CHAPTER - III

DETERMINATION OF PALLADIUM (II)

3.1 INTRODUCTION

Palladium and its alloys find wide range of applications both in chemical industry and in instrument making. As a catalyst, it is principally used in organic synthesis, oxidation, hydrogenation, dehydrogenation etc. In many chemical reactions, surfaces of palladium which are normally deposits of palladium on inert supporting material, function as excellent catalysts. In homogeneous catalysis, in a liquid phase, palladium compounds and salts soluble in the reacting liquids are widely used. Numerous investigations have shown that many of the impurities in the palladium alter its catalytic activity. Palladium is used in stainless steel and high chromium steel from 1 to 10%. Alloys of palladium with other precious metals have found uses in dentistry and jewellery. Alloys of palladium with noble and rare metals are used as electrical contacts, resistances, thermoelectrodes, solders etc. The properties of the alloys of palladium are strictly governed by the concentration of palladium and hence estimation of the palladium content of the alloy is of analytical importance.

The literature is rich in methods for the spectrophotometric determination of Pd(II). Several spectrophotometric reagents have been proposed for the determination of palladium, but only a few are selective and sensitive. In the present investigation it was observed that BPG is comparable with other known reagents for Pd(II). It is superior to some known reagents which suffer from slow rate of complex formation, whereas BPG forms complex instantaneously. As far as the interferences are concerned, some of the reported reagents like 6-HNQDT[1] and furil-α-dioxime[2] are more advantageous as compared to BPG.

Beamish[3] has reviewed the spectrophotometric determination of palladium. Some reagents are not selective though sensitive. Reagents like 2-mercaptoquinoline[4], bismuthol II[5], 2-diethylaminoethanethiol hydrochloride[6] and crystal violet[7] suffer from numerous interfering ions.

Due to low sensitivities, reagents like dimethyl glyoxime[8] (0.06 µg/cm^2), 8-aminoquinoline[9] (0.04 µg/cm^2) and acenaphthene quinone monoxime[10] (0.084 µg/cm^2) are not suitable for trace determination of palladium.

In case of N,N'-bis(2-sulphoethyl) dithio-oximide[11] and 2-diethylaminoethane thiol hydrochloride[12] rate of complex formation is slow. Moreover they are not selective.

Due to low kinetic stability, complex formation in case of 4-methyl cyclohexane-1:2 dioxime[13], 5-amino-2-benzimidazole thiol[14], aluminon[15], phthalimide dioxime[16], procaine[17], chrome azurol S[18], dimethyl glyoxime[19] and azorubine[20] takes place after 30 to 90 minutes. Rate of formation of complexes is slow in case of nitroso-R-salt[21], glycine thymol blue[22], 3-nitroso-pyridine-2, 6-diol[23], malamine[24] and tropolon[25] and hence requires heating.

Reagents like 2-mercaptobenzoic acid[26], o-mercaptobenzoic acid[27], benzoyl methyl glyoxime[28], 1-(2-pyridylazo)-2-naphthol[29], palladiazo[30] and eriochrome cyanine R[31] are selective and sensitive, and hence can be successfully used for the trace determination of palladium.

Though furylpentadienal thiosemicarbazone[32], 6-methyl picolinaldehyde thiosemicarbazone[33], phthalimide bis-thiosemicarbazone[34], bis-acetylbis-4-phenyl-3-thiosemicarbazone[35], p-ethylsulphophenyl benzaldehyde thiosemicarbazone[36] and glyoxal-bis-thiosemicarbazone[37] are used for colorimetric determination of palladium, but none of them is free from the above discussed defects.

Recently, palladium was determined by the reagents such as arylidene-2-pyridylhydrazones derivatives[38], butylene diamine tetramethylene phosphoric acid[39], 2-methyl-1, 4-naphthoquinone monoxime[40], 2-(5-bromo-2-pyridylazo)-5-(diethylamino) phenol[41], triethylene tetramino hexamethylene phosphoric acid[42], o,o'-diamino azobenzene[43], indane-1,2,3-trione trioxime[44] mandelazo I[45], 1,5-diphenylcarbazide[46], 2-(4,5-dimethyl-2-triazolylazo) 5-dimethylamino phenol[47], chlorophosphonazo II[48], 1,8-dihydroxy-2-[(4-chloro-2-phosphonophenyl)azo]-7 [(6,8-disulphonaphthyl)azo] naphthalene[49], 4-carbamoyl-1-[3-(2-hydroxyiminomethyl-1-pyridino)-oxapropyl] pyridinium dichloride (HI-6)[50], 2(4',5'-dimethyl-2' thiazolylazo)-5-dimethyl amino aniline[51], 2-(2-benzothiazolylazo) 5-dimethylamino-4-tolylarsonic acid[52], 5-phenylazo-8-aminoquinoline[53], 5-(2'-benzothiazolylazo)-8-aminoquinoline[54], semixylenol orange[55], 5-(4' amino-2'-hydroxybenzeneazo) tetrazole[56], 2-(2-benzothiazolylazo)-5-dimethylamino-4-tolylarsonic acid[57], 1-(5-bromo-2-pyridylazo)-2-naphthol-6-sulfonic acid[58], 7-(2-pyridylazo)-5-chloro-8-hydroxyquinoline[59] and o-hydroxyacetophenone thiosemicarbazone[60].

