
CHAPTER - V

DETERMINATION OF OSMIUM (VIII)

5.1 INTRODUCTION

Osmium is one of the minor constituents of the natural platinum deposits. It occurs in association with other platinum metals in the form of osmiridium alloy. It exhibits +8 stable oxidation state in osmium tetroxide. Osmium tetroxide is an excellent hydrogenation catalyst, and is also used for hydroxylation of double bonds in the synthesis of certain organic compounds. Osmiridium alloy is used for making pen points. Osmium is encountered only as a component of special alloys in chemical analysis.

Numerous reagents have been proposed for the spectrophotometric determination of osmium. The various methods differ considerably in sensitivity, selectivity, tolerance to other ions, useful concentration range etc., and there appears to be scope for the development of further procedures giving enhanced sensitivity and selectivity.

Beamish¹⁻³ has critically reviewed the methods proposed for the spectrophotometric determination of osmium and other platinum metals. The methods for extraction and photometric determination of osmium have also been reviewed by various authors⁴⁻⁶.

Thiourea and its derivatives have been used for spectrophotometric determination of osmium. But thiourea is not very sensitive ($S = 50 \mu\text{g}/\text{cm}^2$) and also Ru(III) and Pd(II) interfere⁷. Os(IV) reacts with thiourea much more rapidly than does Os(VIII). Based on this, the procedure was developed by Rao et al. in which Os(VIII) was reduced by traces of As(III) before its complexation in a medium of 10% sulphuric acid⁸. Khopkar et al⁹ have

developed a procedure which involves the extraction of Os(IV) into TBP from 1.25 M HCl medium. But the sensitivity of the method is very low ($S = 100 \mu\text{g}/\text{cm}^2$). Ru(III), Pb(II), Sb(III), Te(IV) and many other anions interfere.

Various substituted thiourea which have been proposed for osmium determination are 1-benzoyl-3-(2-pyridyl)-2-thiourea¹⁰, 1-benzoyl-3-(2-hydroxyethyl) and 1-benzoyl-3,3-bis(2-hydroxyethyl) thiourea¹¹, 1-benzoyl-3-(*o*-tolyl) thiourea¹², 1-benzoyl-3-(5-bromo-2-pyridyl) thiourea¹³, N-hydroxymethyl- and N N'-bis(hydroxymethyl)-thiourea¹⁴. For trace determination of osmium, new procedures based on its catalytic effect in specific redox reactions have been proposed¹⁵⁻¹⁷.

In some of the methods, the formation of the complexes is quite slow in aqueous media at room temperature, and condition for obtaining reproducible colour development are usually critical e.g. quinoxaline-2,3 dithiol¹⁸ (1.5 hours), 1-naphthylamine 4,6,8-trisulphonic acid¹⁹ (4 hours), tetramethyl thiourea disulphide²⁰ (2 hours), N-(4-hydroxy-3-methoxybenzilidene)-*p*-morpholinoaniline²¹ (1 hour), thiocyanate²² (1 hour), 2-aminocyclopentane-1-carbodithioic acid²³ (10 minutes), phthalimide bis-thiosemicarbazone²⁴ (30 minutes) and *o*-hydroxy thiobenzhydrazide¹⁸ (10 minutes).

The reagents which require heating of the aqueous phase for full colour development are ferrozine²⁵ (4 hours), 1-benzoyl-3-(*o*-tolyl) thiourea¹² (30 minutes), quinisatin oxime²⁶ (1-5 hours), acenaphthene quinone monoxime²⁷ (90 minutes at 100°C), 3-nitrosopyridine-2,6-diol²⁸ (30 minutes), ammonium thiocyanate²⁹, 1-naphthyl amine-4,6,8-trisulphonic acid¹⁹ (45 minutes at 40°C), pyrogallol³⁰ (30 minutes), 2,4,5-(triaminopyrimidine-6-ol)³¹ (20 minutes), tiron³² (15 minutes) and thiocyanate-rhodamine-6G³³ (20 minutes).

The following reagents form the complexes with osmium which have either low stability or low sensitivity e.g. o-arsanilic acid³⁴ (S = 110 $\mu\text{g}/\text{cm}^2$), pyrocatechol³⁵ (S = 48 $\mu\text{g}/\text{cm}^2$), 2-amino-8-naphthol-3,6-disulphonic acid³⁶ (S = 200 $\mu\text{g}/\text{cm}^2$), 1-benzoyl-3-(5-bromo-2-pyridyl) thiourea¹³ (S = 53 $\mu\text{g}/\text{cm}^2$), 2-mercaptopyrimidine-3-ol³⁷ (S = 58 $\mu\text{g}/\text{cm}^2$) and promethazine hydrochloride³⁸ (stability 35 minutes in 4M HCl).

Sanke Gowda et al have reported the series of organic azine compounds including promethazine hydrochloride³⁸, chlorpromazine hydrochloride³⁹, thioridazine hydrochloride⁴⁰, diethazine hydrochloride⁴¹, trifluoperazinedihydrochloride⁴² and promazine hydrochloride⁴³ for the photometric determination of osmium in HCl medium. However there are interferences of Pd(II), Au(III), Fe(III), Pt(IV) and other platinum metals and a large number of common anions.

For photometric determination of osmium in aqueous medium, various reagents have been recommended. These are quinoxaline-2,3-dithiol¹⁸, trichloro perazine dihydrochloride⁴², naphthalene 2,3-diol⁴⁴, 3-nitrosopyridine-2,6-diol²⁸, m-aminobenzoic acid⁴⁵ and 1-naphthylamine-4,6,8-trisulphonic acid¹⁹. Although these methods appear to be sensitive, they are subject to interferences from many metal ions including transition as well as platinum group metals.

