CHAPTER - IV

DETERMINATION OF RUTHENIUM (III)

4.1 INTRODUCTION

The common valence states for ruthenium are (II), (III) and (IV). Its complexes are usually octahedral. Ru(III) occurs as the volatile oxide RuO_4. Most of the analytically important reactions of ruthenium involve Ru(III).

Ruthenium finds wide applications as a versatile catalyst in organic synthesis. It is one of the most effective hardeners in high density alloys. It is alloyed with other platinum metals to make electrical contacts for severe wear resistances. It is also used in jewellery. It is resistant to common acids including aqua-regia. It may be electrodeposited from molten salt bath for electroplating of brass metals. Complex ruthenium alloys with and without osmium, are very hard and are used for pen tips, nonmagnetic instrument pivots and similar items. Because of its commercial importance, numerous reagents have been proposed for its spectrophotometric determination. The various methods differ considerably in sensitivity selectivity, tolerance limits of cations and anions, rate of reactions, useful concentration range, stability etc. and there appears to be scope for the development of further procedures giving good sensitivity and accuracy.

Beamish[1] has reviewed the reagents used upto 1965 for the spectrophotometric determination of ruthenium. One of the widely utilised photometric methods for Ru(III) is based upon the formation of the blue complex with thiourea[2] in an alcoholic acid 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) and Pd(II) interfere and the sensitivity is low.

Several modified procedures have been developed. Dithio-oximide[3], p-nitrosodimethylaniline[4] and 1,10-phenanthroline[5] are largely used for determination of Ru(III). The use of dithio-oxamide[6] has been recommended for the extractive photometric determination of Ru(III). 1-Naphthylamino-3, 5,7-trisulphonic acid[7] (S = 100 μg/cm^2) and 2-mercaptobenzimidazole[8] (S = 50 μg/cm^2) are less sensitive. 1-Nitroso-2-naphthol[9] and 2-nitroso-1-naphthol[10] have been used for determining Ru(III) in HCl-H$_2$SO$_4$ medium. Acenaphthenequinone mono-oxime[11] is highly sensitive but many anions including EDTA, hydroxylamine, tartrate, citrate, thiocyanate interfere. Pyridine-2-aldoxime[12] and thiophene-2-carboxaldoxime[13] methods suffer interference from many metal ions and also low tolerance limit for platinum metals. Benzil-α-oxime[14] method requires to keep the reaction mixture for 1 hour for full colour development. Isonitroso benzoyl acetone[15] extracts Ru(III) into MIBK at pH 3.5-4.5 and is measured at 470 nm but Pt(IV), Pd(II) and Fe(III) interfere.

Recently, thiocyanate[16] method has been successfully used for the extraction, separation and spectrophotometric determination of ruthenium and osmium. Oximidobenzotetronic acid[17], thio-salicylamide[18] and 8-quino-linol[19] have been used for determination of Ru(III). But these methods are less sensitive. Diphenylthiovioluric acid[20] reagent is quite selective only in presence of masking agents. Rhodamine 6G thiocyanate[21] and furil-α-dioxime[22] methods suffer from the interferences of platinum metals and base metals.

Sanke Gowda et al. have reported a series of organic azine compounds including promethazine hydrochloride[23], chlorpromazine

hydrochloride[24], thioridazine hydrochloride[25], diethazine hydrochloride[26], trifluoperazine dihydrochloride[27], mepazine hydrochloride[28] and phenothiazone[29] for photometric determination of Ru(III) in aqueous acid medium. Various organic thiohydrazides[30-32] have been explored as analytical reagents by Shome et al. These reagents are highly sensitive but lack selectivity and require longer time of heating for full colour development.

In case of some reagents, the heating of the aqueous phase is necessary for attaining full colour intensity of the ruthenium complex e.g. 3-nitrosopyridine-3,6-diol[33] (1 hour), 3,4-diamino benzoic acid[34] (1 hour) glycine[35] (1 hour), ferrozine[36] (3 hours), 2-methyl-1,4-naphthaquinone monoxime[37] (90 minutes), diphenylcarbazone[38] (45 minutes) β-dithionaphthoic acid[39] (30 minutes), acetothio acetanilide[40] (30 minutes), furfil-α-monoxime[41] (10 minutes), tropolone[42] (16 minutes), ammonium thiocyanate[43] (16 minutes), N-phenyl N'-acetylthiourea[44] (10 minutes), 2-thiobarbituric acid[45] (35 minutes) and 3-hydroxy-2-methyl-1,4-naphthaquinone monoxime[46] (45 minutes).

Serious interferences are observed either of platinum or base metals or both in the determination of Ru(III) with the reagents such as nitroso-R-salt[47], anthranilic acid[48], 3-nitrosopyridine-2,6-diol[33], glycine[35], β-dithionaphthoic acid[39], acetothio acetanilide[40] etc. As the complexation reaction of Ru(III) with some reagents are found to be slow, waiting is required for full colour intensity of the complex e.g. selenourea[49] (30 minutes), peroxide-EDTA[50] (10 minutes) etc.

Recently, Ru(III) was determined spectrophotometrically with the reagents such as 2-(5-bromo-2-pyridylazo) 5-(N-propyl-3-sulpho-propylamine) phenol[51], 3-phenylazohydroxylamine[52], porphyrin[53], rhodamine 6 G[54],

ethylisobutrazine hydrochloride[55], α, β, γ, δ -tetrakis(3-methoxy-4-hydroxy-phenyl) porphine[56], 2-2'dipyridyl and 1-10 phenanthroline[57], bis(thiophene-2-aldehydo) tricarbohydrazone[58], meso-tetrakis(p-sulfophenyl) porphyrin[59], n-amylthioglycolate[60] and halogen derivatives of mono and bisphenylazo chromotropic acid[61].