Palladium(II) was determined by extractive spectrophotometric method with the reagents such as pyronine B[61], 5,5-methylene bis-thiosalicylic acid[62], N,N'-diphenyl propane dithioamide[63], 4-(2-pyridylazo)-resorcinol and tetraphenyl arsonium[64], 2-hydroxynaphthalene-4-phenyl-3-thiosemicarbazone[65], pyridine-2-acetaldehyde salicyloylhydrazone[66], 5-chloro-salicylaldoxime[67], 2-allylthiourea[68], furilacrolein oxime[69], 2-mercaptobenzamide[70], diphenyl thiovioluric acid[71], cetyltrimethyl ammonium bromide[72], 2 N-(2-mercaptophenyl)-1,2,3-benzothiadizoline[73], 2,2'-dipyridyl-1-phthalazinohydrazone[74], 2N-(2,mercapto-4-chlorophenyl)-6-chloro, 1,2,3-benzothiadiazoline[75] and iso-nitrosomalondianilide[76].

Palladium(II) was also determined spectrophotometrically as Pd(II)-KI-rhodamine 6G-PVA[77] system, Pd(II)-tin(II) chloride-crystal violet[78] system Pd(II)-picoline amidoxime[79] system, Pd(II)-5-Br-PADAP-triton-x-100[80] system, Pd(II)-CPA-mA-CTMAN[81] system and Pd(II)-1,10-phenanthroline-cadion A-peregal-0[82] system.

By spectrophotometric extraction, Pd(II) was determined as Pd(II)-thiocyanate-tetrabutyl ammonium[83] ion pair and Pd(II)-PAR-xylometazoline hydrochloride[84] ion pair.

3.2 EXPERIMENTAL

3.2.1 Standard Solutions :

Standard palladium(II) solution :

A stock solution of palladium (1 mg/ml i.e. 9.396×10^{-3}M) was prepared by dissolving 0.168 grams of A.R. grade palladium(II) chloride in 100 ml distilled water containing a few mls of concentrated hydrochloric acid. The solution was standardised with dimethylglyoxime gravimetrically[85]. Further dilutions for experimental purposes were done with distilled water.

Reagent (BPG) solution :

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

Buffer solution :

Buffer solution was prepared by dissolving appropriate amounts of borax.

Potassium thiocyanate solution :

4.0% of KCNS in distilled water.

3.2.2 Recommended Procedure :

An aliquot of the solution containing 50.0 µg of palladium(II) was taken in a 10 ml volumetric flask. To it, 0.6 ml of the reagent (BPG) solution of concentration 2.5 x 10^{-3}M and 1.0 ml of 4% potassium thiocyanate solution were added. The pH of the solution was adjusted to 8.5 with buffer solution. It was then diluted upto the mark with distilled water The absorbance of the palladium(II)-BPG complex was measured at 415 nm against reagent blank. The concentration of palladium in an unknown solution was determined from a calibration curve obtained under identical conditions.

3.3 RESULTS AND DISCUSSION

3.3.1 Spectral Characteristics :

The absorption spectrum of Pd(II)-BPG complex of concentration 4.699 x 10^{-5}M was recorded at pH 8.5 against reagent blank. The complex has absorption maximum at 415 nm and molar extinction coefficient of the complex is 0.6609 x 10^4 l $\mathrm{mole}^{-1}\mathrm{cm}^{-1}$. The reagent does not absorb in this region. Absorption spectra of the complex and the reagent are shown in figure 3.1. Observations are given in table 3.1.

Table 3.1 : Absorbances and molar extinction coefficients of Pd(II)-BPG complex and reagent (BPG)

Wavelength λ, nm	Absorbance		Molar extinction coefficient, ϵ	
	Pd(II)-BPG complex 4.699×10^{-5}M	BPG, reagent 2.5×10^{-4} M	Pd(II)-BPG complex $\epsilon \times 10^{4}$ l mole^{-1}cm^{-1}	BPG, reagent $\epsilon \times 10^{4}$ l mole^{-1}cm^{-1}
365	0.240	0115	0.5117	0.0460
375	0.255	0.110	0.5437	0.0446
390	0.270	0.105	0.5746	0.0420
400	0.290	0.095	0.6183	0.0380
410	0.305	0.090	0.6503	0.0360
415	0.310	0.085	0.6609	0.0340
420	0.305	0.075	0.6503	0.0300
430	0.295	0.065	0.6289	0.0260
440	0.285	0.055	0.6076	0.0220
450	0.265	0.045	0.5650	0.0180
460	0.250	0.035	0.5330	0.0140
480	0.190	0.030	0.4051	0.0120
500	0.130	0.020	0.2771	0.0080
520	0.095	0.010	0.2025	0.0040
540	0.090	0.005	0.1958	0.0020
560	0.080	-	0.1705	-
580	0.070	-	0.1492	-
600	0.060	-	0.1279	-
620	0.055	-	0.1172	-
640	0.050	-	0.1064	-

