Chapter-IV

Photometric Determination of Ruthenium(III)with 5-Methyl Salicylaldehyde Thiosemicarbazone

CHAPTER IV

PHOTOMETRIC DETERMINATION OF Ru(III) WITH 5-METHYL SALICYLALDEHYDE THIOSEMICARBAZONE

Critical reviews on methods for the separation and determination of noble metals are published by Beanish (1,2,3). The literature reveals that although the numerous reagents are reported for determination and separation of Ru(III), very few methods can be recommended for routine analysis. Some of the promising reagents investigated include oximes (4,6,10,16,21,22,25,30,31,32,42,43,) substituted ureas (8,15,24,56),thiosemicarbazones(11),dyes (7,12 23,29,35), substituted azines (17,18,20,26,28,34,36,37,39,41,45, 47,48,50), azides (14,57) and thiazoles (27). These reagents suffer from either low sensitivity or interference of platinum metals and base metals, prolong heating time for the development of the colour, or low stability of the complex.

However ,the present method described here is free from the drawbacks mentioned above. The method is simple,selective and reproducible. 5-Methyl SAT reagent in alcohol reacts with Ru(III) at 6M HCl when the reaction mixture was heated on a boiling water bath for 20 min to form green complex which is measured at 590 nm against simultaneously prepared reagent blank.

A summary of the methods reported for determination of Ru(III) is given in Table No.1 describing reagents, conditions,characteristics of the complex,interferences of diverse ions alongwith special remarks.

A Summary of the Reagents Reported for Ru(III)

Sr.No.	Reagent	Medium	Conditions	λmax;molar extinction coeff;Beer's range and sensitivity	Interferences	Remarks	Ref No.
1.	2.	3.	4.	5.	6.	7.	8.
1.	Furil-α-dioxime	Aqueous	3M-HCl,2ml of 0.126MR in propanol,0.67M $SnCl_2$ OR 0.14M thiourea	λmax=545 mm,upto 12 ppm	Pt,Os,Ir,Pd, and Fe interfere	Heating 6-8 min, used for detg.Ru in films and waste waters from the catalyst manufg.	4
2	2-Thiobarbituric acid	Ethanolic	30m MR	λmax=338 nm;ϵ=11,000 upto 28 ppm,detection limit =0.17 ppm	Distill off Ru as RuO_4	Heating 35 min at 75°	5
3	3-Hydroxy-2-methyl-1-1,4 naphthaquinone monoxime	Ethanolic	pH =6.5	λmax =490 nmϵ=1.4x10^4 1 to 8.71 ppm, S=7.2 ng Cm^{-2}	Rh^{III} and citrate interfere	Heating 45 min at 100°	6
4	5-Chloro-2-hydroxy-3-(4-oxo-2-thioxothiazolidin 5-ylazo)benzene sulphonic acid;I	Aqueous	3.3 M HCl,8.5M acetic acid	λmax=520 nm,ϵ=15,000 0.4 to 10 ppm	-	Heating 30 min at 70° suitable for Ru-detn from soln containing CI, SO_4^{2-} and PO_4^{3-}	7
5	N-phenyl-N'-acetylthiourea	Ethanolic	6M-HCl,3-4ml of 0.01M R	λmax=650nm,ϵ=4700, 2 to 18 ppm	-	Warming 10 min stability 48 hrs.	8

1	2	3	4	5	6	7	8
6	Hexamethyl phosphoramide	MIBK	3M-HCl,2M-NH_4SCN	λmax=570 nm upto 4 ppm	Au and thiourea interfere	Heating 6 min	9
7	Benzyl-α-monoxime	$CHCl_3$	pH=9 5mMR,0.5M Na_2CO_3	λmax=480 upto 0.5 to 7.6 ppm	Sequencial separation from Rh and Ir	Waiting 1 hr; C.V.= 0.6% for ≈ 50 μg of Ru	10
8	Phenanthraquinone mono thiosemicarbazone	$CHCl_3$	4 ml of 0.05% R in DMF +2M acetic acid	λmax=660 nm, ϵ=4740 upto 1-15 ppm S=0.02 μg Cm^{-2}	Cd interferes most seriously	Heating 10 min C.V.=1.2% for 50 μg	11
9	N-(4-Aminobenzamido)-N'-(Benzenesulphonyl benzamidine	Butanol	pH=0.5 to 1.5,6-fold molar excess of R	max=460 nm, =5370 0.1 to 5 ppm	-	1:1 complex, C.V.= 2.1%	12
10	1,10-Phenanthroline and thiocynate	$CHCl_3$ or Isoamylalcohol orMIBK	>6m MR,0.25 to 2M HCl,0.6% of hydrazine chloride followedby NH_4SCN	λmax=490nm,ϵ=8000 0.2 to 10ppm	Pd interferes	Heating 15 min at 1000^o,1:2:2 chloroform extraction required 1 hr.	13
11	1.5-Dibenzylidene-3-thiocarbo hydrazide	$CHCl_3$	1)Brown complex-pH =5.2 to 6.5 acetate buffer	1)λmax=370nm, ϵ=33,200 0.7 to 2.2 ppm	-	1)C.V.=0.86% for 33.1 μg	14
		Ethanolic	2)Ethanolic Pink complex - 1 to 2.5 M HCl	2)λmax=530nmm ϵ=13,300 1.8to 5.0 ppm	-	2)C.V.=0.57% for 67.5 μg	
12	1-Benzyl-3-tolyl-2-selenourea	Aqueous	2 ml of 0.01H R, 1 to 3M HCl	λmax=460nm,0.65 to 9.81 ppm	EDTA or tartarate used for masking base metals	-	15