Ru(III) was determined by extractive photometric method by various analytical reagents such as isonitrosomalondianilide[62] and 2,4,6-tris(2-pyridyl) -1,3,5-triazine[63] and picrate. The extraction of thiocyanato complexes of Ru(III) by bis(2-ethylhexyl) amine[64] in 1,2-dichloroethane was also studied.

By spectrophotometric method, ruthenium(III) was determined as Ru(III)-SCN-rhodamine 6 G ternary complex[65] system, Ru(III)-SnCl$_2$-crystal violet[66] system, Ru(III)-SnCl$_2$-malachite green[67] system and Ru(III)-thiocyanate ethyl violet[68] system.

Catalytic spectrophotometric determination of ruthenium was studied by oxidation of phthalin[69] with H$_2$O$_2$ and oxidation of benzylamine[70] by alkaline hexacyanoferrate(III). A new method was established based on the catalytic effect of Ru(III) on the oxidative fading between 3-(4-carboxyl azobenzene)-6(4-acetylcarboxylazo-p) and potassium periodate[71].

However, the present method is free from the disadvantages mentioned for the above methods. The method is highly selective, simple and reproducible. The proposed reagent 2-benzoyl pyridine guanylhydrazone (BPG) reacts with Ru(III) in aqueous acidic medium in presence of potassium thiocyanate to form reddish violet coloured complex. The complex is measured at 520 nm against reagent blank. The method is applicable for the multicomponent synthetic mixtures.

4.2 EXPERIMENTAL

4.2.1 Standard Solutions :

Standard ruthenium (III) solution :

A stock solution of Ru(III) (1 mg/ml i.e. 9.894 x 10^{-3}M) was prepared by dissolving 0.259 g of ruthenium(III) chloride trihydrate (M/s. Johnson Matthey, London) in 1 M analar hydrochloric acid and diluting to 100 ml with distilled water and then was standardised[72]. Working solutions of lower concentration were made from it by diluting the stock solution with distilled water as required.

Reagent (BPG) solution :

0.6 mg/ml in distilled ethyl alcohol (2.5 x 10^{-3}M).

Buffer solution :

Buffer solution was prepared by dissolving appropriate amounts of sodium hydroxide.

Potassium thiocyanate solution :

2.0 % KCNS in distilled water.

4.2.2 Recommended Procedure :

An aliquot of the solution containing 250 μg of ruthenium(III) was taken in a 10 ml volumetric flask. To it, were added 3.0 ml of the reagent (BPG) solution of concentration 2.5 x 10^{-3}M and 2.5 ml of 2.0 % KCNS solution. The pH of the solution was adjusted to 4.0 with buffer solution. It was then diluted upto the mark with distilled water. The absorbance of the ruthenium(III)-BPG complex was measured at 520 nm against reagent blank. The concentration of ruthenium in an unknown solution was determined from a calibration curve obtained under identical conditions.

4.3 RESULTS AND DISCUSSION

4.3.1 Spectral Characteristics :

The absorption spectrum of Ru(III)-BPG complex (2.0×10^{-4}M) was recorded at pH 4.0 against reagent blank. (Table 4.1; Figure 4.1). The complex has absorption maximum at 520 nm and molar extinction coefficient of the complex is 0.2650×10^4 l mole^{-1}cm^{-1}. The molar extinction coefficient of the reagent blank at 520 nm is negligible i.e. 0.004×10^4 l mole^{-1}cm^{-1}.

Table 4.1 : Absorbances and molar extinction coefficients of Ru(III)-BPG complex and reagent (BPG)