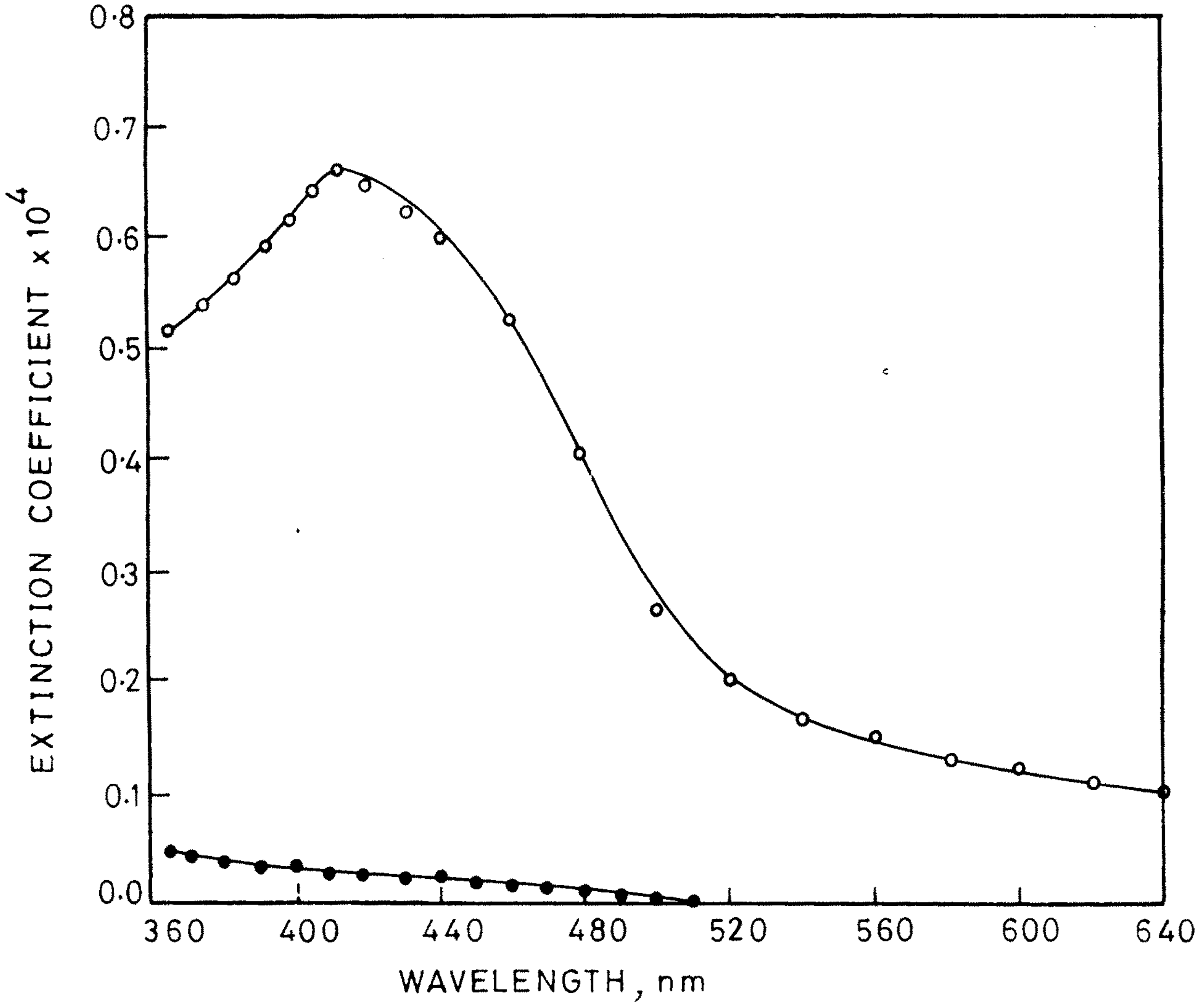


FIG. 3·1 – ○—○ ABSORPTION SPECTRUM OF PALLADIUM(II)-BPG COMPLEX.

●—● ABSORPTION SPECTRUM OF REAGENT (BPG).

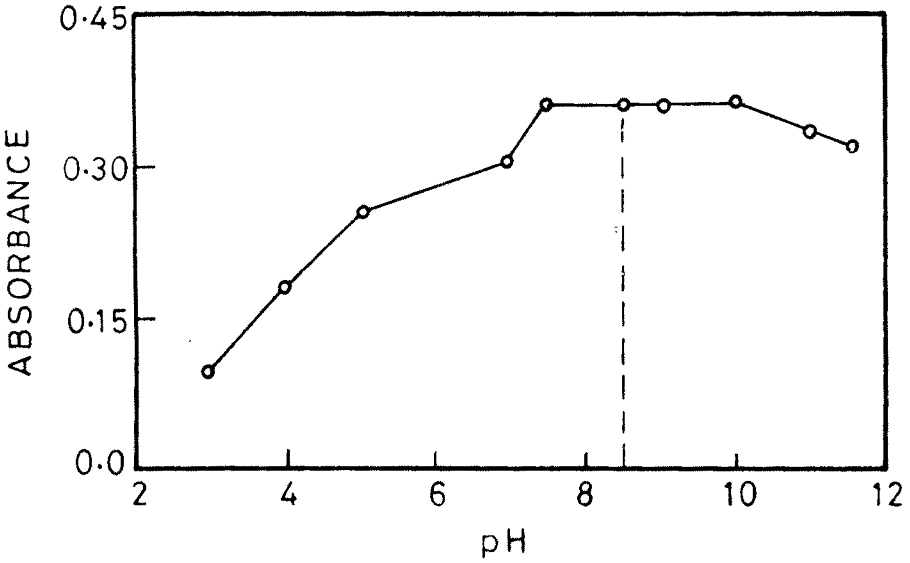


FIG. 3·2 – EFFECT OF pH.