Some extractive spectrophotometric methods which suffer from the interferences are tetramethyl thiourea disulphide²⁰, 2-(3-benzoyl thioreido) benzoic acid⁴⁶, thiosemicarbazone of 6-methyl piconaldehyde⁴⁷, bismuthiol-II⁴⁸ and thiobenzhydrazide⁴⁹.

Singh et al. reviewed the analytical aspects of the chemistry of substituted pyrimidine thiol⁵⁰ as selective reagents for determination of osmium. The complexes have sensitivities ranging from 6 to 13 $\mu\text{g}/\text{cm}^2$. No attempts were made to investigate the application of the method.

Recently, spectrophotometric determination of osmium(VIII) was studied by the reagents as 2-methyl, 1,4-naphthoquinone-4-oxime⁵¹, 2-thio-barbituric acid⁵², 4-sulfo-2-aminobenzene thiol⁵³, pyrocatechol and hydroxy-amidine⁵⁴, N'-benziloyl-N-sulphonyl hydrazine⁵⁵, 1-hydroxy-2-pyridinethione⁵⁶ (sodium salt), 4-(2-pyridylazo) resorcinol⁵⁷, 2,2'-diaminodiphenyl disulfide⁵⁸, 2,3,7-trihydroxy-9-(p-nitrophenyl) fluorone⁵⁹, 3-(4-phenyl-2-pyridyl)-5,6-diphenyl-1,2,4-triazine⁶⁰ with sodium tetraphenyl borate and 1,5-diphenylcarbazine⁶¹

Osmium(VIII) was determined by extractive photometric methods by the reagents such as 3,4-dihydro-4,4,6-trimethyl-2-(1H) pyrimidinethione⁶², thiopyrine⁶³, aza analogs of dibenzo-18-crown-6⁶⁴, N'-(2-hydroxybenzoyl)-N-(4-tolysulphonyl) hydrazine⁶⁵, 4-(2-pyridylazo) resorcinol⁶⁶, and N'-benziloyl-N-phenyl sulfonyl hydrazine⁶⁷.

Sensitive spectrophotometric determination of osmium(VIII) in Os(VIII)-tin(II) chloride-rhodamine B^{68,69} system, Os(VIII)-SnCl₂-malachite green⁷⁰ system, Os(VIII)-SCN-ethyl violet⁷¹ system and Os(VIII)-halide (or SCN)-methylene blue⁷² system were also studied.

By spectrophotometric method, Os(VIII) was determined by means of catalytic effects on the oxidation of pyrogallol red⁷³ by potassium bromate and on the oxidation of phthaline⁷⁴ with hydrogen peroxide.

The yellowish orange complex of osmium with proposed reagent 2-benzoyl pyridine guanylhydrazone (BPG) is formed at pH 3.0 and measured at 435 nm, against the reagent blank. The method is highly selective and can also be applied for the determination of osmium in synthetic mixtures.

5.2 EXPERIMENTAL

5.2.1 Standard Solutions :

Standard osmium(VIII) solution :

Osmium tetroxide is volatile and reacts with skin and eyes to form a deposits of metallic osmium. Therefore, direct contact with the solid and its vapour should be avoided.

Osmium(VIII) solution was conveniently prepared as described by Ayres and Wells⁷⁵ as follows : A 1.0 g ampule of osmium tetroxide (Johnson-Matthey) was scratched with a file and then weighed. The weighed ampule is dropped into a thick walled glass stoppered bottle containing about 100 ml of 0.2 M sodium hydroxide solution. The bottle is shaken until the glass ampule breaks. When all the osmium tetroxide is dissolved to give an orange-red solution, most of the supernatant liquid is carefully transferred into a 1 litre volumetric flask. The glass stoppered bottle is rinsed with successive portion of 0.2 M sodium hydroxide. The washings are transferred to the same volumetric flask. Care should be taken so that no harm is done in leaving all the glass fragments inside the bottle. The solution is made upto volume with 0.2 M sodium hydroxide solution. The glass fragments are dried and weighed. The weight of the osmium tetroxide used to prepare the solution is thus obtained by difference.

This solution was standardised by the method of Klobbie⁷⁶ as follows:

To 25 ml of the solution, 15 ml of 6 M sulphuric acid and 2.0 gm of potassium iodide were added. The liberated iodine was titrated with standardised 0.01 N sodium thiosulphate. The difficulty in determining the end point on account of the green colour of the reduced osmium was circumvented by adding 5 ml of benzene and titrating with standard sodium thiosulphate until a colourless layer of benzene was obtained. The working solution (90 $\mu\text{g}/\text{Os(VIII)}/\text{ml}$) was prepared by appropriate dilution of the stock solution with distilled water.

Reagent (BPG) solution :

0.6 mg/ml in distilled ethyl alcohol ($2.5 \times 10^{-3}\text{M}$).

Buffer solution :

Buffer solution was prepared by dissolving appropriate amounts of citric acid and disodium hydrogen phosphate.

Potassium thiocyanate solution :

4.0 % of KCNS in distilled water.

5.2.2 Recommended Procedure :

In a 10 ml volumetric flask, an aliquot of the solution containing 137 μg of osmium(VIII) was taken. To it, 1.5 ml of the reagent (BPG) solution ($2.5 \times 10^{-3}\text{M}$) and 0.6 ml of 4.0 % KCNS solution were added. The pH of the solution was adjusted to 3.0 with buffer solution. It was then diluted upto the mark with distilled water. The absorbance of the Os(III)-BPG complex was measured at 435 nm against reagent blank. The concentration of osmium was determined from a calibration curve.