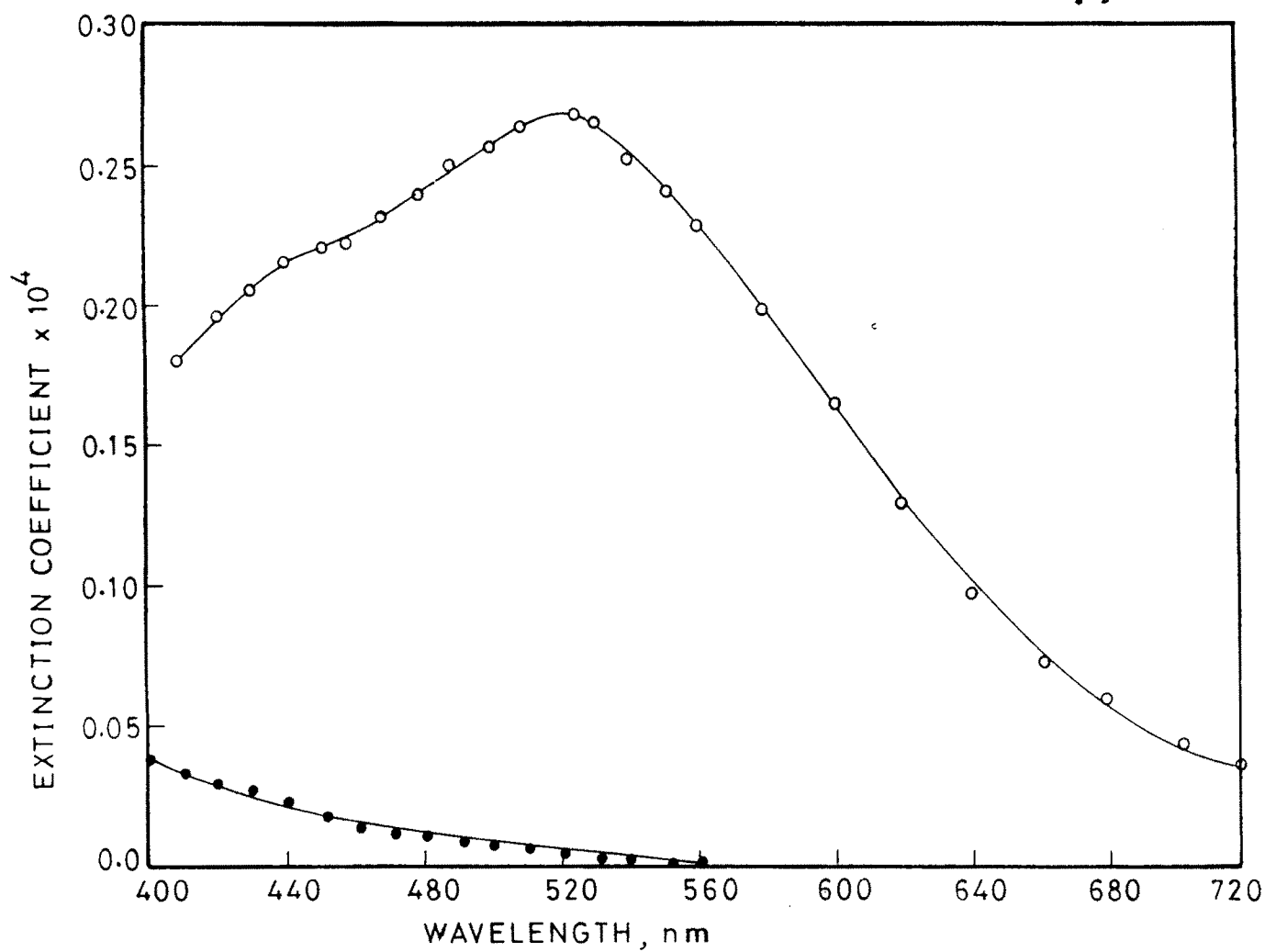| Wavelength λ, nm	Absorbance		Molar extinction coefficient, $\in$	
	Ru(III)-BPG complex 2.0x10^{-4} M	BPG, reagent 2.5x10^{-4} M	Ru(III)-BPG complex $\in$ x10^4 l mole^{-1}cm^{-1}	BPG, reagent $\in$ x10^4 l mole^{-1}cm^{-1}
400	0.340	0.095	0.1700	0.0380
410	0.360	0.090	0.1800	0.0360
420	0.390	0.075	0.1950	0.0300
430	0.410	0.065	0.2050	0.0260
435	0.420	0.060	0.2100	0.0240
440	0.430	0.055	0.2150	0.0220
450	0.440	0.045	0.2200	0.0180
460	0.445	0.035	0.2225	0.0140
470	0.460	0.030	0.2300	0.0120
480	0.480	0.030	0.2400	0.0120
490	0.500	0.025	0.2500	0.0100
500	0.510	0.020	0.2550	0.0080
505	0.520	0.020	0.2600	0.0080
510	0.525	0.015	0.2625	0.0060
515	0.530	0.015	0.2650	0.0060
520	0.530	0.010	0.2650	0.0040
525	0.530	0.010	0.2650	0.0040
530	0.525	0.010	0.2625	0.0040
535	0.510	0.010	0.2550	0.0040
540	0.500	0.005	0.2500	0.0020
550	0.480	0.005	0.2400	0.0020
560	0.460	–	0.2300	–
580	0.400	–	0.2000	–
600	0.330	–	0.1650	–
620	0.260	–	0.1300	–
640	0.195	–	0.0975	–
660	0.150	–	0.0750	–
680	0.120	–	0.0600	–
700	0.090	–	0.0450	–
720	0.070	–	0.0350	–

FIG. 4·1 — o——o   ABSORPTION SPECTRUM OF RUTHENIUM (III)-BPG COMPLEX.

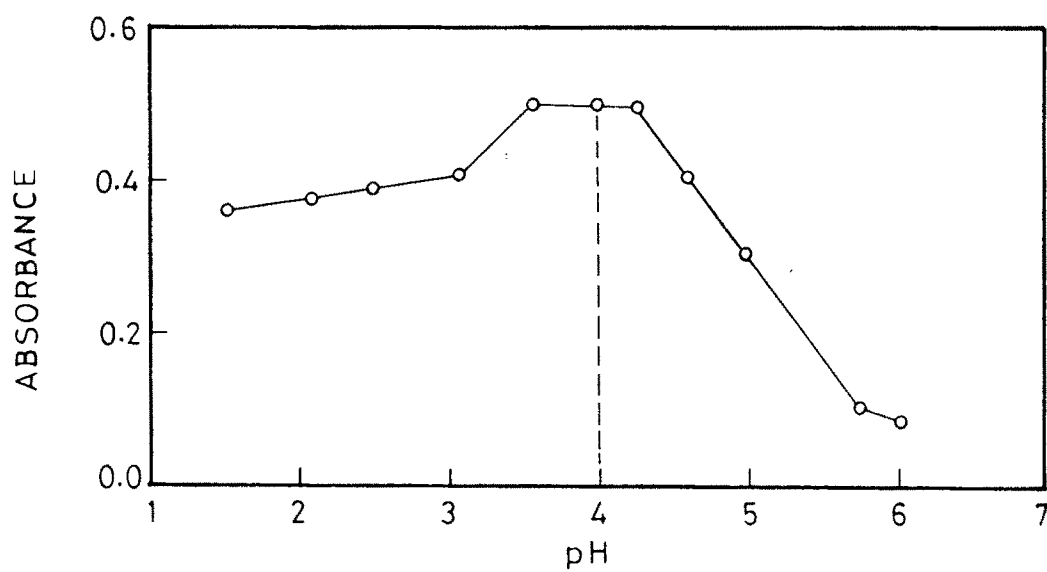●——●   ABSORPTION SPECTRUM OF REAGENT (BPG).