1	2	3	4	5	6	7	8
13	Thiophen-2-carboxaldoxime	40% acetone medium	pH=10.4 to 10.7	λmax=360nm,0.5to 10;0ppm,S=0.015 µg cm^{-2}	Many metals interfere	-	16
14	2,4,5-Triamino pyrimidin 6-ol	Aqueous	pH=4 to 5,0.1M-KCl and 60fold amount of R	λmax=570 nm,0.8 to 3ppm,S=3.6 ng Cm^{-2}	No_2^-,$S_2O_3^{2-}$,Fe^{2+} and Cu interfere	Heating 20 min	17
15	Phenothiazine	Aqueous	pH=3,acetate+HCl buffer,15 fold molar R in acetone	λmax=500 nm ϵ=3620, 0.16to 3.4ppm, S=27 ng Cm^{-2}	-	1:1 complex	18
16	Thiocynate	MIBK	1M-HCl;0.3M-SCN	λmax=570nm,ϵ=5500, upto 20 ppm	Separated from Os(VIII)	-	19
17	3-(4-Dimethyl-aminophenyl)-3 hydroxy-1-phenyltriazen	Aqueous	pH=7.7to 7.8,40 fold excess R	λmax=490nm ϵ =2.5x10^4 2 to 400 µm	Rh,Pd,Fe,Cu Ni,Co,Ti and V interfere	1:1 complex std.deviation = 0.52%	20
18	1,3-Diphenyl-propanetrione 2-oxime	$CHCl_3$	pH=4.5,5ml of 0.05% 1R	λmax=530nm,1-12ppm	-	Heating 10 min stability 48hrs std.deviation 0.0015	21
19	2-Methyl-1,4-napthaquinone monoxime	Butanol	pH=7.2to 8.4,1.4 ml of 0.01M of R	λmax=470nm ϵ =27,600 1.9 to 34 ppm	-	Heating 90 min, stability 748 hrs.Reagent blank needed	22
20	Chrome Azurols +Hexadecylpyridinium bromide	$CHCl_3$	pH=3 ±0.2,25 fold excess of R	λmax=615 -625	-	Tertiary complex reproducibility is inadequate for quantitative analysis	23
21	Monothiourea-3-nitrophthalic-acid	Ethanolic (40%)	7M-HCl,9% R	max=598nm =3,900 2.25 ppm	-	Heating 15min at 85°	24

1	2	3	4	5	6	7	8
22	Furil-α-monoxime	Aqueous	pH=6to 7 acetate buffer,25 fold molar R	λmax=555 nm,ϵ=16,000 1 to 25 ppm	-	1:2 complex,Heating 10 min at 100°,C.V.=7.8% for 0.9% of Ru	25
23	Mepazine (pecazine) hydrochloride	-	2mlof 0.2% aqueous R, 1) 1M H_2SO_4 or 2) 2M HCl	λmax=515nm ϵ=4480 and 6700 for H_2SO_4 and HCl medium,upto 12.8ppm	Pd^{II},Os^{VIII} Ag and Au^{III} interfere	Waiting 10 and 25min for H_2SO_4 and HCl respectively Reagent blank needed	26
24	2-Mercaptobenzothiazole	Butanol	H_2O +DMF,pH=3to5	λmax=460nm,ϵ=2000	-	2:2 complex	27
25	2,4,6-Tri-(2-pyridyl)1,3,5-triazine	Nitrobenzene	0.5 M $HClO_4$	λmax=543 mm 4.40 µg	-	Heating 35min at 100° 1:2 complex application.	28
26	N(α-benzene sulphonylhydrazo) benzylidene)benenesulphonamide	-	pH=11-12,10mM R in alkali	max=650 nm,2-32 ppm	-	Waiting 15 min	29
27	Pentyl,4,6-dihydroxy-5-nitrosonicotinate		pH=4.5	λmax=535nm,ϵ=42,000	Interference of Co,Fe and Pd removedby extraction into MIBK	Heating 1 hr at 85°	30
28	2-Hydroxyimino acetophenone	3-Methylbutanol	pH -4.5 to 9	λmax=535nm,0.5to7ppm	-	Heating 5min at 98° C.V.=8.8% for 2.7µg in presence of 25 fold of Pd, Pt,Ru and Ir.	31
29	Hydroxyliminoacetyl acetone	-	-	λmax=538nm, =4592 1-12 ppm,S=22ng Cm^{-2}	-	Std.deviation= 0.006 stability 36 hrs.	32

30	Thio-antipyrine	Ethanolic + Aqueous	pH=3(acetate buffer+2.5% R(15 ml)	λmax=700 nm 0 to 20ppm	O_s^{VIII} interfers,seriously	Prior reduction to Ru (III)by alcohol.Heating 15 min at 80°, 1:6 complex	33
31	Promazine hydrochloride	-	1.5M H_2SO_4,4.5 mlof 0.2% R	λmax=515 nm 0.2 to 12ppm S=15.8ng Cm^{-2}	-	Waiting 10 min	34
32	1,(2-pyridylazo)phenanthren -Ol	$CHCl_3$	pH=4.7 to 6.1 Methanolic R	λmax=615,0.8 to 3 ppm,S=4.9 ng Cm^{-2}	Many metal interfere	-	35
33	Promethazine hydrochloride	H_2SO_4 or HCl	-	λmax=515 0.4 to 44 ppm or 6.5to 11.6ppm for HCl H_2SO_4 respectively S=16ng Cm^{-2}in 3HCl & 24 in 1.5M H_2SO_4	-	Tolerance levels are higher in H_2SO_4 medium	36
34	Trifluoperazine dihydrochloride	H_2SO_4 or HCl		λmax=500nm,ϵ =4285, 2 to 8ppm,S=23.3ng Cm^{-2}	thiourea $S_2O_3^{2-}$ Pd^{II} ,Au^{III} , Ag V^V & Ce^{IV} interfere at all conc.	-	37
35	Periodate	Aqueous	2M-KOH,KIO_4(1to2g) 30to 40fold molar excess of R.	λmax=400nm 4to 40 ppm	In,Rh,Os,Pd and Pt interfere	C.V.=1.9%,Heating 50min at 80°.Analysis of catalyst.	38