5.3 RESULTS AND DISCUSSION

5.3.1 Spectral Characteristics :

The absorption spectrum of the complex of Os(III)-BPG having the concentration $7.20 \times 10^{-5} \text{M}$ was recorded at pH 3.0 against reagent blank. (Table 5.1, Figure 5.1). The spectrum of the complex has an absorption maximum at 435 nm. The molar extinction coefficient of the complex is $0.2986 \times 10^4 \text{ l mole}^{-1} \text{cm}^{-1}$. The reagent does not absorb in this region.

Table 5.1 : Absorbances and molar extinction coefficients of the Osmium(III)-BPG complex and reagent (BPG)

Wavelength λ , nm	Absorbance		Molar extinction coefficient, ϵ	
	Os(III)-BPG complex 7.20×10^{-5} M	BPG, reagent 2.5×10^{-4} M	Os(III)-BPG complex $\epsilon \times 10^4$ l mole $^{-1}$ cm $^{-1}$	BPG, reagent $\epsilon \times 10^4$ l mole $^{-1}$ cm $^{-1}$
400	0.155	0.095	0.2152	0.0380
410	0.160	0.090	0.2222	0.0360
415	0.170	0.080	0.2361	0.0320
420	0.180	0.075	0.2500	0.0300
425	0.195	0.070	0.2638	0.0280
430	0.205	0.065	0.2847	0.0260
435	0.215	0.060	0.2986	0.0240
440	0.210	0.055	0.2916	0.0220
445	0.200	0.050	0.2777	0.0200
450	0.190	0.045	0.2638	0.0180
460	0.180	0.035	0.2500	0.0140
470	0.175	0.030	0.2430	0.0120
480	0.165	0.030	0.2291	0.0120
500	0.135	0.020	0.1875	0.0080
520	0.100	0.010	0.1388	0.0040
540	0.070	0.005	0.0972	0.0020
560	0.050	-	0.0694	-
580	0.030	-	0.0417	-
600	0.025	-	0.0347	-
620	0.015	-	0.0208	-
640	0.010	-	0.0138	-
680	0.010	-	0.0138	-

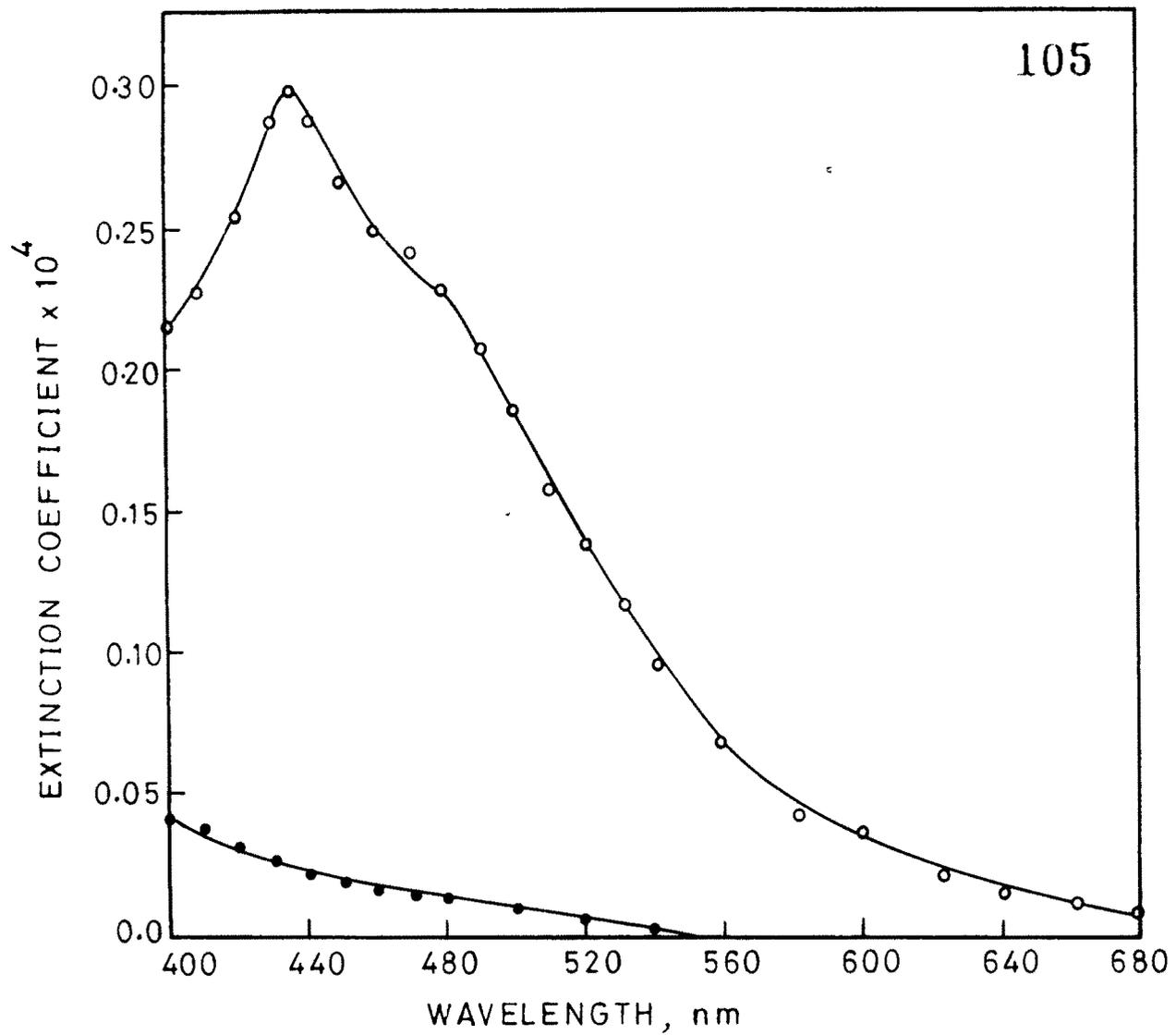


FIG. 5.1 — ○—○ ABSORPTION SPECTRUM OF OSMIUM(III)-BPG COMPLEX.
●—● ABSORPTION SPECTRUM OF REAGENT (BPG).