FIG. 4·2 —   EFFECT OF pH.

4.3.2 Effect of pH :

A series of solutions of different pH from 1.5 to 6.0 was prepared as per the recommended procedure. It was found that complex shows maximum and constant absorbance from pH 3.6 to 4.3 in acidic medium (Table 4.2; Figure 4.2). And therefore the study of ruthenium(III)-BPG complex was carried out at pH 4.0.

Table 4.2 : Effect of pH

$[Ru(III)] = 2.47 \times 10^{-4}M; \quad [BPG] = 7.5 \times 10^{-4}M$

pH	Absorbance at 520 nm
1.5	0.36
2.1	0.38
2.5	0.39
3.1	0.40
3.6	0.50
4.0	0.50
4.3	0.50
4.6	0.40
5.0	0.30
5.7	0.10
6.0	0.08

4.3.3 Effect of Reagent Concentration :

A series of solutions containing constant concentration of ruthenium $(2.47 \times 10^{-4}M)$ and different amounts of reagent (BPG) ranging from 0.4 ml

to 3.5 ml of 2.5 x 10^{-3}M concentration were prepared. Complex was developed as per recommended procedure and its absorbance was measured at 520 nm. Results in table 4.3 show that three fold molar excess of the reagent was sufficient for full colour development of 25.0 ppm of ruthenium (Figure 4.3).

Table 4.3 : Effect of reagent concentration

$[Ru(III)]$ = 25.0 ppm; $[BPG]$ = 2.5 x 10^{-4}M

Amount of BPG added, ml	Absorbance at 520 nm
0.4	0.34
0.8	0.38
1.0	0.40
1.4	0.43
1.8	0.45
2.0	0.47
2.5	0.49
3.0	0.52
3.5	0.52
4.0	0.52
4.5	0.52

4.3.4 Effect of Potassium Thiocyanate Concentration :

A series of solutions were prepared in which the volume of 2.0 % KCNS was varied from 0.4 ml, to 4.0 ml, while the concentration of ruthenium (2.47 x 10^{-4}M) and 3.0 ml of reagent, BPG (2.5 x 10^{-4}M) were
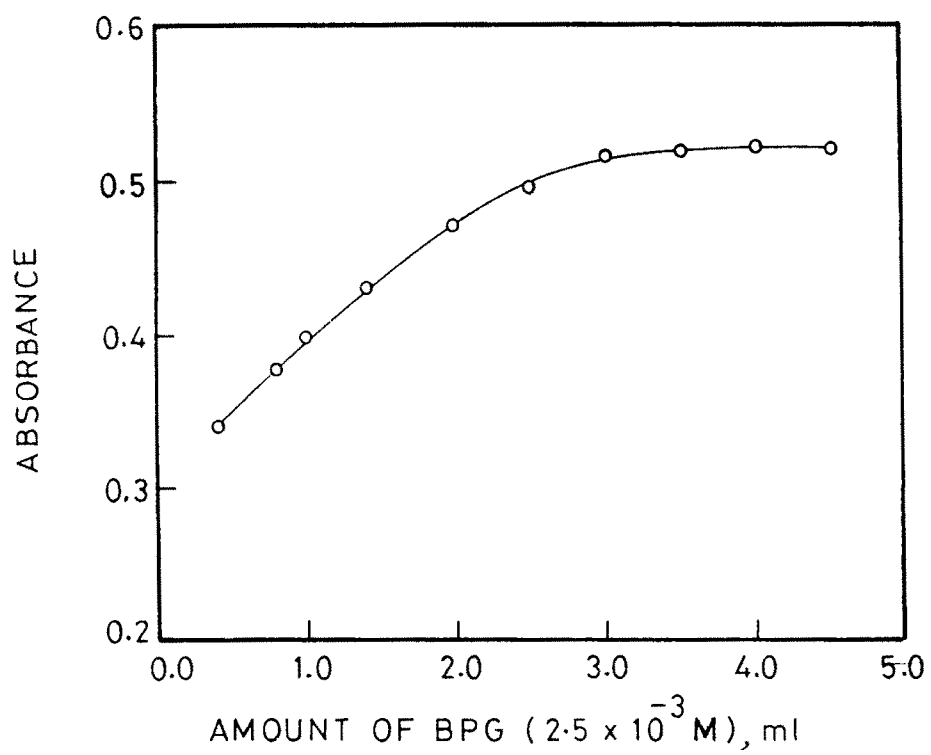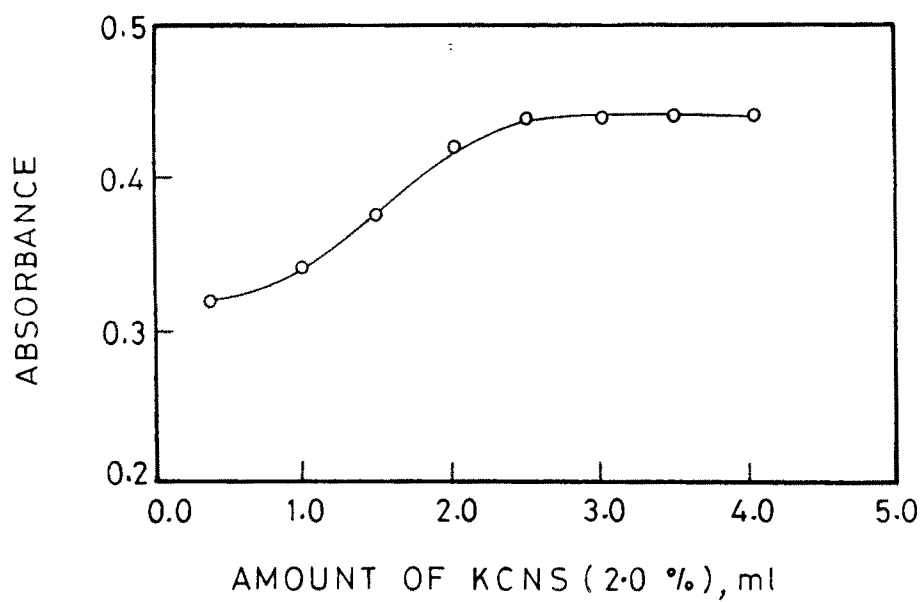
FIG. 4·3 — EFFECT OF REAGENT CONCENTRATION.