1	2	3	4	5	6	7	8
36	Chloropromazine hydrochloride	Aqueous	2N-HCl or H_2SO_4 15-fold R	λmax=530nm,0.4 to 12ppm in H_2SO_4 and 0.2to4.8 ppm in HCl	I^-,Fe^{III},Pd^{III}, Ag, Os^{VIII} and Au^{III} interfere	Waiting 20 min stability 55 min std.deviation =0.002	39
37	Acetothioacetanilide	$CHCl_3$	1.2to 4.5N H_2SO_4 0.05 M Ethanolic R	λmax=420 nm,0.9 to 3.1 ppm	Many metals interfere	Heating 30 min at 50°,Reagent blank needed	40
38	Diethazine hydrochloride	Aqueous	H_2SO_4,5ml of aqueous R(0.2%)	λmax=515 nm,2to 9ppm	$S_2O_3^{2-}$,Os^{VIII} Pd^{II},Au^{III},Ce^{IV} Fe^{III} or V^{V}	1:1 complex,C.V. =0.45% at 4 ppm.	41
39	Pyridine-2-aldoxime	Aqueous	pH-4.5,0.05% of aqueous R	λmax=420 nm to 430 nm	-	Boiling 5 min	42
40	Ethyl α-isonitrosoacetoacetate	Benzyl alcohol	pH=4 to 6,10M-Licl(5ml) 2 ml aqueous R(5%)	λmax=470 nm,0.1 to 8 ppm	Fe^{II},Fe^{III} and Cr^{III} need masking with tartrate.Measurement at 540 nm reduces the interference of Pd^{II} Pt^{IV},Rh^{III} and Ir^{IV}	Boiling 15 min std. deviation =0.1 µg at 0.5 ppm	43
41	6-Amino-2-mercapto-5-nitroso-pyrimidin-4-ol	Aqueous	pH=2.8 to 4.8, 5 mM R	max=530nm, =15,300 upto 2.7ppm S=6ng cm-2	Pd^{II}, Hg^{II} and No_2^- interfere	-	44
42	Ferrozine	-	pH=2.5(acetate buffer) 7 ml R (0.02 M)	λmax=480nm upto 2.8 ppm	Many metal interfere	Heating 3hrs	45

1	2	3	4	5	6	7	8
43	-2,2':6',2"-Terpyridyl	-	—	I-Ru(III)-λmax=690nm ϵ=8300,S=12ng Cm^{-2} II=Ru(II) λmax=475nm ϵ=14,500,S=6.9ng Cm^{-2}	-	Std.deviation =0.001 and0.002	46
44	Prochloroperazine maleate	Aqueous	1.5M H_2SO_4,5 ml HCl soln of R 0.2 %	λmax=530nm,ϵ =6733 upto 10 ppm	Many metals interfere	Waiting 1 hr. Reagent blank needed	47
45	Thioridazine hydrochloride	Aqueous	0.75M H_2SO_4 Aqueous R(0.2%)	λmax=640nm ϵ=4580, upto 8ppm,S=22ng Cm^{-2}	Pt-group metals Au^{III},V^{V},Ce^{IV} $S_2O_3^{2-}$ and I^- interfere and HNO_3 oxidises the reagent	Waiting 10 min stability 30 min	48
46	B-Dithionaphtholic acid	$CHCl_3$	pH=5.6(acetate buffer) 1mM ethanolic R(10 ml)	λmax=490nm, ϵ=23,600 0.05 to 2.4 ppm	Os,Pt,Au,Ni,Co and Cu interfere seriously	1:3 complex Heating 30min Reagent blank needed	49
47	5-6-Diphenyl-3-(2-pyridyl -1,2,4-triazine	Aqueous	pH=5(acetate buffer) 2 ml ethanolic R (0.1%)	λmax=485nm,ϵ =21,000 5 to 35 ppm	Numerous ions interfere	Heating 30 min at 85°,1:2 complex	50
48	Glycine	Aqueous	pH=3,0.1N in glycine	For Ru-III λmax=600 to 620nm,ϵ=60,1mM-10mM For Ru(IV)λmax=295nm ϵ=3300 ,0.07 to 9.9mM	Fe,Rh,Pt,Ir, and Pd, interfere	1:3 complex Heating 1 hr, C.V.=$<$2.3 %, Stability=2hrs.	51
49	Arsenazo-I	Aqueous	pH=6,(Hexamine buffer) mM aqueous R(2ml)	λmax=580 nm,upto 7ppm	Many metal ions interfere	Reagent blank needed	52

1	2	3	4	5	6	7	8
50	4,5 Diamino 6-hydroxylpyrimidium sulphate	Aqueous	pH=3.2(acetate buffer)6ml R (0.3 %)	λmax=530 nm, ϵ=6500,upto 20ppm	Other Pt-group metals and transition metals interfere	Heating 75 min std.deviation 1% Reagent blank needed stability=upto 8 days	53
51	3-Nitroso-4-hydroxy-5:6-benzo coumarin	Butanol	pH-5.5to 8, 2M-NaClO$_4$(1ml), 2mM R in acetone (5ml)	λmax=520, 11 to 63 ppm	Co must be absent	Heating 40 min	54
52	2-Amino-3-hydroxy-pyridine	H$_2$O + methanol	pH=5.5(acetate buffer)5 ml methanolic R(0.02M)	max=520 nm, 0.5 to 12ppm S=0.22ug/Cm^{-2}	-	Warming 45 min 1:1 complex stability=3 hrs.	55
53	Phenyl or diphenyl thiourea	CHCl$_3$	4.0M-HCl,15 ml Ethanolic R (0.025M)	λmax=670 nm, 0.28 to 24 ppm	Os interfere	Heating 20 min at 90°	56
54	O-Hydroxythiobenzhydrazide	Aqueous	6.8M HCl,Ethanolic 0.01M R	λmax=540 nm 0.44-8.8 ppm	-	Heating 25-30 min	57

Experimental

Standard Ruthenium (III) Solution :

Standard ruthenium (III) solution was prepared by dissolving 1 g ruthenium (III) chloride hydrate (M/s Johnson Matthey,London), in dilute AR hydrochloric acid (1M) and diluting to 1000 ml with distilled water and then standardised (3).Working solutions of lower concentration were made from it by diluting the stock solution with distilled water as required.

Reagent Solution :

A 0.5 gm of the reagent 5-methyl SAT was dissolved in 100 ml of hot ethyl alcohol to obtain 0.024 M reagent solution.

Standard solutions 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 absorbances measurements were carried out with a specol (Carlzeiss Jena made in Germany DDR)equipped with 1 cm glass or quartz cells.

Recommended Procedure :

To an aliquot of the solution containing 400 µg of ruthenium, enough hydrochloric acid was added so as to make it 6M in a final volume of 25ml followed by the addition of 6 ml ethanolic reagent solution. This solution was heated for 20 min on boiling water bath,cooled and then quantitatively transferred to 25 ml volumetric flask. It was made up to volume with double distilled water. The optical density of ruthenium(III) complex was measured against reagent blank prepared in the same manner excluding ruthenium at 590 nm.

Results and Discussion :

Spectral Properties :

Fig.1 shows the absorption spectrum of ruthenium (III)-5 methyl SAT complex containing 1.58 x 10^{-4} M RUTHENIUM and 5.74 x 10^{-3} M of reagent using the reagent blank. Absorption measurements were made in spectral range 450 to 700 nm. From Fig.1 it is observed that the complex has absorption maximum at 590 nm, at which the molar extinction coefficient is 2398.0 L $mole^{-1}$ cm^{-1}.