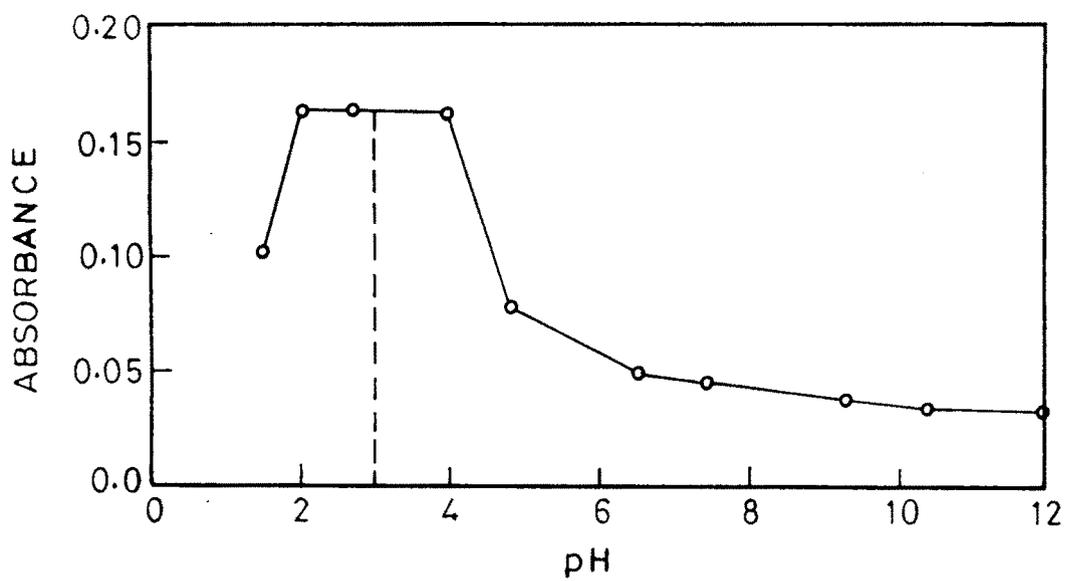


FIG. 5.2 — EFFECT OF pH .

5.3.2 Effect of pH :

The effect of pH of the solution on the absorbance of the complex was studied by preparing a series of solutions containing 1.0 ml of 0.07 mg/ml of osmium(VIII) and 0.8 ml of $2.5 \times 10^{-3}M$ reagent (BPG) at different pH values from 1.5 to 12.0. The absorbances were measured at 435 nm against corresponding reagent blank. At the pH range 2.0 to 4.0, maximum and constant absorbance was observed. Therefore pH 3.0 was selected as the optimum pH for further studies. The observations are given in table 5.2 (Figure 5.2).

Table 5.2 : Effect of pH

$$[\text{Os(VIII)}] = 3.68 \times 10^{-5}M; [\text{BPG}] = 2.0 \times 10^{-4}M$$

pH	Absorbance at 435 nm
1.5	0.100
2.0	0.165
2.7	0.165
3.2	0.165
4.0	0.165
4.8	0.085
6.5	0.050
7.4	0.045
9.3	0.041
10.4	0.035
11.5	0.035
12.0	0.035

5.3.3 Effect of Reagent Concentration :

A series of solutions were prepared in which the volume of $2.5 \times 10^{-3} \text{M}$ reagent was varied from 0.4 ml to 2.4 ml, while the concentration of osmium was kept constant at $7.61 \times 10^{-5} \text{M}$. The complex was developed as per recommended procedure. The results in the table 5.3 show that six fold molar excess of the reagent is sufficient for full colour development (Figure 5.3).

Table 5.3 : Effect of reagent concentration

$$[\text{Os(VIII)}] = 14.0 \text{ ppm}; \quad [\text{BPG}] = 2.0 \times 10^{-4} \text{M}$$

ml of reagent	Absorbance at 435 nm
0.5	0.08
0.8	0.12
1.0	0.13
1.5	0.15
2.0	0.15
2.5	0.15

5.3.4 Effect of Potassium Thiocyanate Solution :

A series of solutions were prepared in which the volume of 4.0 % KCNS was varied from 0.1 ml to 1.0 ml. The concentrations of osmium at 7.0 ppm, and 0.8 ml of the reagent, BPG ($2.5 \times 10^{-4} \text{M}$) were kept constant. The complex was developed as per recommended procedure. The results in table 5.4 show that 0.6 ml of 4.0 % KCNS was sufficient for full colour development of Osmium (III)-BPG complex (Figure 5.4).