FIG. 4·4 — EFFECT OF KCNS CONCENTRATION.

kept constant. The complex was developed as per recommended procedure. The results in table 4.4 show that 2.5 ml of 2.0 % KCNS was sufficient for full colour development of Ru(III)-BPG complex (Figure 4.4).

Table 4.4 : Effect of potassium thiocyanate concentration

$[Ru(III)]$ = 25.0 ppm; $[BPG]$ = 7.5 x 10^{-4}M; KCNS = 2.0%

Amount of KCNS added, ml	Absorbance at 520 nm
0.4	0.32
0.8	0.33
1.0	0.34
1.5	0.37
2.0	0.42
2.5	0.44
3.0	0.44
3.5	0.44
4.0	0.44

4.3.5 Stability and Reaction Rate :

Complex formation of Ru(III)-BPG is instantaneous and colour of the complex is stable for several hours. Complex formation is independent of temperature.

4.3.6 Validity of Beer's Law :

The measurement of the absorbance of Ru(III)-BPG complex at pH 4.0 containing varying amounts of ruthenium and same amount of reagent (BPG) i.e. 3.0 ml of 2.5 x 10^{-4}M showed that Beer's law is valid upto 33.0 ppm of Ru(III) (Table 4.5; Figure 4.5).
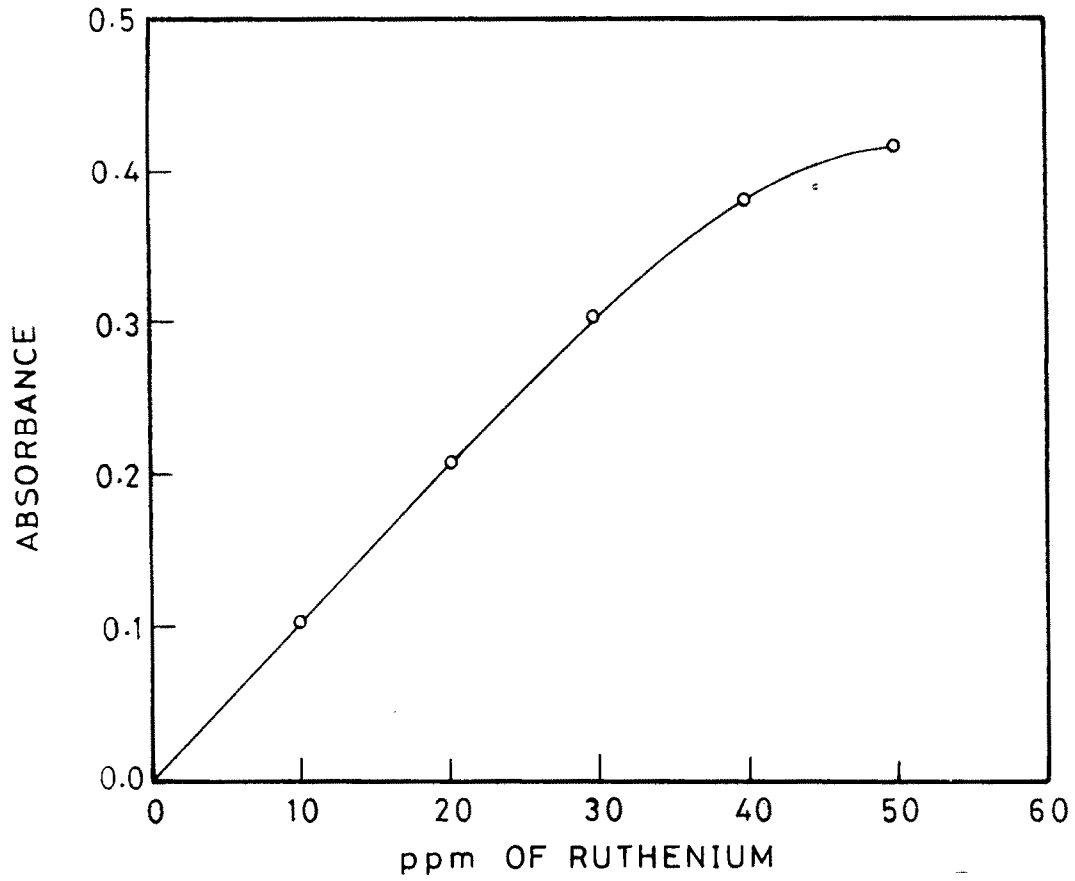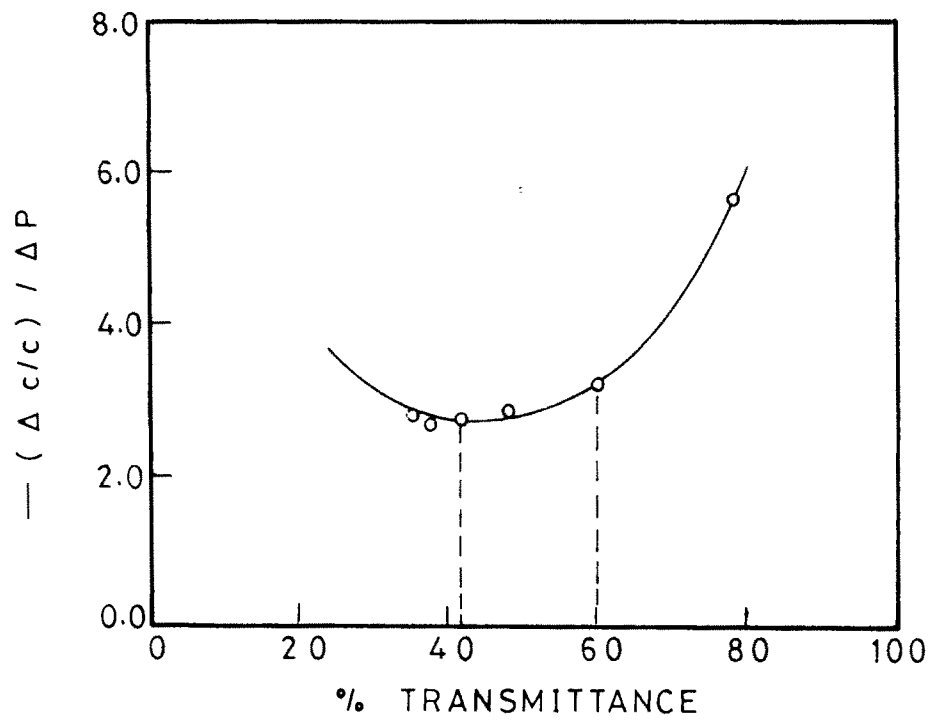
FIG. 4·5 — VALIDITY OF BEER'S LAW.