Effect of Acidity :

A series of solutions containing 1.58 x 10^{-4} M ruthenium and 5.74 x 10^{-3} M reagent solution but varying in acidity from 4M to 9M were prepared and the absorbance measurements were recorded at 590 nm.

It was observed from fig.2 that the absorbance of the complex at 590 nm was found maximum and constant at 6M HCl.At less than 4M acidity the reaction mixtures becomes turbid and hence the measurements could not be made. However, there is a small decrease in absorbance at higher acid concentration.

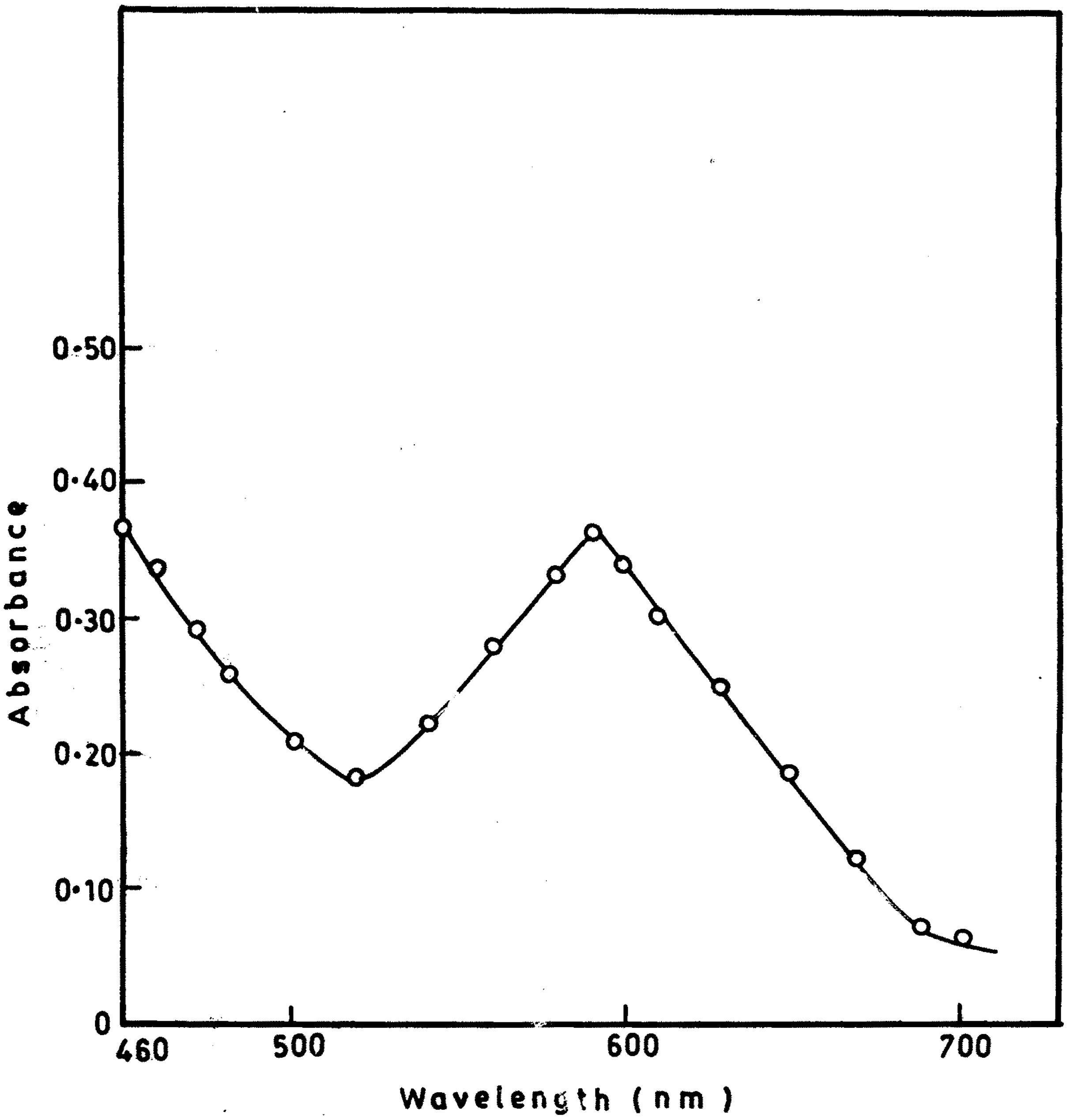

Fig. 1 — ABSORBANCE CURVES OF
Ru(III)-5-METHYL SAT COMPLEX.
Ru(III) : 16 ppm

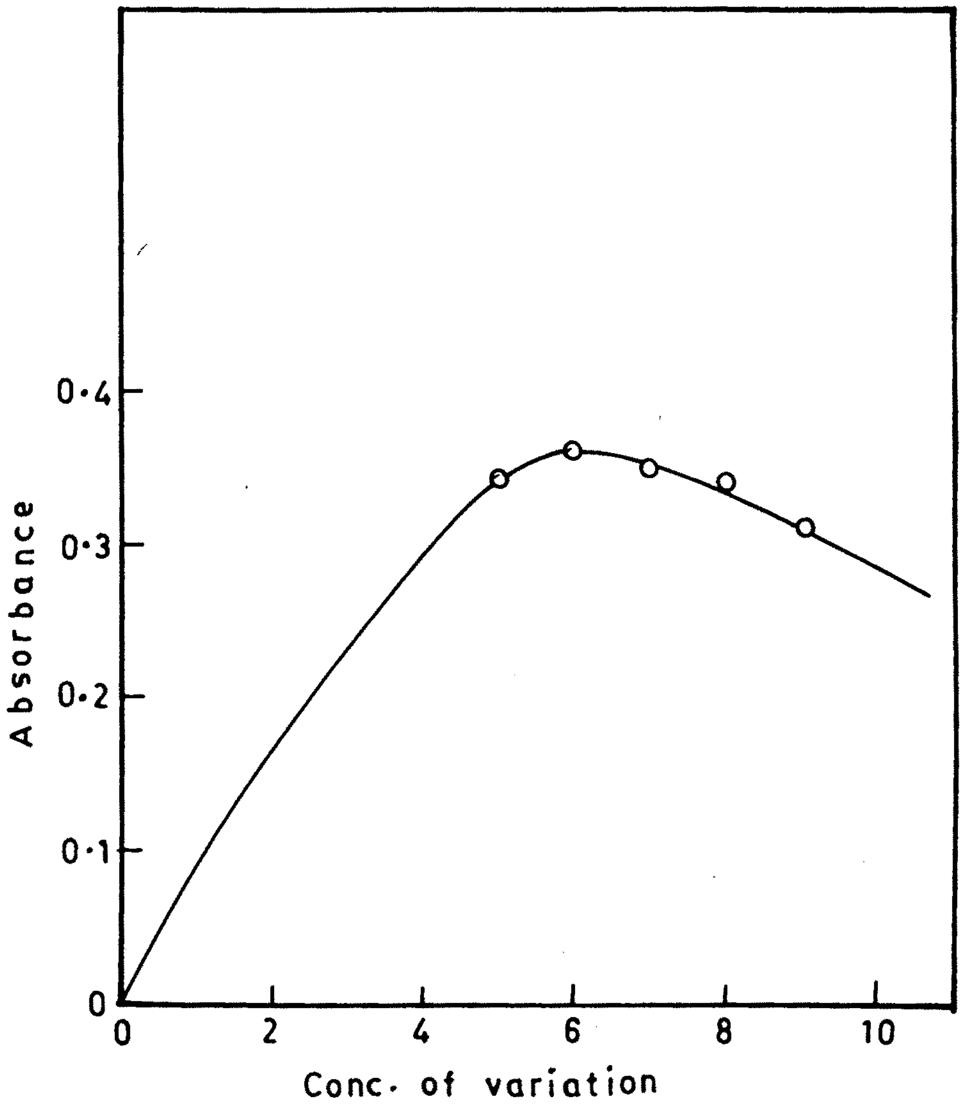

Fig. 2 — EFFECT OF ACIDITY ·

Ru (III) : 16 ppm

Effect of Reagent Concentration:

Solutions containing 1.58 x 10^{-4} M ruthenium (III) but different amounts of reagent varying from 1-10 ml of 0.024 M alcoholic reagent were prepared. Acidity of the solution was adjusted to 6M with hydrochloric acid and heated for 20 min on water bath. After cooling, the solution was made upto 25 ml, with double distilled water. Absorbance measurements were recorded at 600 nm against simultaneously prepared reagent blank. From Fig.3 it is seen that 16 ppm