreases the intensity of Rh(III) complex.

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 1,2,3,4,5,7,10,12,15,20 min. The results plotted in the Fig.5 indicated that the heating of the aqueous phase in the range 8 to 12 min was necessary for full complexation. The MIBK extracts of Rh(III) pyrimidinethiol complex when measured at regular intervals of time was found to remain constant for more than 24 hr.

Effect of Solvent

Of the various solvents examined as an extractants for Rh(III) - pyrimidinethiol II complex, it was observed that the complex was extractable into solvents such as MIBK, benzene, toluene, chloroform, carbontetrachloride, amyl acetate, amyl alcohol, n butanol, isobutyl alcohol. However, MIBK was chosen as an extractant because of high distribution ratio of the complex in it.

Validity of Beer's Law

The solutions containing Rh(III) in the concentration range upto 40 ppm were used for the study of the validity of
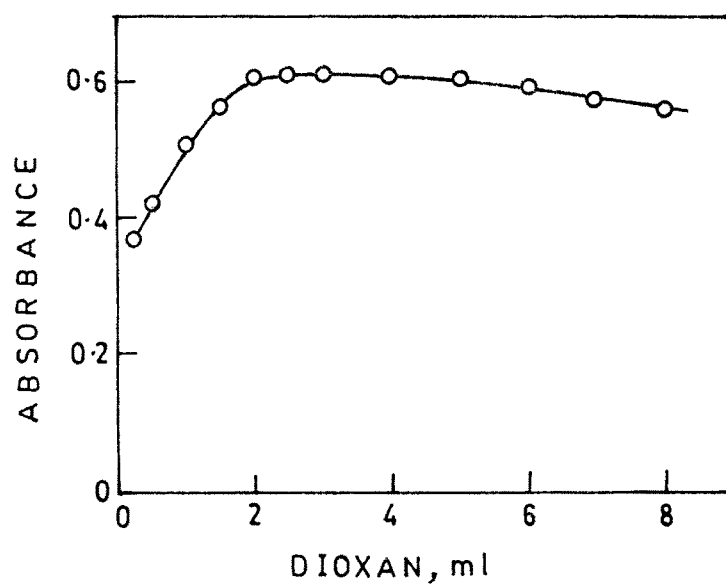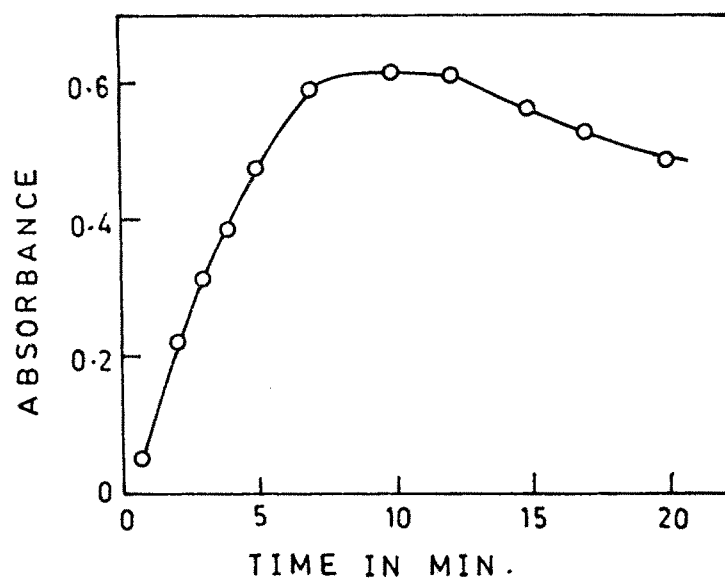
FIG. 4 —
EFFECT OF
DIOXAN CONC.
Rh(III) = 24 ppm

FIG. 5 —
EFFECT OF
TIME OF
HEATING.
Rh(III) = 24 ppm

Beer's law. The colour of the complex was developed as described in the general procedure. The extracted complexes were measured at 355 nm against reagent blank. The absorbance was plotted against the ppm of Rh(III) taken (Fig.6). The curve indicates that there is a rectilinear relationship between the absorbance and the concentration of Rh(III) in the concentration range 2 to 32 ppm. However, the optimum condition range was found to be 8 to 28 ppm.