FIG. 4·6 — RINGBOM PLOT.

The optimum concentration range for ruthenium was studied from Ringbom Plot[73] (Figure 4.6) and was found to be 20.0 to 30.0 ppm at the conditions chosen for the experiment.

Table 4.5 :   Validity of Beer's law

$$[BPG] = 7.5 \times 10^{-4}M$$

Amount of Ru(III), ppm	Absorbance at 520 nm	Transmittance, %	$-(\Delta c/c)/\Delta P$
10.0	0.105	78.5	5.60
20.0	0.210	61.6	3.26
30.0	0.310	49.0	2.88
40.0	0.375	42.2	2.75
50.0	0.410	38.9	2.73
60.0	0.440	36.4	2.77

4.3.7   Composition of the Complex :

The combining ratio of BPG to Ru(III) was determined by Job's method of continuous variation[74], mole ratio method[75] and slope ratio method[76]. For Job's method, a series of solutions were prepared by mixing equimolar solutions of ruthenium and reagent (BPG) in which mole fraction of the reagent was kept between 0.1 to 0.9 keeping all other parameters constant.   The reddish violet complexes at pH 4.0 were measured against a reagent blank.   The plot of the absorbance at 520 nm against mole fraction of the reagent indicated a 1:2 complex (Figure 4.7).   The observations were recorded at $2.0 \times 10^{-4}M$ concentration (Table 4.6).

In mole ratio method, equimolar solutions of BPG and ruthenium were mixed to give a series of solutions in which mole ratio of the reagent to ruthenium was varied from 0.0 to 4.0 ml of concentration 2.0×10^{-4}M (Table 4.7). The absorbance curve at 520 nm confirms that metal ion to ligand ratio is 1:2 of the formation of complex. (Figure 4.8). Slope ratio method also confirms 1:2 complex of Ru(III)-BPG.