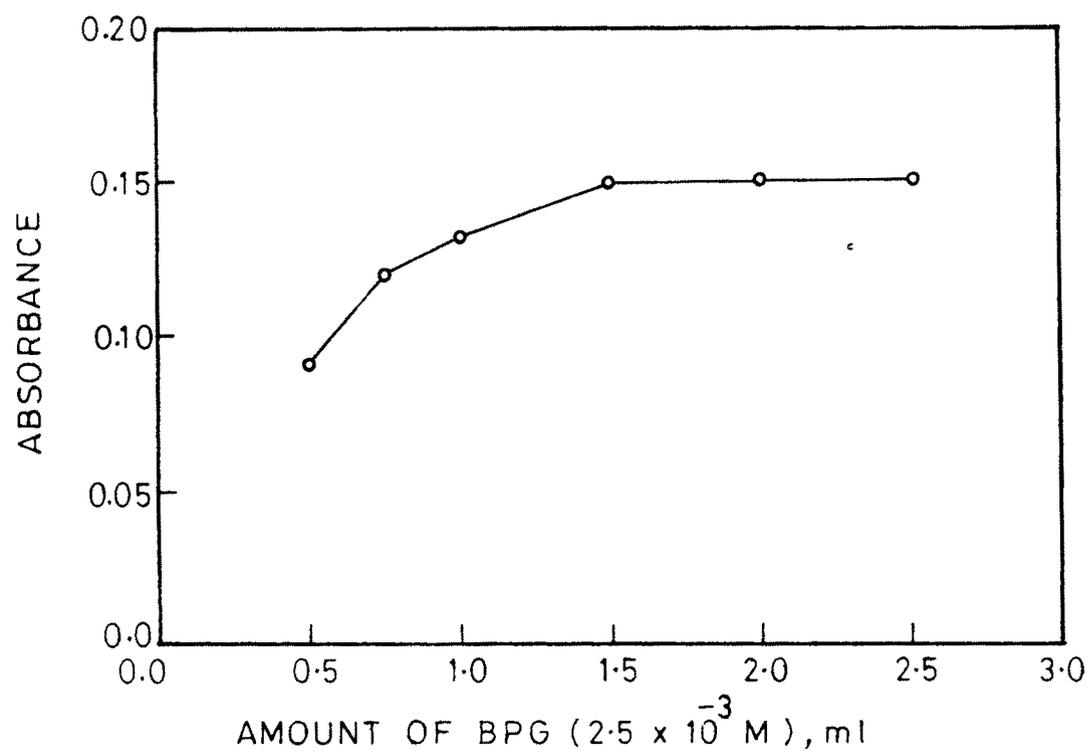


FIG.5.3 — EFFECT OF REAGENT CONCENTRATION.

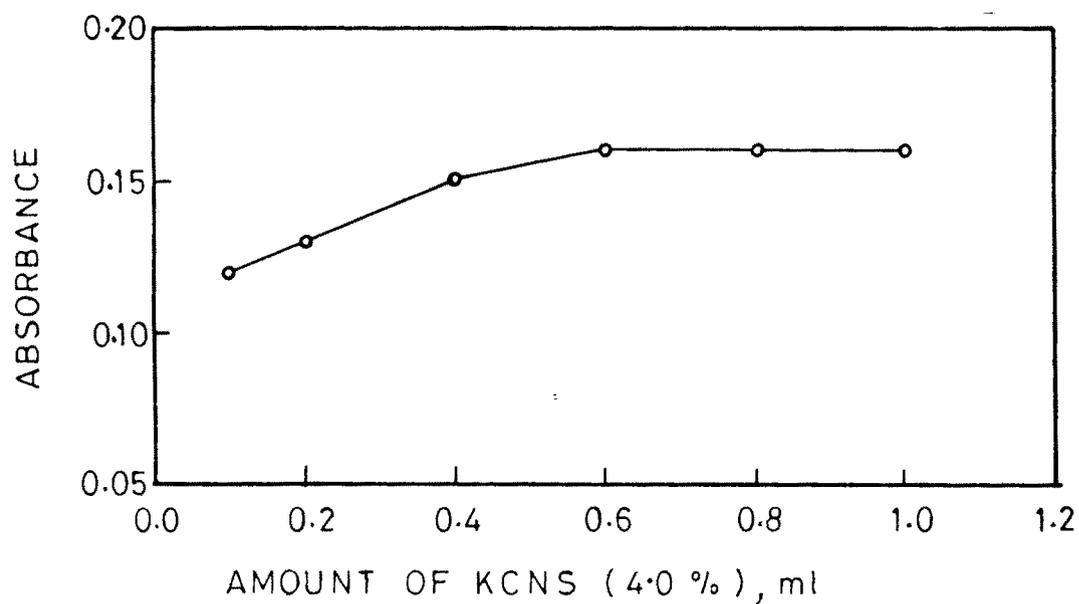


FIG.5.4 — EFFECT OF KCNS CONCENTRATION.

Table 5.4 : Effect of potassium thiocyanate concentration

$$[\text{Os(VIII)}] = 7.0 \text{ ppm}; \quad [\text{BPG}] = 2.5 \times 10^{-4} \text{ M}; \quad \text{KCNS} = 4.0 \%$$

Amount of KCNS added, ml	Absorbance at 435 nm
0.1	0.12
0.2	0.13
0.4	0.15
0.6	0.16
0.8	0.16
1.0	0.16

5.3.5 Stability and Time Effect :

The complex formation is instantaneous and independent upon temperature. The colour of the complex is stable for several hours.

5.3.6 Validity of Beer's Law :

The measurement of the absorbance of Os(III)-BPG complex at 435 nm from the solution containing various amounts of osmium and same amount of reagent (BPG) i.e. 3.0 ml of $5.0 \times 10^{-5} \text{ M}$ showed that Beer's law is valid upto 22.0 ppm of Os(VIII). (Table 5.5, Figure 5.5).

Ringbom plot⁷⁷ as obtained by plotting the percentage transmittance at 435 nm against $-\Delta c/c/\Delta P$ revealed the optimum concentration range, where the curve has greatest slope to be 9.0 to 22.0 ppm of metal (Figure 5.6).