3.3.2 Effect of pH :

The effect of variation in pH on the absorbance of Pd(II)-BPG complex was studied over the pH range 3.0 to 11.6. The complex has maximum and constant absorbance over the pH range 7.5 to 10.0. Therefore pH 8.5 was selected as the optimum pH for further studies. The observations are given in table 3.2 (Figure 3.2).

Table 3.2 : Effect of pH

$[\mathrm{Pd(II)}] = 4.699 \times 10^{-5}$M; $[\mathrm{BPG}] = 2.5 \times 10^{-4}$M

pH	Absorbance at 415 nm
3.0	0.095
4.0	0.180
5.0	0.255
7.0	0.30
7.5	0.36
8.5	0.36
9.0	0.36
10.0	0.36
11.0	0.33
11.6	0.32

3.3.3 Effect of Reagent Concentration :

It was observed that the amount of excess of reagent was the least critical. About three fold excess of molar concentration relative to the metal ion concentration was satisfactory. A series of solutions were prepared in which the concentration of reagent was varied from 0.1 ml to 1.0 ml of 2.5 x 10^{-4}M concentration, while the concentration of palladium(II) was kept constant at 4.699 x 10^{-5}M. The pH value was adjusted and the solution was made upto the mark in 10 ml volumetric flask. The absorbance was measured at 415 nm wavelength against reagent blank. The results are given in table 3.3 (Figure 3.3) which shows that three fold molar excess of the reagent was sufficient for full colour development of 5.0 ppm palladium.

Table 3.3 : Effect of reagent concentration

$[\text{Pd(II)}]$ = 5.0 ppm; $[\text{BPG}]$ = 2.5 x 10^{-4}M

Amount of BPG added, ml	Absorbance at 415 nm
0.1	0.225
0.2	0.300
0.3	0.355
0.4	0.400
0.5	0.425
0.6	0.435
0.7	0.435
0.8	0.435
1.0	0.435

3.3.4 Effect of Potassium Thiocyanate Solution :

A series of solutions were prepared in which the volume of 4.0% KCNS was varied from 0.2 ml to 1.6 ml, while the concentration of palladium (4.699 x 10^{-5}M) and 0.6 ml of reagent (BPG) (2.5 x 10^{-4}M) were

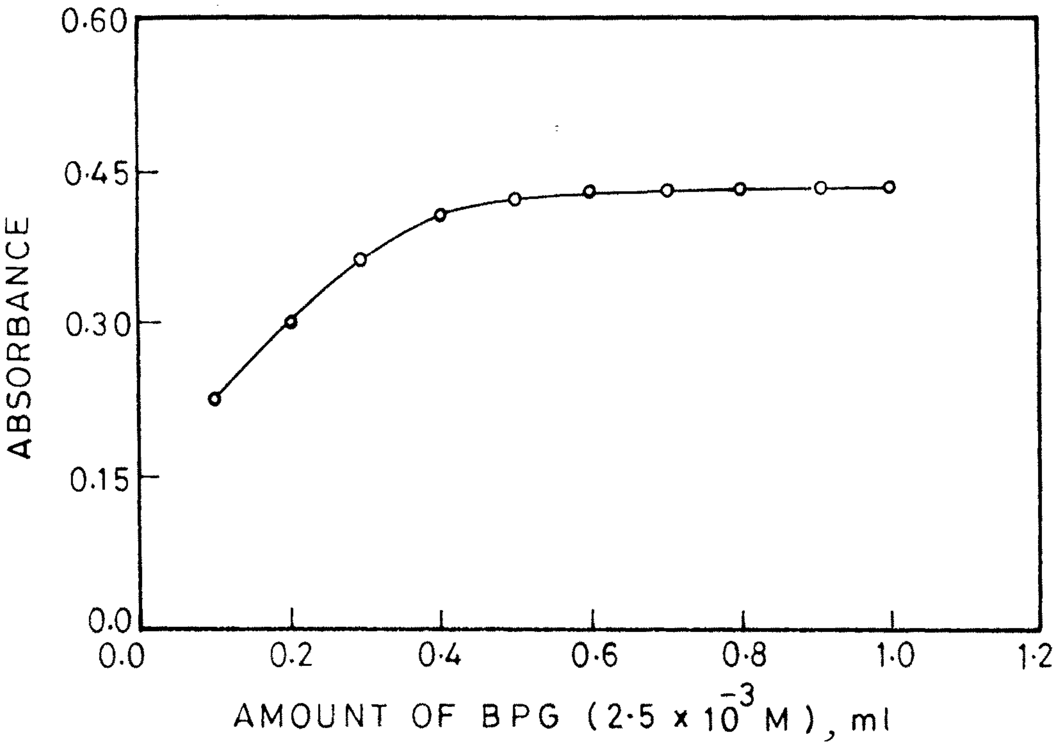


FIG. 3·3 – EFFECT OF REAGENT CONCENTRATION.