Table 4.6 : Job's continuous variation method

$$[Ru(III)] = [BPG] = 2.0 \times 10^{-4}M$$

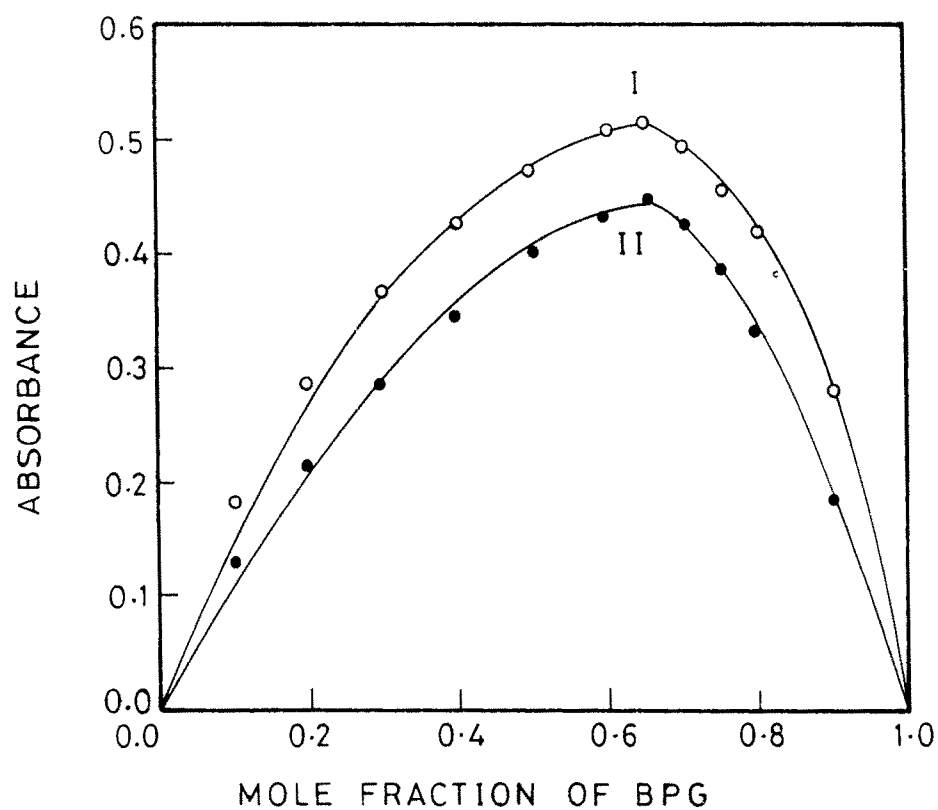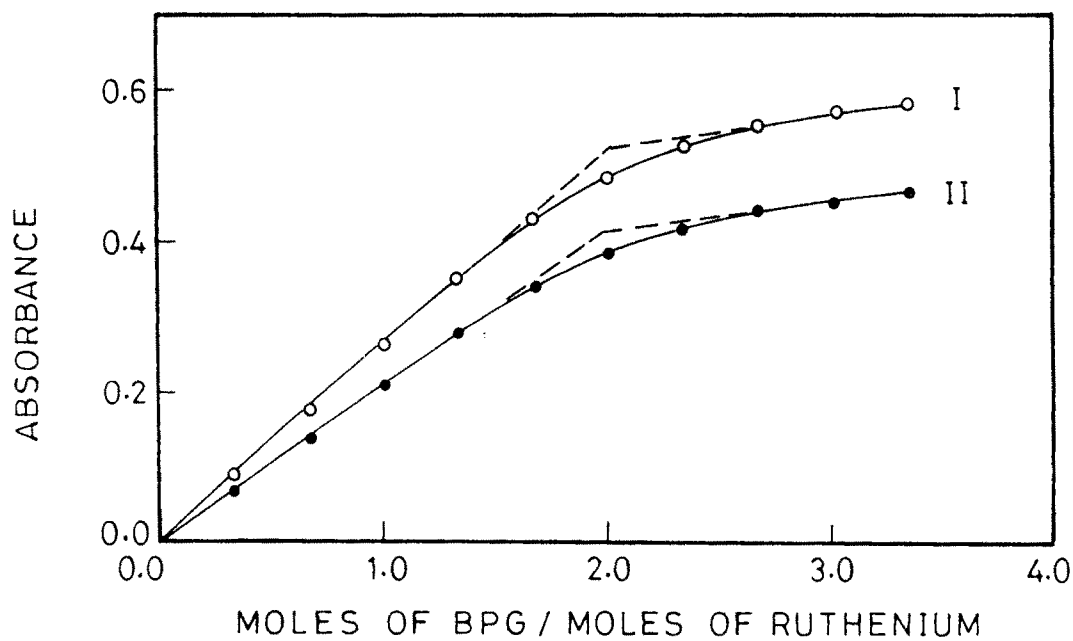| [Ru(III)], ml	[BPG], ml	$\dfrac{[BPG]}{[Ru(III)] + [BPG]}$	Absorbance at λ	
			520 nm	540 nm
4.0	0.0	-	-	-
3.6	0.4	0.10	0.185	0.130
3.2	0.8	0.20	0.285	0.215
2.8	1.2	0.30	0.375	0.285
2.4	1.6	0.40	0.430	0.340
2.0	2.0	0.50	0.470	0.395
1.6	2.4	0.60	0.505	0.435
1.33	2.66	0.66	0.510	0.445
1.2	2.8	0.70	0.495	0.420
1.0	3.0	0.75	0.460	0.385
0.8	3.2	0.80	0.415	0.330
0.4	3.6	0.90	0.285	0.185
0.0	4.0	1.00	-	-

FIG. 4·7 – JOB'S CONTINUOUS VARIATION METHOD

I — 520 nm;   II — 540 nm

FIG. 4·8 — MOLE RATIO METHOD.

I — 520 nm; II — 500 nm .