of ruthenium required a 30 mg of reagent dissolved in 6 ml of alcohol for maximum colour development. At this reagent concentration, the reagent to metal ratio in terms of moles is approximately 40:1 . At high reagent concentration the turbidity was formed and the absorbance could not be measured.

Effect of time of heating and Stability of the Complex:

The development of the colour of Ru(III)-5-methyl SAT complex containing 16 ppm of Ru and 6 ml of 0.024 M alcoholic reagent at 6 M HCl was carried out by heating on water bath over a period from 1-60 min. The complex was measured at 590 nm against the simultaneously prepared reagent blank. Results plotted in Fig.4 indicate that, the heating of the aqueous phase for 20 min was enough for complete complexation. But there is no effect of heating on the absorbance of the complex upto 60 min. Heating the aqueous phase for 20 min was recommended for studies.

The absorption measurements were recorded at different time intervals, at 590 nm. It was observed that the absorbance of the complex remained constant over a period 6 hours. Hence the time of absorbance measured is not critical.

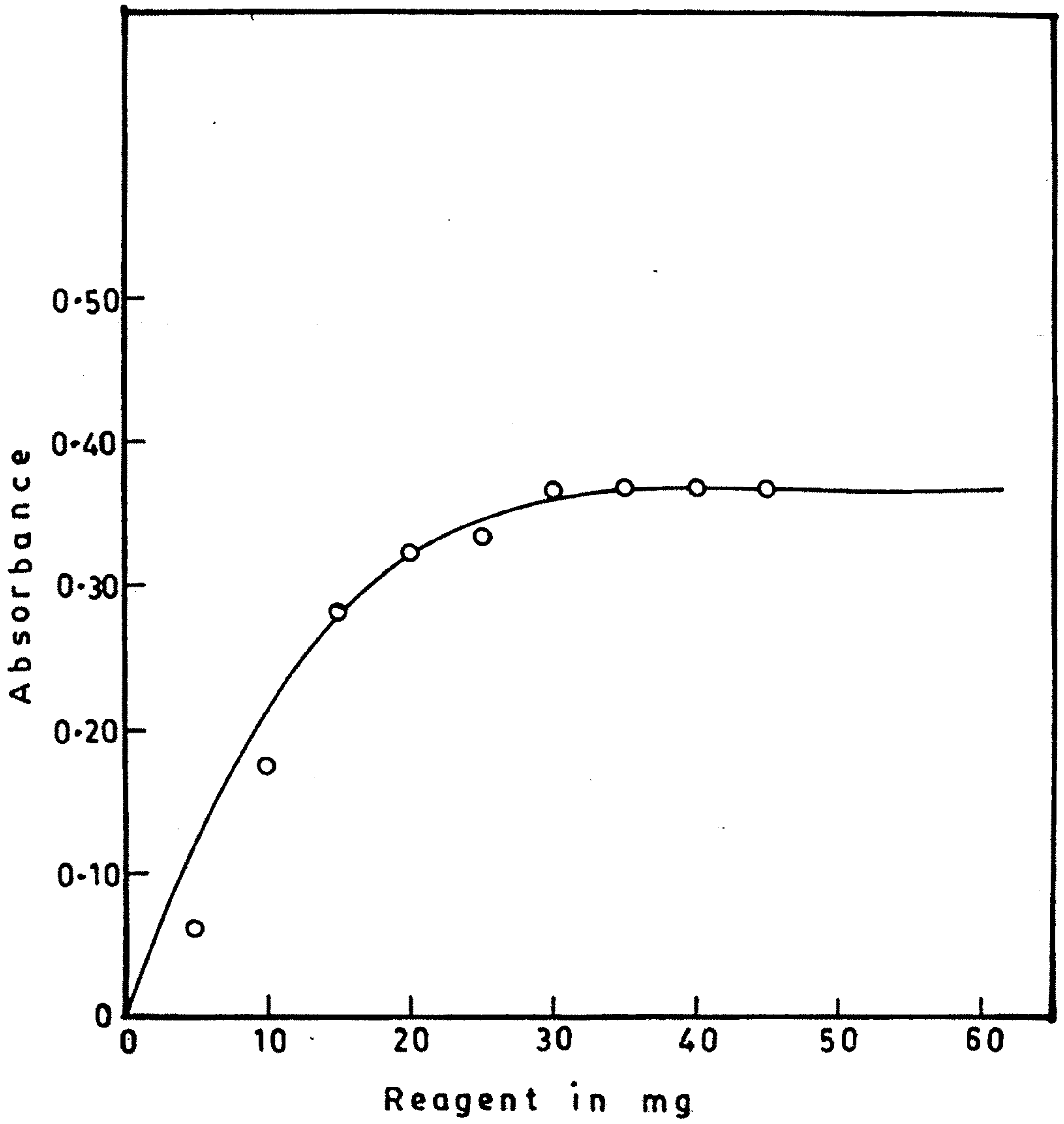

Fig. 3 — EFFECT OF REAGENT CONCENTRATION .