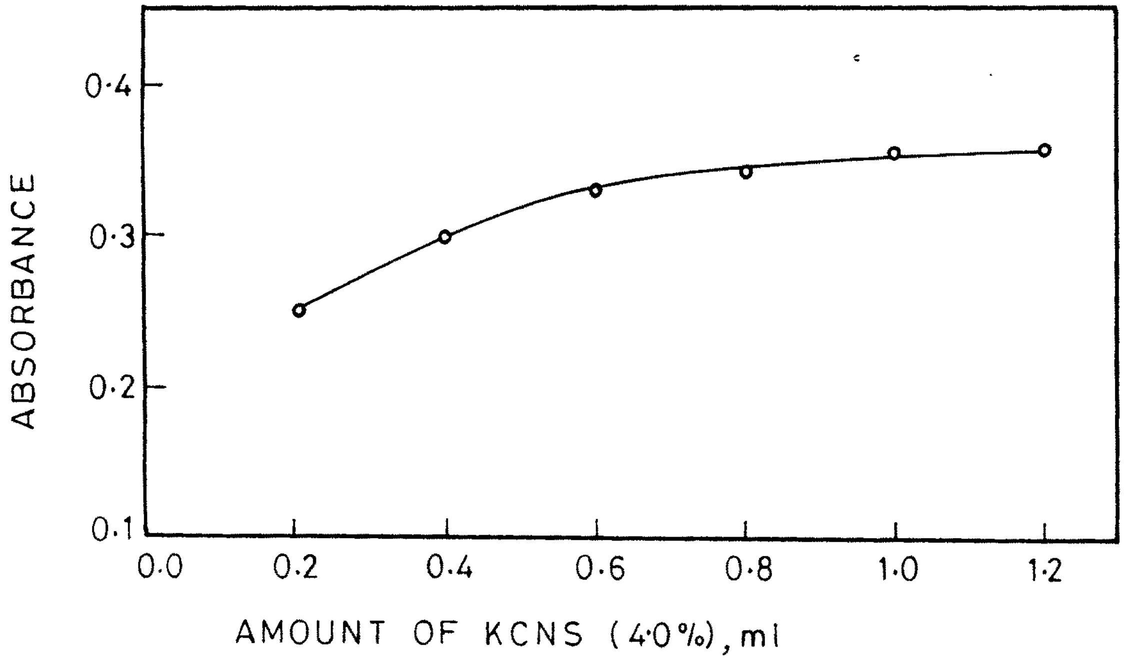


FIG. 3·4 – EFFECT OF KCNS CONCENTRATION.

kept constant. The complex was developed as per recommended procedure. The results in table 3.4 show that 1.0 ml of 4% KCNS was sufficient for full colour development of Pd(II)-BPG complex (Figure 3.4).

Table 3.4 : Effect of potassium thiocyanate concentration
[Pd(II)] = 5.0 ppm; [BPG] = 2.5 x 10^{-4}M; KCNS = 4.0%

Amount of KCNS added, ml	Absorbance at 415 nm
0.2	0.25
0.4	0.30
0.6	0.33
0.8	0.34
1.0	0.355
1.2	0.355
1.4	0.355
1.6	0.355

3.3.5 Stability and Reaction Rate :

Pd(II)-BPG complex is stable for several hours. Complex formation is instantaneous and is independent of temperature.

3.3.6 Validity of Beer's Law :

The solutions containing different amounts of palladium and same amount of reagent (1.692 x 10^{-4}M) were studied at pH 8.5 for varification of Beer's law. The absorbance measurements were recorded at 415 nm against corresponding reagent blank (Table 3.5; Figure 3.5). It was found that Beer's law is obeyed upto 6.0 ppm of palladium.