Composition of the Complex

The composition of the Rh(III)-pyrimidinethiol II complex was determined by the methods of Job's of continuous variation and mole ratio. Equimolar solutions of metal and ligand (2.5 x 10^{-3}M) were used. For Job's method, solutions were prepared by keeping the sum of the molar concentrations of Rh(III) and pyrimidinethiol II constant, while varying the mole fraction of metal in different solutions. The colour of the Rh(III)-pyrimidinethiol II complex was developed as per the recommended procedure. The plot of absorbance at 355 nm versus the mole fraction of metal (Fig.7) indicated the formation of 1:2 metal ligand complex. This was further confirmed from the studies of mole ratio method (Fig.8).

Effect of Diverse Ions

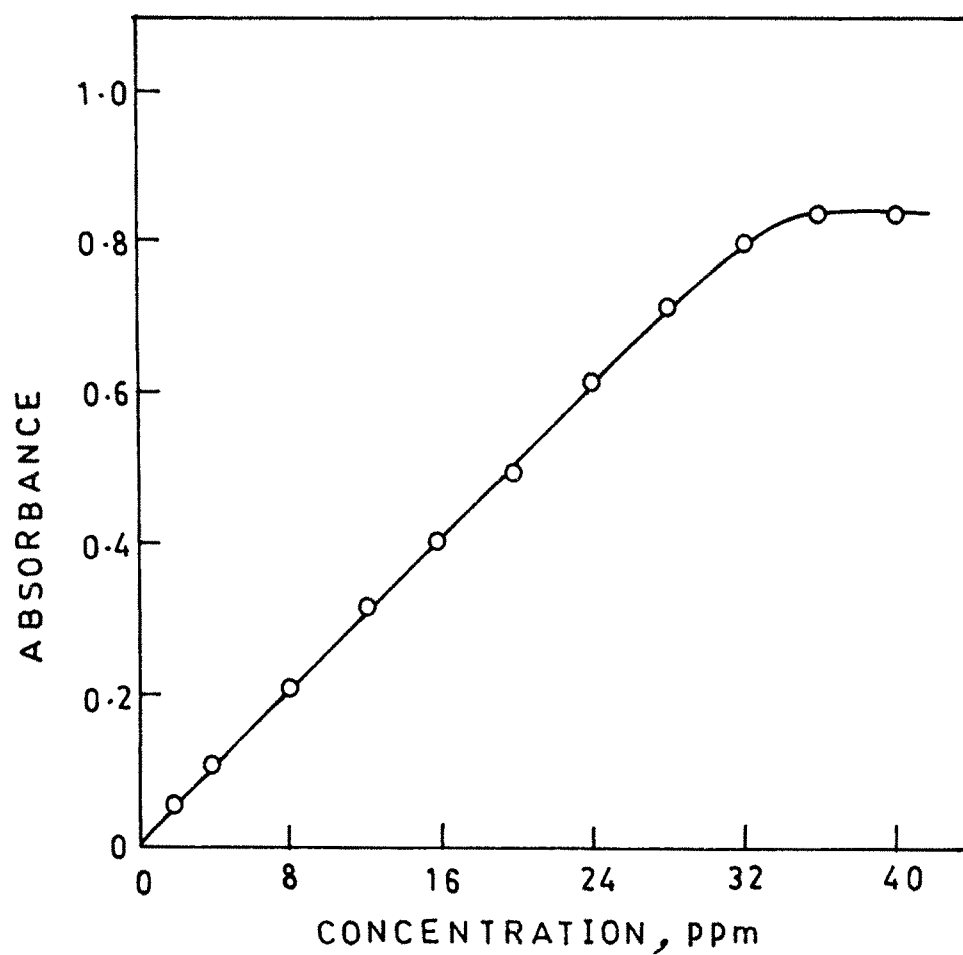The effect of large number of diverse ions on the determination of 24 ppm of Rh(III) with the reagent was investigated