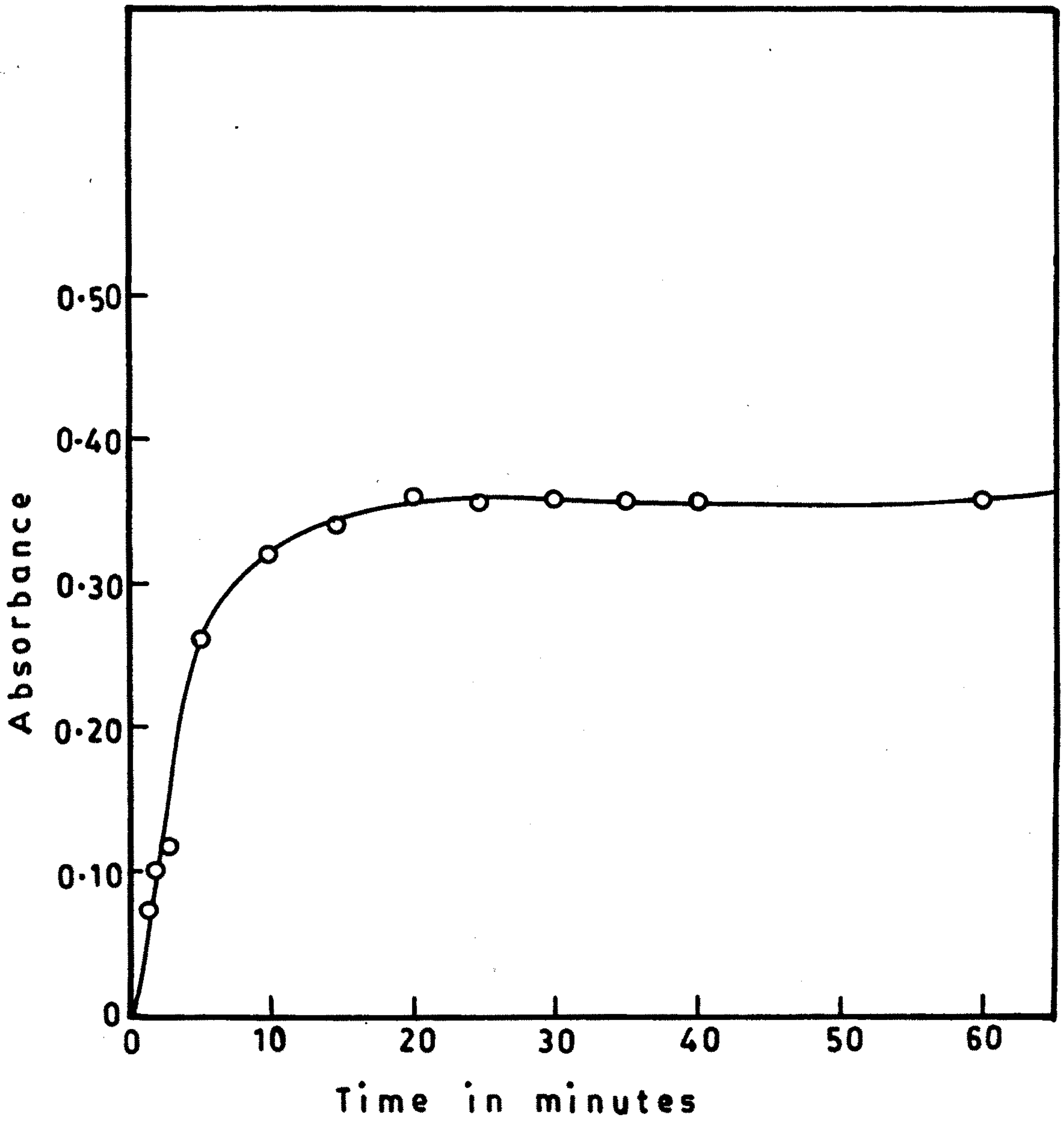

Fig. 4 — EFFECT OF TIME OF HEATING.

Ru(III) : 16 ppm

Effect of Alcohol :

In order to find out the amount of alcohol needed during the complexation of Ru(III)-5-methyl SAT complex, the amount of alcohol was varied between 1-10 ml in a total volume of 25 ml. It was found from fig.5 that the absorbance of the complex remained maximum and constant between 3-8 ml alcohol in the reaction mixture. Hence 6 ml of alcohol was recommended for future studies.

Study of Validity of Beer's Law :

The solutions containing ruthenium (III) in the concentration range from 2-24 ppm were used for the study of Beer's law. The colour of the complex was developed as described in general procedure using 5.74×10^{-3}M reagent and 6M HCl and was measured at 590 nm against simultaneously prepared reagent blank. The absorbance was plotted against the ppm of Ru(III) taken (Fig.6). The curve indicates that, there is a rectilinerar relationship between the absorbance and the concentration of ruthenium(III) in the range 2-20 ppm.

The Sandell sensitivity (Sg) of the reaction as calculated from Beer's plot is found to be 42 ng Ru(III) cm^{-2} at 590 nm for log Io/I= 0.001.

Reproducibility, Accuracy and Precision :

For the study of reproducibility and accuracy of the method, absorbance measurements with 10 different identical solutions containing 16 ppm ruthenium(III) each, were performed as per recommended procedure and concentrations was determined by using calibration curve. The results are shown in Table-2.