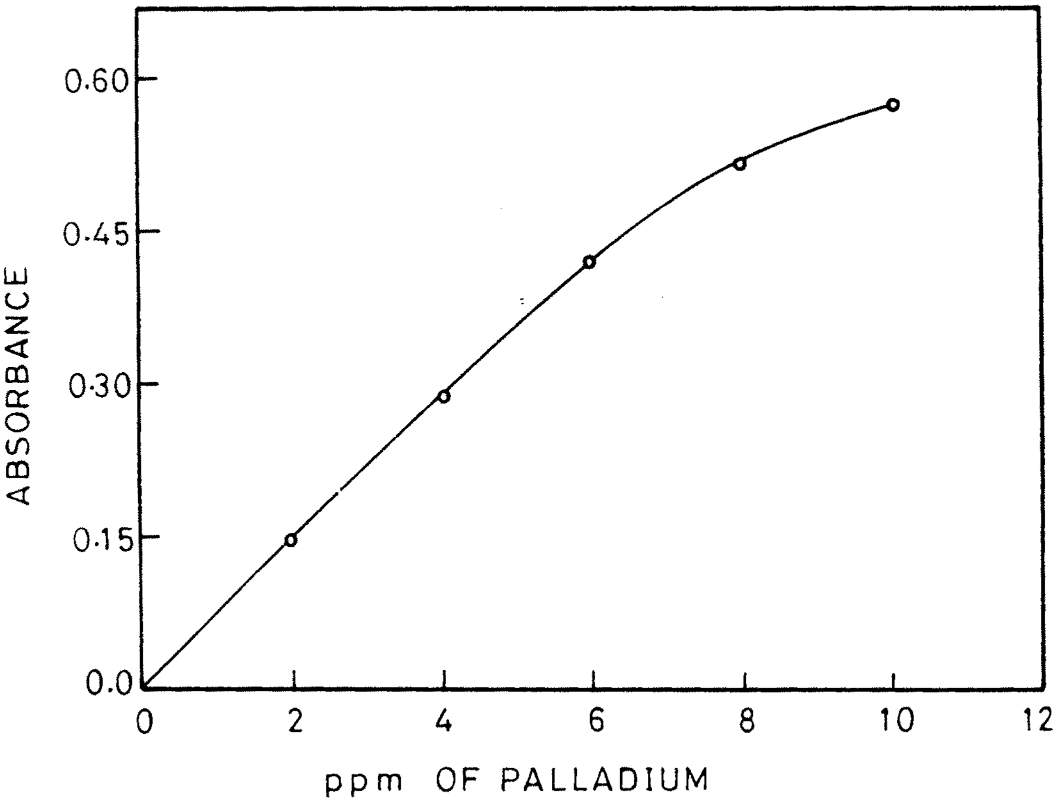


FIG. 3·5 — VALIDITY OF BEER'S LAW.

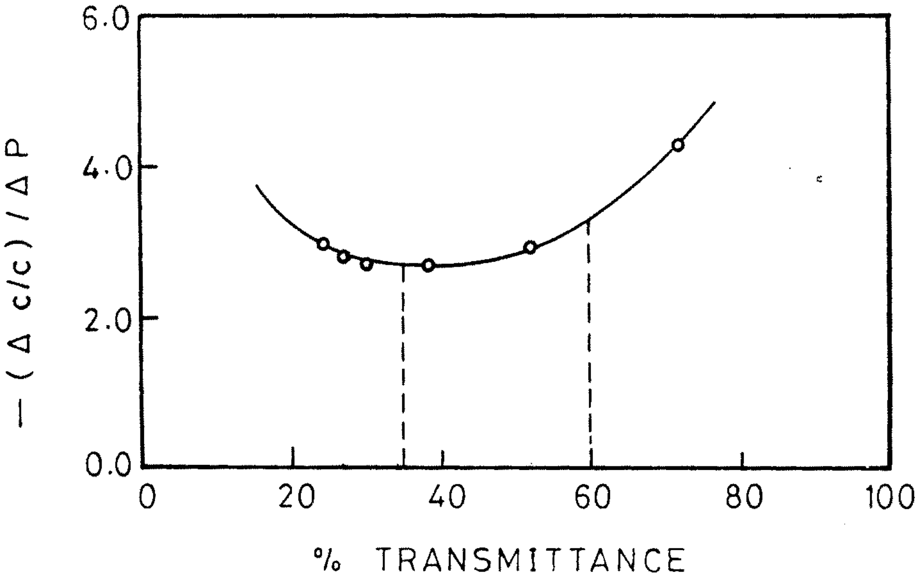


FIG. 3·6 — RINGBOM PLOT.

The Ringbom Plot[86] (Figure 3.6) indicated that the optimum concentration range to be from 3.0 to 6.0 ppm of palladium.

Table 3.5 : Validity of Beer's law

$[\mathrm{BPG}^-] = 1.692 \times 10^{-4}\mathrm{M}$

Amount of Pd(II), ppm	Absorbance at 415 nm	Transmittance, %	$-(\Delta c/c)/\Delta p$
2.0	0.14	72.4	4.32
4.0	0.28	52.5	2.96
6.0	0.42	38.0	2.73
8.0	0.515	30.5	2.77
10.0	0.57	26.9	2.80
12.0	0.61	24.5	3.00

3.3.7 Composition of the Complex :

Job's method of continuous variation[87], mole ratio method[88] and slope ratio method[39] were used to determine the composition of the complex. For these methods, equimolar solutions of the reagent and metal were used. The Job's plot of absorbance against mole fraction of reagent (Table 3.6; Figure 3.7) indicated the existance of 1:1 (metal:ligand) complex. This composition was confirmed by mole ratio study (Table 3.7; Figure 3.8) and slope ratio study.

Table 3.6 : Job's continuous variation method

$[Pd(II)] = [BPG] = 7.5 \times 10^{-5}M$

[Pd(II)], ml	[BPG], ml	$\frac{[BPG]}{[Pd(II)] + [BPG]}$	Absorbance at λ	
			415 nm	460 nm
2.0	0.0	-	-	-
1.8	0.2	0.1	0.20	0.145
1.6	0.4	0.2	0.305	0.25
1.4	0.6	0.3	0.38	0.32
1.2	0.8	0.4	0.44	0.37
1.0	1.0	0.5	0.49	0.41
0.8	1.2	0.6	0.40	0.355
0.66	1.33	0.66	0.36	0.31
0.6	1.4	0.7	0.335	0.27
0.5	1.5	0.75	0.29	0.195
0.4	1.6	0.8	0.19	0.12
0.2	1.8	0.9	0.09	0.05
0.0	2.0	1.0	-	-