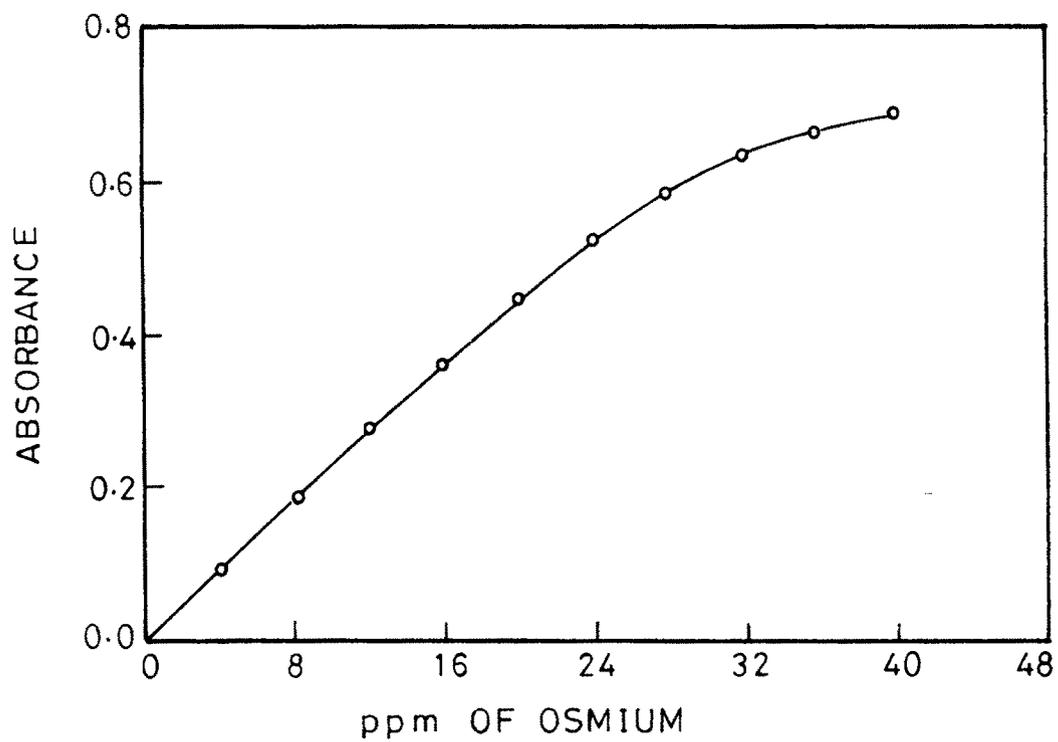


FIG. 5.5 — VALIDITY OF BEER'S LAW.

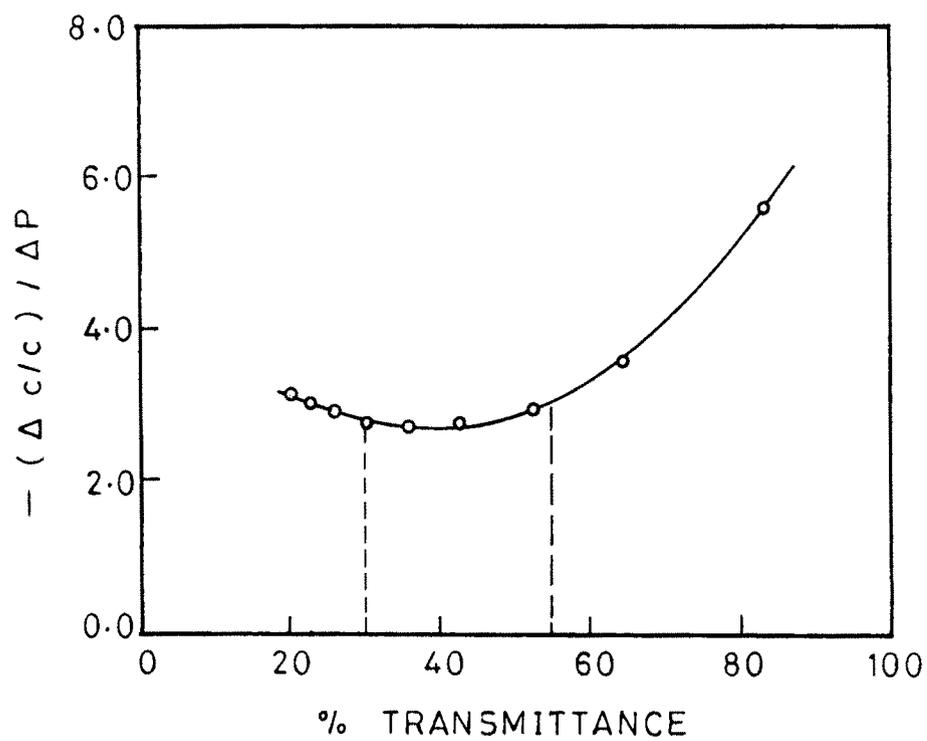


FIG. 5.6 — RINGBOM PLOT.

Table 5.5 : Validity of Beer's law

$$[\text{BPG}] = 5.0 \times 10^{-5} \text{M}$$

Amount of Os(VIII), ppm	Absorbance at 435 nm	Transmittance, %	$-(\Delta c/c)/\Delta p$
4.0	0.095	80.3	5.60
8.0	0.19	64.6	3.57
12.0	0.28	52.5	2.96
16.0	0.36	43.6	2.78
20.0	0.44	36.3	2.72
24.0	0.52	30.2	2.77
28.0	0.58	26.3	2.89
32.0	0.64	22.9	3.00
36.0	0.67	21.3	3.10
40.0	0.69	20.4	3.11

5.3.7 Composition of the Complex :

The composition of the Os(III)-BPG complex was studied by Job's method of continuous variation⁷⁸ (Table 5.6, Figure 5.7) mole ratio method⁷⁹ (Table 5.7, Figure 5.8) and slope ratio method⁸⁰. Job's plot indicated the formation of 1:1 complex of Os(III)-BPG and this composition was confirmed by mole ratio and slope ratio methods.