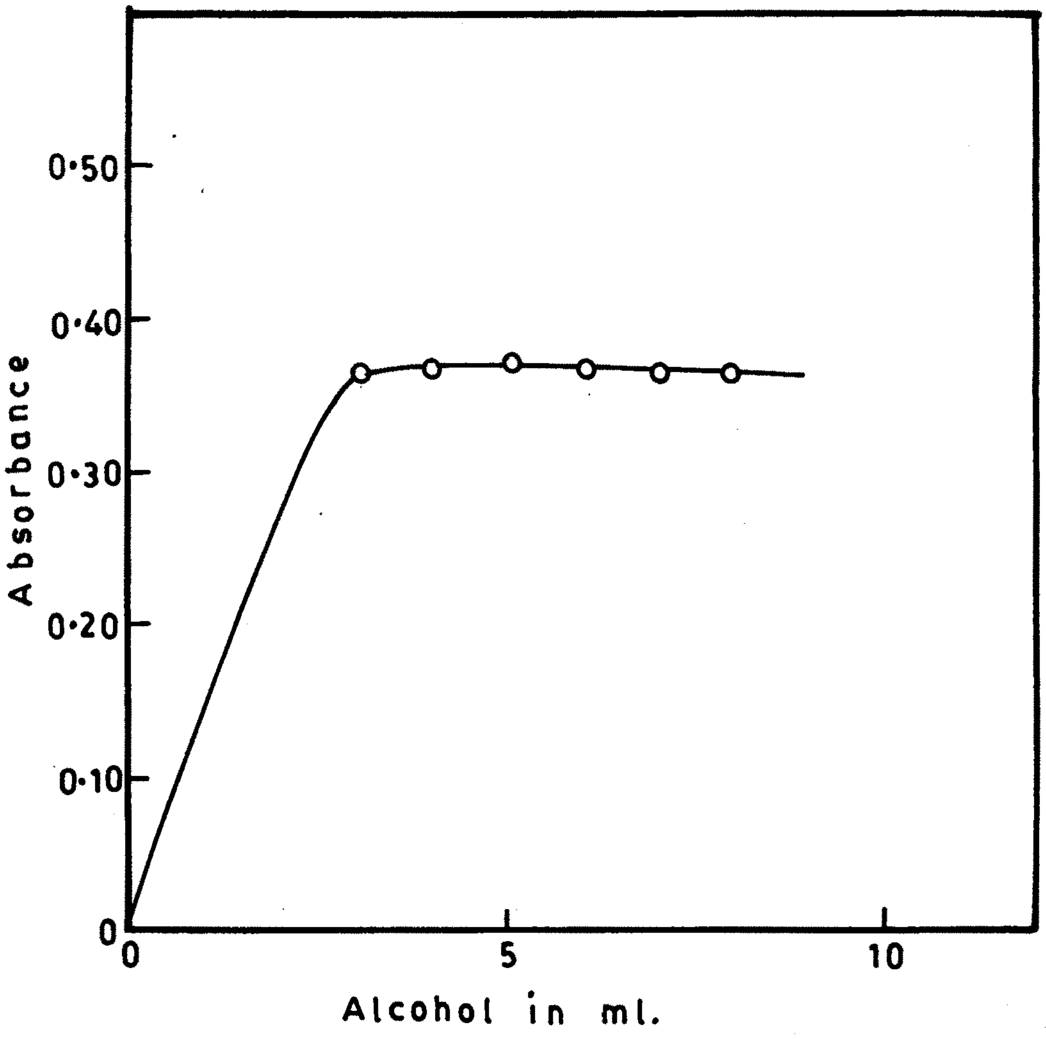

Fig. 5 — EFFECT OF ALCOHOL.