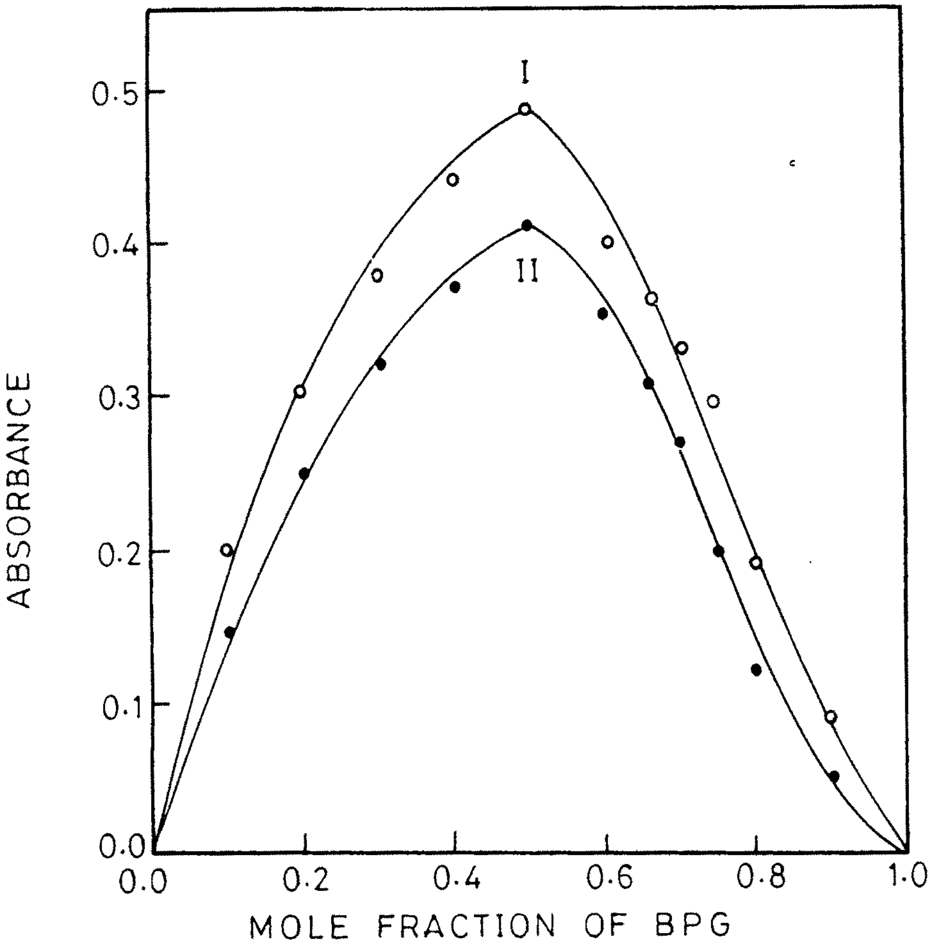


FIG. 3·7 – JOB'S CONTINUOUS VARIATION METHOD.

I – 415 nm ; II – 460 nm

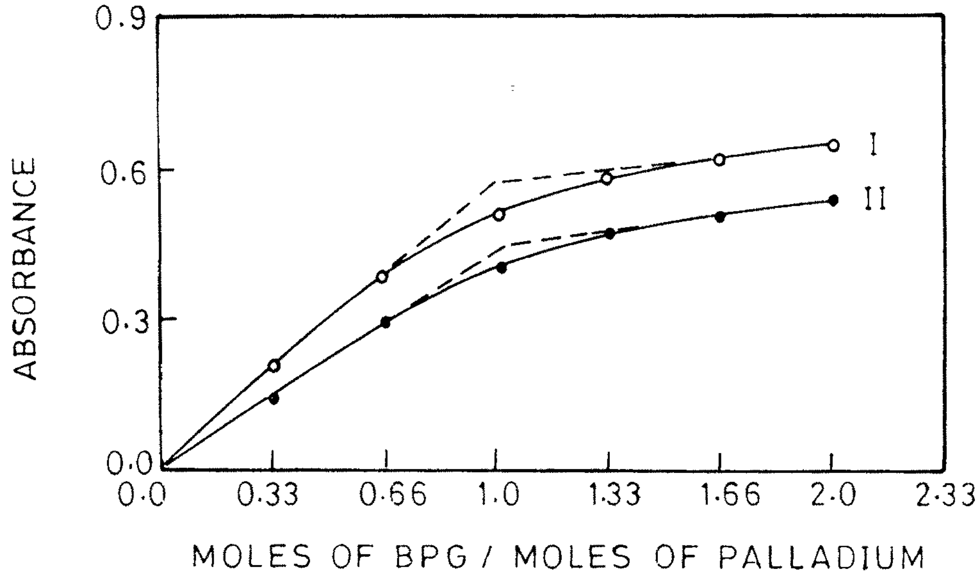


FIG. 3·8 – MOLE RATIO METHOD.