Table 5.6 : Job's continuous variation method

$$[\text{Os(VIII)}] = [\text{BPG}] = 10.5 \times 10^{-5} \text{M}$$

[Os(VIII)], ml	[BPG], ml	[BPG]		Absorbance at λ	
		[Os(VIII)] + [BPG]		435 nm	455 nm
4.0	0.0	-	-	-	-
3.6	0.4		0.1	0.27	0.19
3.2	0.8		0.2	0.46	0.33
2.8	1.2		0.3	0.54	0.42
2.4	1.6		0.4	0.60	0.49
2.0	2.0		0.5	0.62	0.51
1.6	2.4		0.6	0.52	0.47
1.33	2.66		0.66	0.46	0.38
1.2	2.8		0.7	0.42	0.36
1.0	3.0		0.75	0.39	0.34
0.8	3.2		0.8	0.28	0.23
0.4	3.6		0.9	0.18	0.12
0.0	4.0		1.0	-	-

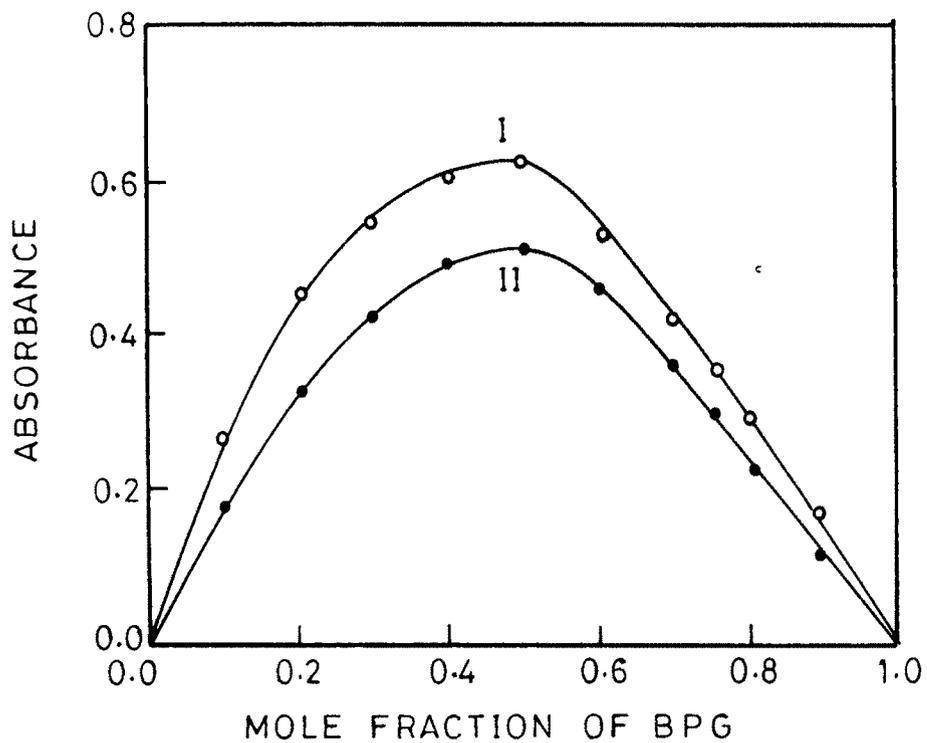


FIG.5.7 — JOB'S CONTINUOUS VARIATION METHOD.

I — 435 nm ; II — 455 nm .

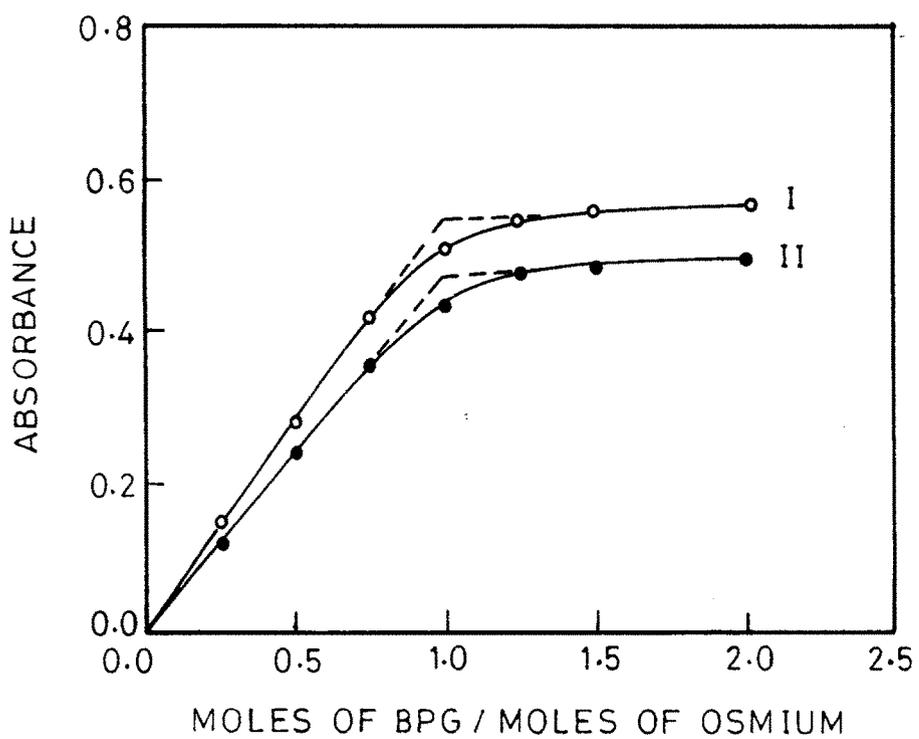


FIG.5.8 — MOLE RATIO METHOD.