Table 4.7 : Mole ratio method

$$[Ru(III)] = [BPG] = 2.0 \times 10^{-4}M$$

[Ru(III)], ml	[BPG] ml	$\dfrac{[BPG]}{[Ru(III)]}$	Absorbance at λ	
			520 nm	500 nm
1.5	0.0	-	-	-
1.5	0.5	0.33	0.080	0.070
1.5	1.0	0.66	0.175	0.150
1.5	1.5	1.00	0.270	0.220
1.5	2.0	1.33	0.350	0.280
1.5	2.5	1.66	0.415	0.340
1.5	3.0	2.00	0.480	0.390
1.5	3.5	2.33	0.520	0.420
1.5	4.0	2.66	0.545	0.440
1.5	4.5	3.00	0.565	0.455
1.5	5.0	3.33	0.575	0.465
1.5	5.5	3.66	0.580	0.470
1.5	6.0	4.00	0.585	0.475

Hence, the probable structure for Ru(III)-BPG complex may be shown as :
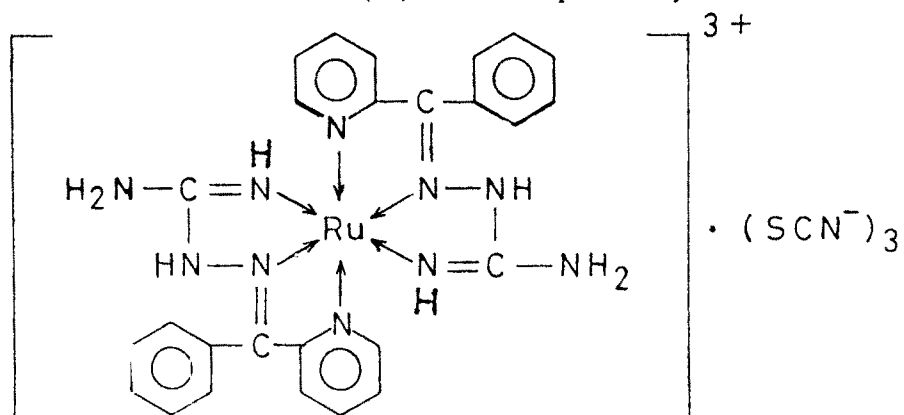
4.3.8 <u>Sensitivity</u> :

Reagent (BPG) or Ru(III)-BPG complex do not show any effect due to light.

The photometric sensitivity was calculated by the method of Sandell[77] and was found to be 0.2844 $\mu g/cm^2$ at 520 nm.

4.3.9 <u>Degree of Dissociation and Instability Constant</u> :

The degree of dissociation was obtained from mole ratio plot (Figure 4.8). The value of α, the degree of dissociation was found to be 0.0943.

The apparent instability constant[78] was found to be 3.33 x 10^{-10} for Ru(III)-BPG complex.

4.3.10 <u>Precision and Accuracy of the Method</u> :

To test the precision and accuracy of the method, different amounts of ruthenium were determined in five identical samples. The results show that there is a good agreement in the experimental values (Table 4.8).

Table 4.8 : Precision and accuracy of the method

Ruthenium(III), ppm	Mean absorbance of five observations	Standard deviation	Coefficient of variation, %
5.0	0.050	0.002	4.0
15.0	0.155	0.006	3.8
25.0	0.250	0.008	3.2

4.3.11   Effect of Diverse Ions :

To study the effect of diverse ions of ruthenium(III)-BPG complex, various cations and anions were added to the solution containing 25.0 ppm of Ru(III).   Colour was developed at pH 4.0 and measured at 520 nm.

It is observed that Cu(II), Ni(II), Co(II), Bi(III) and thiourea interfere seriously.   The interferences were removed by addition of proper masking agents.   Copper(II) is masked with sodium thiosulphate.   The tolerance limit of Zn(II) is 32 ppm.   The results are given in table 4.9.

Table 4.9 : Effect of diverse ions

$[Ru(III)]$ = 25.0 ppm; $[BPG]$ = 7.5 x 10^{-4}M .

Foreign ions	Added as	Tolerance limit, ppm
Cations :		
Zn(II)	$ZnSO_4 . 7H_2O$	32
Ba(II)	$BaCl_2 . 2H_2O$	14
V(V)	V_2O_5	11
Cu(II)	$CuSO_4 . 5H_2O$	None
Tl(I)	TlCl	3
Sn(II)	$SnCl_2 . 2H_2O$	7
In(III)	$InCl_3 . 4H_2O$	5
Mg(II)	$MgCl_2 . 6H_2O$	10
Se(IV)	Na_2SeO_3	13
Pb(II)	$Pb(NO_3)_2$	2
Mn(II)	$MnCl_2$	8
Zr(IV)	$ZrSO_4$	12
Te(IV)	Na_2TeO_3	14
U(VI)	$UO_2(NO_3)_2.6H_2O$	17
Ni(II)	$NiSO_4 . 6H_2O$	None
Co(II)	$CoSO_4 . 7H_2O$	None
Bi(III)	$BiCl_3$	None
Anions :		
Phosphate	Potassium hydrogen phosphate	3
Thiosulphate	Sodium thiosulphate	4
Oxalate	Potassium oxalate	8
$EDTA^{-4}$	Disodium salt	6
Borate	Sodium borate	5
Acetate	Sodium acetate	11
Thiourea	Thiourea	None

4.4 APPLICATIONS

Determination of Ruthenium (III) in Synthetic Mixtures :

To establish the reliability and applicability of the proposed method, recovery experiments were performed on laboratory mixtures containing other metals. This was done because authentic samples containing trace amounts of ruthenium were not available.

Several synthetic mixtures were prepared and analysed in triplicate. The results of analyses are summarised in table 4.10.

Table 4.10 :   Determination of Ru(III) in synthetic mixtures

Composition of synthetic mixture, μg	Ru(III) found, μg	Relative mean error, %
Ru(III) - 30.5 Pt(IV) - 20.3 Mo(VI) - 10.6	30.27	0.75
Ru(III) - 50.0 Ir(III) - 35.8 Sb(III) - 40.4	49.31	1.38

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