FIG. 6 — BEER'S LAW FOR Rh(III)-PYRIMIDINE-
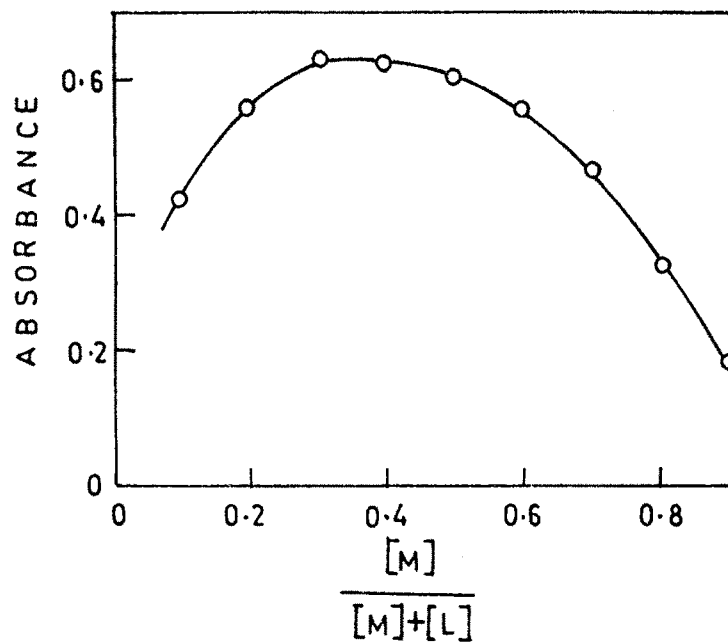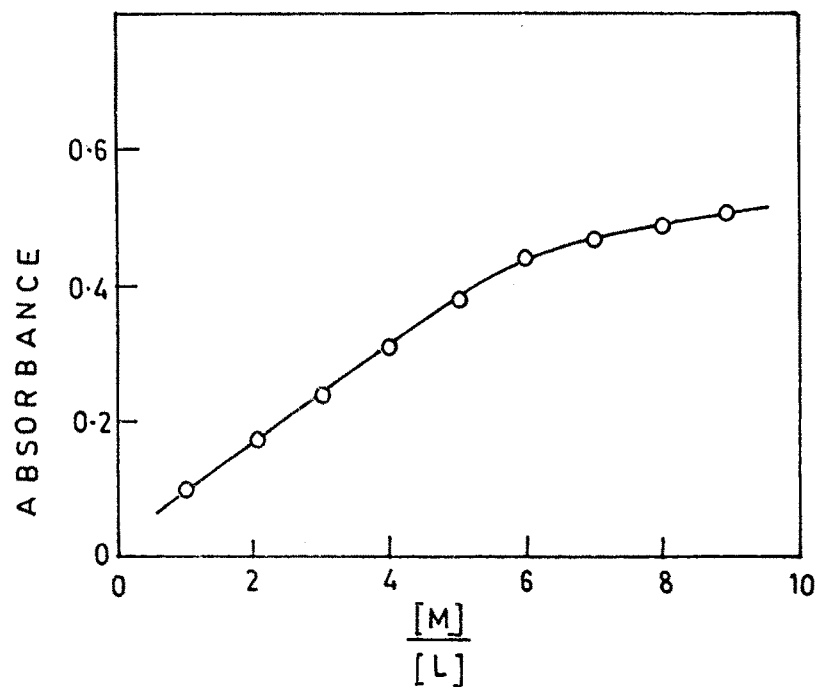-THIOL(II) COMPLEX .

FIG. 7 —

JOB'S PLOT

$[M] = [L] =$

$2 \cdot 5 \times 10^{-3} M$

FIG. 8 —

MOLE RATIO

$[M] = [L] =$

$2 \cdot 5 \times 10^{-3} M$

following the recommended procedure. Initially foreign ion was added to the Rh(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 limit was set at that amount of foreign ion which gave an error less than 2% in the absorbance of the complex at 355 nm. The tolerance limit of ions tested were shown in Table 2.

The anions are tolerable in fairly large amount except thiourea, borax, glycine, phosphate. It is evident that the method permits the determination of Rh(III) even in presence of base and noble metals.

Reproducibility, Accuracy and Precision :

For study of reproducibility and accuracy of the method, absorbance measurements with 10 different identical solutions containing 24 ppm rhodium (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 was calculated. Also the Sandell's sensitivity was calculated from Beer's law graph.