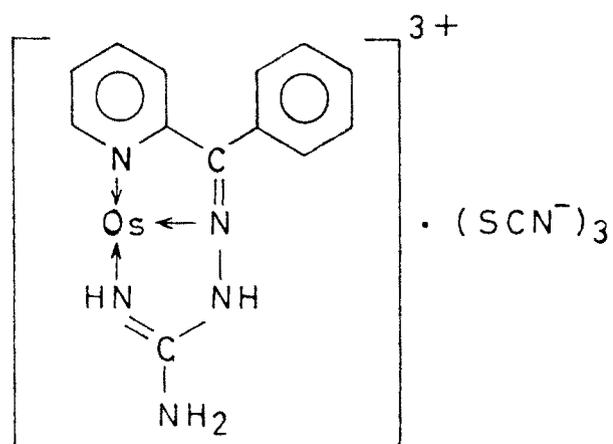
I — 435 nm ; II — 460 nm .

Table 5.7 : Mole ratio method

$$[\text{Os(VIII)}] = [\text{BPG}] = 8.5 \times 10^{-5} \text{M}$$

[Os(VIII)], ml	[BPG], ml	$\frac{[\text{BPG}]}{[\text{Os(VIII)}]}$	Absorbance at λ	
			435 nm	460 nm
2.0	0.0	-	-	-
2.0	0.5	0.25	0.175	0.12
2.0	1.0	0.50	0.28	0.24
2.0	1.5	0.75	0.42	0.36
2.0	2.0	1.00	0.505	0.43
2.0	2.5	1.25	0.54	0.475
2.0	3.0	1.50	0.55	0.485
2.0	3.5	1.75	0.565	0.50
2.0	4.0	2.00	0.565	0.50

Hence, the probable structure for Os(III)-BPG complex may be shown as :



5.3.8 Sensitivity :

The osmium (III) complex of BPG does not show sensitivity towards light. The Sandell's sensitivity⁸¹ of the complex was found to be 0.2020 $\mu\text{g}/\text{cm}^2$ at 435 nm.

5.3.9 Degree of Dissociation and Instability Constant :

The degree of dissociation was calculated from the mole ratio plot. The value of degree of dissociation (α) was found to be 0.0818. The apparent instability constant⁸² was found to be 7.288×10^{-7} for Os(III)-BPG complex.

5.3.10 Reproducibility of the Method :

In order to study the reproducibility of the method, different amounts of osmium were determined. The results in table 5.8 show that the method is reproducible.

Table 5.8 : Reproducibility of the method

Osmium(VIII), ppm	Mean absorbance of five observations	Standard deviation	Coefficient of variation, %
6.0	0.13	0.0018	1.384
10.0	0.22	0.0026	1.181
14.0	0.31	0.0040	1.290
18.0	0.41	0.0048	1.170

5.3.11 Effect of Diverse Ions :

Various ions were added to a sample containing a fixed amount of osmium (28.0 ppm) and the colour was developed and measured as per recommended procedure. The tolerance limit was assumed to be the amount of foreign ion needed to cause an error less than 2% in absorbance values.

It is found that Cu(II), Ni(II), Fe(III), thiosulphate ion, EDTA^{-4} and thiourea interfere seriously and can be tolerated in presence of appropriate masking agents. For example; Cu(II) was masked by using sodium thio-sulphate. The tolerance limits of Pb(II) and acetate ion are 110 and 160 ppm respectively. The tolerance limits of other ions are listed in table 5.9.

Table 5.9 : Effect of diverse ions

$$[\text{Os(VIII)}] = 28.0 \text{ ppm} \quad [\text{BPG}] = 2.5 \times 10^{-4} \text{M}$$

Foreign ions	Added as	Tolerance limit, ppm
<u>Cations :</u>		
Zn(II)	ZnSO ₄ · 7H ₂ O	18
Ba(II)	BaCl ₂ · 2H ₂ O	12
Bi(III)	BiCl ₃	28
Zr(IV)	ZrSO ₄	14
Tl(I)	TlCl	92
Se(IV)	Na ₂ SeO ₃	60
Mg(II)	MgCl ₂ · 6H ₂ O	85
Sn(II)	SnCl ₂ · 2H ₂ O	40
Pb(II)	Pb(NO ₃) ₂	110
In(III)	InCl ₃ · 4H ₂ O	24
U(VI)	UO ₂ (NO ₃) ₂ · 6H ₂ O	32
Mn(II)	MnSO ₄ · H ₂ O	16
Cu(II)	CuSO ₄ · 5H ₂ O	None
Ni(II)	NiSO ₄ · 6H ₂ O	None
Fe(III)	FeCl ₃ · 6H ₂ O	None
<u>Anions :</u>		
Phosphate	Potassium hydrogen phosphate	105
Thiosulphate	Sodium thiosulphate	None
Oxalate	Potassium oxalate	90
EDTA ⁻⁴	Disodium salt	None
Borate	Sodium borate	25
Acetate	Sodium acetate	160
Thiourea	Thiourea	None

5.4 APPLICATIONS

Determination of Osmium(VIII) in Synthetic Mixtures :

In order to confirm the usefulness of the reagent, the proposed method was applied for the determination of Os(VIII) in various synthetic mixtures.

Various synthetic mixtures were prepared. Suitable aliquots were taken and analysed as per recommended procedure. The results of analyses are summarised in table 5.10.

Table 5.10 : Determination of Os(VIII) in synthetic mixtures*

Composition of synthetic mixture, μg	Os(VIII) found, μg	Relative mean error, %
Os(VIII) - 100	99.1	0.90
Ir(III) - 50		
Mo(VI) - 75		

Os(VIII) - 200	198.9	0.55
Pt(IV) - 30		
Sb(III) - 100		

* Triplicate determinations.



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