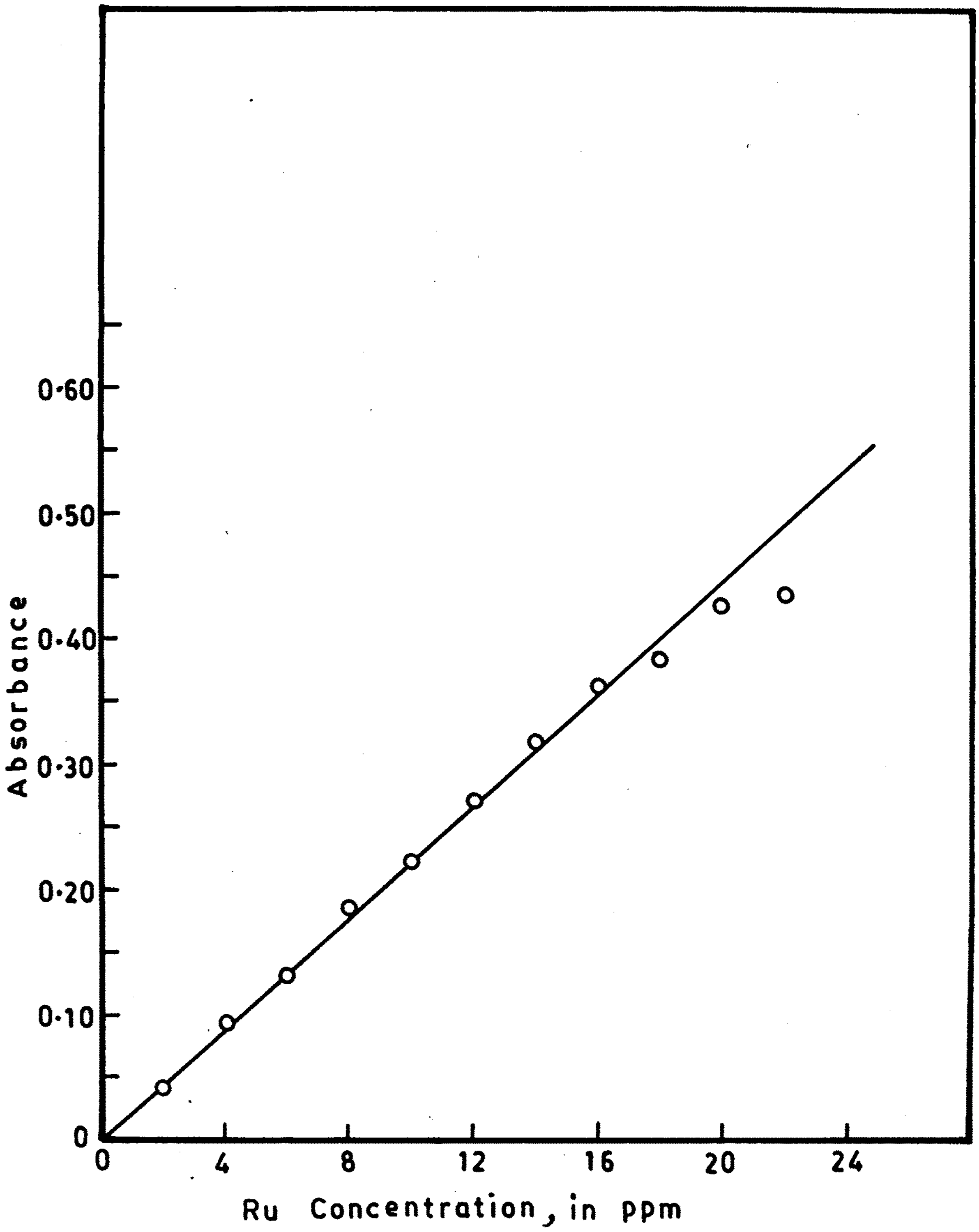

Fig. 6 — VALIDITY OF BEER'S LAW FOR Ru(III)-5-METHYL SAT COMPLEX.

Table No.2: Precision and Accuracy of the Method

Amount of Ru(III): 16 ppm; 5 Methyl SAT = 5.74×10^{-3}M
Aqueous phase = 6M HCl, λmax = 590 nm

Sr.No.	Absorbance observed	ppm of Ru(III) found X	$X - \bar{X}$	$(X-\bar{X})^2$
1	0.385	15.88	- 0.06	0.0036
2	0.38	16.01	+ 0.07	0.0049
3	0.375	15.80	- 0.14	0.0196
4	0.37	15.58	- 0.36	0.1296
5	0.385	16.29	+ 0.35	0.1225
6	0.38	16.01	+ 0.07	0.0049
7	0.375	15.80	- 0.14	0.0196
8	0.382	16.08	+ 0.14	0.0196
9	0.39	16.43	+ 0.49	0.2401
10	0.37	15.58	- 0.36	0.1296
		$X = 159.46$		0.694
		$\bar{X} = \frac{159.46}{10}$		0.0694 mean
		$\bar{X} = 15.94$		

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

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

$$= \sqrt{\frac{0.694}{9}}$$

$$= \sqrt{0.07711}$$

$$= 0.2776$$

Reproducibility with 95% Confidence limit :

$$\bar{x} \pm 2.26 \times \frac{\delta}{n}$$

$$= 15.94 \pm 2.26 \times \frac{0.2776}{9}$$

$$= 15.94 \pm 0.0665$$

Error = Observed value - Actual value

= 15.44 - 16.00

= 0.06

% Relative Error (Accuracy)

$$= \frac{E \times 100}{10}$$

$$= \frac{0.06 \times 100}{10}$$

$$= 0.6 \%$$

Molar Extinction Coefficient :

$$\epsilon = \frac{A}{C \times l}$$

$$= \frac{\text{Absorbance} \times 1000 \times \text{At. Wt.}}{\text{ppm}}$$

$$= \frac{0.36 \times 1000 \times 101}{16}$$

$$= 2272.5 \ \text{l mol}^{-1} \ \text{cm}^{-1}$$

ϵ from graph = Slope x 1000 x 96

$$= 2398 \ \text{l mol}^{-1} \ \text{cm}^{-1}$$

Sandell's Sensitivity :

$$S = 10^3 \times \text{At.wt} \times C \qquad C = \frac{D \text{ min}}{E \times b}$$

$$= 10^3 \times 101 \times \frac{0.001}{2398 \times 1}$$

$$= 0.042 \ \mu g/\ cm^2$$

$$= 42 \ ng \ cm^{-2}$$

% Coefficient of Variation

$$C.V. = \frac{\delta \times 100}{\bar{X}} \qquad \delta = \text{Std.deviation}$$

$$= \frac{0.2776 \times 100}{15.94}$$

$$= 1.7415$$

Effect of diverse ions:

The effect of diverse ions was studied using 0.4 mg Ru(III) and 5.74×10^{-4} M reagent in final volume of 25 ml at 6 M acidity. An error of less than 2 % in absorbance was considered to be tolerable. The samples were prepared as outlined in the general procedure. The absorbance was measured at 590 nm against reagent blank. The tolerance for the various foreign ions tolerated is shown in Table-3.

It was observed that the cations which did not interfere when present in 10 fold excess relative to Ru(III) were Co(II), Fe(III), Ni(II), Mg(II), K(I),Al(III),Ba(II), W(VI),V(V),Ca(II), Zn(II), Na(I), Li(I),Sn(II),Fe(II),Sb(III),Be(II),As(III),Mo(VI), The cations which are tolerable in 1:1 ratio were Pd(II), Os(VIII), Rh(IV),U(VI). The ions showing interference were Cu(II),Hg(II), Ce(IV),Cd(II),Bi(III), Se(IV), In (III), Tl(I),Pt(IV),Au(III),and thiosulphate.Relatively large amounts of anions could be tolerated in the determination of 0.4 mg of Ru(III).

Table No.3 : <u>Effect of Diverse Ions</u>

Ru(III) = 400 ug; 5-Methyl SAT = 5.74×10^{-3} M
Aqueous phase = 6M HCl, λmax= 590 nm

o. Foreign ion added	Toleronce limit in mg	Sr. No.	Foreign ion added	Tolerance limit inmg
Co (II)	5	23	U(VI)	1
Cu(II)	Interfere	24	Sn(II)	5
Fe(III)	5	25	Fe(II)	5
Ni(II)	5	26	Sb(III)	5
Mg(II)	5	27	Be(II)	5
K(I)	5	28	In(III)	Interfere
Al(III)	5	29	Mo(VI)	5
Ba(II)	5	30	Pd(II)	1
Hg(II)	Interfere	31	Pt(IV)	Interfere
W(VI)	5	32	Os(VIII)	1
Pb(II)	Interfere	33	Rh(III)	1
V(V)	5	34	Au(III)	Interfere
Ce(II)	Interfere	35	Oxalate	100
Cd(II)	Interfere	36	Thiosulphate	Interfere
Bi(II)	Interfere	37	EDTA	100
Tl(I)	Interfere	38	Acetate	100
Ca(II)	5	39	Citrate	100
Se(IV)	Interfere	40	$-NO_2$	Interfere
Zn(II)	5	41	thiourea	100
Na(I)	5	42	thiocynate	Interfere
Li(I)	5	43	pot dihydrogen	100
As(III)	5			

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