Table - 2 :   Effect of Foreign Ions on the Determination
of Rh(III) with Pyrimidinethiol II
Rh(III) = 0.240 mg, λ max = 355 nm

Tolerance limit in mg	Foreign ions added
10	Fe(III), Ni(II), Cu(II), Ca(II), Pb(II), Mo(II), V(V), Ba(II), Sn(II), Mg(II), Cr(VI), Co(II), K(I), Mn(II), Ti(IV), Pb(II), U(VI)
5	Zr(II), Cr(III), Zn(II), Te(IV), W(VI), Se(IV)
1	Cd(II), Ag(I) Au(III).
100	EDTA, Salicylate, Acetate, Citrate, Tartrate, Oxalate, SCN^-, $S_2O_3^{-2}$, Urea, I^- .

<u>Table - 3</u> :   Precision and Accuracy of the Method

Amount of Rh(III) = 24 ppm, λ_{max} = 355 nm

Sr.No.	Absorbance observed	ppm of Rh(III)found	$X - \bar{X}$	$(X-\bar{X})^2$
1	0.618	24.000	0.058	0.00336
2	0.610	23.689	−0.253	0.0640
3	0.609	23.650	−0.292	0.0853
4	0.620	24.077	0.135	0.0182
5	0.619	24.039	0.097	0.0094
6.	0.618	24.000	0.058	0.003364
7	0.615	23.883	−0.059	0.003481
8.	0.613	23.806	−0.136	0.0185
9	0.621	24.117	0.175	0.03063
10.	0.622	24.155	0.213	0.0454
	Total	239.416		0.281635

Average value $\bar{X}$ = $\dfrac{239.416}{10}$

= 23.942

Standard deviation

$$S = \sqrt{\frac{(x_1-\bar{x})^2 + (x_2-\bar{x})^2 \ldots (x_n-\bar{x})^2}{n-1}}$$

$$S = \sqrt{\frac{0.281635}{9}}$$

$$= \sqrt{0.03129}$$

$$= 0.17689$$

Percentage coefficient of variation

$$C.V. = \frac{S \times 100}{\bar{X}}$$

$$= \frac{0.17689 \times 100}{23.942}$$

$$= 0.7388$$

Error (E) = Observed reading − Actual reading

$$= 23.942 - 24.00$$

$$= 0.058$$

Relative error % $= \dfrac{0.058 \times 100}{24}$

$$= 0.2416$$

Reproducibility with 95% confidence

$$= \bar{X} \pm 2.26 \times \frac{S}{\sqrt{n}}$$

$$= 23.942 \pm 2.26 \times \frac{0.17689}{\sqrt{10}}$$

$$= 23.942 \pm 2.26 \times \frac{0.17689}{3.162}$$

$$= 23.942 \pm 0.1264$$

Molar Extinction Coefficient

$$\varepsilon = \frac{Absorbance}{ppm} \times 1000 \times Atomic\ Weight$$

$$= Slope \times 1000 \times Atomic\ weight$$

$$= 0.02562 \times 1000 \times 102.91$$

$$= 2637\ L\ mole^{-1}\ cm^{-1}$$

Sandell's sensitivity (S)

$$S = 10^3 \times Atomic\ weight \times C_{min}$$

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

$$S = 10^3 \times 102.91 \times \frac{0.001}{2637 \times 1}$$

$$= 0.039\ \mu g\ cm^{-2}$$

$$= 39\ ng\ cm^{-2}$$

References

1. G.H. Ayres and F.L. Johnson, Jr.,

   Anal. Chim. Acta. 23, 448 (1960).

2. E.E. Beamish and J.C. Van Loon

   Analysts of Noble Metal : Overview and selected methods,

   Academic Press New York, pp.113 (1977).

3. S.S. Berman and R. Ironside

   Can. J. Chem., 36, 1151 (1958).

4. Rakovskii E.E., Shvedova N.V. and Berliner L.D.

   Zh. analit. Khim., 29, 2263 (1974).

5. Usatenko Yu. I., Klimkovich E.A. and Machul Skii B.M.

   Khim. Zh., 42, 425 (1976).

6. Shome S.C., Mazumdar M., and Chakrabarti M.K.

   J. Indian Chem. Soc., 54, 225 (1977).

7. Das D.K., Mazumdar M., and Shome S.C.

   J. Indian Chem. Soc., 54, 779 (1977).

8. Usalenko Yu.I., Meshcheryakova N.R. and Pedan V.P.

   Zh. Anal. Khim., 34, 1211 (1979).

9. Uttarwar R.M. and Joshi A.P.

   Indian J.Chem., Sect A, 16, 1113 (1978).

10. Savostina V.M., Shpigum O.A., Parmenova V.A. and

    Peshkova V.M.

    Zh. Anal. Khim. 32, 556 (1977).

11. Paria Praphulla K. and Majumdar Santosh K.

    Indian J. Chem. Sect.A. 15, 157 (1977).

12. Thokdar T.K., Paria P.K. and Majumdar S.K.

    J. Indian Chem.Soc., 66, 918 (1989).

13. Propistsova R.F. and Savvin S.B.

    Zh. analit.Khim., 28, 1768 (1978).

14. Ivanov V.M., Busev A.I. and Figurovskaya V.N.

    Zh. analit. Khim., 29, 2260 (1974).

15. Duchkova H., Cermakova L. and Malat M.

    Analyt. Lett., 8, 115 (1975).

16. Saxana K.K. and Agarwal B.V.

    Indian J. Chem. Sect. A., 14, 634 (1976).

17. Voklova G.V. and Vaisbera A.S.

    Zavod Lab., 43, 25 (1977).

18. Grag B.S., Singh R.P. and Rishi A.K.

    Indian J. Chem. Sect A., 15, 367 (1977).

19. Govoshko G.G., Dedkov Yu. M. and Ermakov A.N.

    Zh. Anal. Khim., 33, 1114 (1978).

20. Marczenko Z. and Kowalczuk E.

    Anal. Chim. Acta, 108, 261 (1979).

21. Shurupora T.I., Iranov V.M. and Golubtsov I.V.

    Vestn. Mosk. Univ.Khim., 20, 459 (1979).

22. Sabartova J., Herrmannova M., Malat M. and Cermakova L.

    Chem. Zvesti, 34, 111 (1980).

23. Liu S., Liu Z. and Zhong W.

    Fenx. Huaxue, 16, 1042 (1988).

24. Pilipanlco A.T., Farkhomenko E.P., Falendysh N.F.,

    Zh. Anal. Khim., 43, 1822 (1988).

25. Alte A., Cermalcova L.

     Chem. Pap., 42, 483 (1988).

26. Gong X., Song Y., Pan Y.

     Gujjinshu, 11, 41 (1990) (China)

27. Yang H.Q., Zhang G., Mu Q.Y., Huang H.

     Fenxi Huaxue, 20, 725 (1992).

28. Yang H.Q., Zhang G., Mu Q.Y., Zhou C.S.

     Huaxue Shiji, 28, 328 (1992).

29. Guzman Chozas M., Perez Bendio D. and Pino Perez F.

     An. Quim. 72, 651 (1976).

30. Kamil Fasihuldin, Sindhwani S.K. and R.P. Singh

     Rev. Roum. Chim., 25, 875 (1980).

31. Sharma Jawahar Lal, Gang B.S., Srivastava J.N. and

     Singh R.P.

     J. Indian Chem. Soc., 54, 407 (1977).

32. Borshch N.A., and Petrukhin O.M.

     Zh. Anal. Khim. 33, 2181 (1978).

33. Pohlandt C. and Hegetschweiler H.

     Natl. Inst. Metall. Repub. South Africa Rep.,

     No. 1940, pp. 22 (1978).

34. Radushev Aleksandr V.,Prochorenko Evgenya N. and

     Koethe Jutta Jutta

     Z. Chemie LPZ, 16, 234 (1976).

35. Patil M.K. and Haldar B.C.
     J. Indian Chem. Soc., 56, 576 (1979).

36. Kulshreshtha H., Singh R.B. and Singh R.P.
     Chem. Ind. (London), 17, 699 (1980).