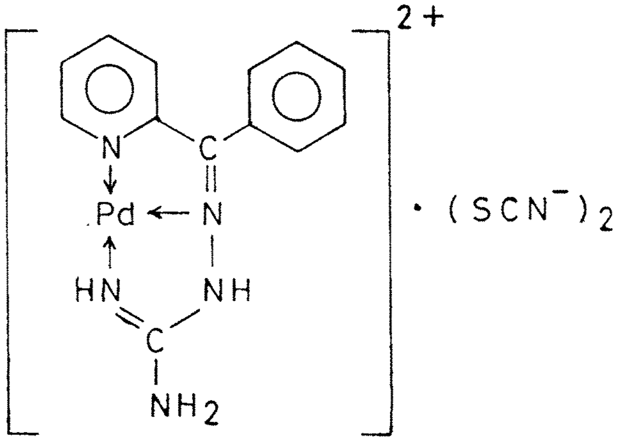
I – 415 nm ; II – 430 nm

Table 3.7 : Mole ratio method

[Pd(II)] = [BPG] = 10.5 x 10^{-5}M

[Pd(II)], ml	[BPG], ml	[BPG] / [Pd(II)]	Absorbance at λ	
			415 nm	430 nm
0.75	0.00	-	-	-
0.75	0.25	0.33	0.21	0.15
0.75	0.50	0.66	0.39	0.30
0.75	0.75	1.00	0.51	0.405
0.75	1.00	1.33	0.585	0.48
0.75	1.25	1.66	0.62	0.51
0.75	1.50	2.00	0.645	0.52

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



3.3.8 Sensitivity :

There is no effect of light on complex and reagent. The photometric sensitivity was calculated by Sandell's[90] method and was found to be 0.0704 µg/cm^2.

3.3.9 Degree of Dissociation and Instability Constant :

The degree of dissociation was obtained from the mole ratio plot (Figure 3.8). The value of α, degree of dissociation was found to be 0.0892.

The apparent instability constant[91] was found to be 7.56 x 10^{-7} for Pd(II)-BPG complex.

3.3.10 Reproducibility of the Method :

The reproducibility of the method was tested by analysing different amounts of palladium as per recommended procedure. The results given in table 3.8 illustrate that the reproducibility of the method is good as the coefficient of variation did not exceed 5% in all measurements. Table 3.8 also contains standard deviation for set of five readings.

Table 3.8 : Reproducibility of the method

Palladium(II), ppm	Mean absorbance of five observations	Standard deviation	Coefficient of variation, %
1.0	0.075	0.002	2.66
3.0	0.210	0.007	3.33
5.0	0.355	0.011	3.098

3.3.11 Effect of Diverse Ions :

The interference from common cations and anions were tested in the determination of Pd(II) at 5.0 ppm level by the recommended procedure in the usual way. The tolerance for foreign ion was taken as the largest amount that could be present to give an error of about 2% in absorbance values.

The results indicate that Bi(III), Sn(II), Cu(II), Ni(II), Fe(III), and Co(II) interfere seriously. Tl(I) and thiosulphate ion have the tolerance limits 90 ppm and 40 ppm respectively. Copper(II) is masked with sodium thiosulphate and Fe(III) is masked with fluoride. The results are given in table 3.9.

Table 3.9 : Effect of diverse ions

$[\mathrm{Pd(II)}] = 5.0$ ppm; $[\mathrm{BPG}] = 2.5 \times 10^{-4}$M.

Foreign ions	Added as	Tolerance limit, ppm
Cations :		
Zn(II)	$ZnSO_4 . 7H_2O$	15
Ba(II)	$BaCl_2 . 2H_2O$	10
Bi(III)	$BiCl_3$	None
Zr(IV)	$ZrSO_4$	3
Tl(I)	TlCl	90
Mg(II)	$MgSO_4 . 7H_2O$	20
Sn(II)	$SnCl_2 . 2H_2O$	None
Pb(II)	$Pb(NO_3)_2$	2
U(VI)	$UO_2(NO_3)_2 . 6H_2O$	32
Mn(II)	$MnSO_4 . H_2O$	28
Cu(II)	$CuSO_4 . 5H_2O$	None
Ni(II)	$NiSO_4 . 6H_2O$	None
Fe(III)	$FeCl_3 . 6H_2O$	None
Co(II)	$CoSO_4 . 7H_2O$	None
Anions :		
Phosphate	Potassium hydrogen phosphate	8
Thiosulphate	Sodium thiosulphate	40
Oxalate	Potassium oxalate	12
$EDTA^{-4}$	Disodium salt	70
Borate	Sodium borate	10
Acetate	Sodium acetate	7
Thiourea	Thiourea	17

3.4 APPLICATIONS

Determination of Palladium in Palladium Chloride of Carbon Catalyst:

Palladium(II) carbon catalyst was prepared by a standard method[92]. This catalyst containing 5.0% of $PdCl_2$ on carbon is prepared by treating 0.046 mole of $PdCl_2$ in 0.24 mole of concentrated HCl in 50 ml water. Solution is diluted with 140 ml of H_2O and poured over 92.0 gram nitric acid washed Darco G-60 in an evaporating dish. After palladium chloride solution has been thoroughly mixed with carbon, the whole mixture is dried first on a steam bath and then in an oven at $100^{o}c$ with occasional mixing until it becomes completely dry. The mass is powdered and stored in a closed bottle.

The catalyst is roasted to convert into fine powder form. Adsorbed Pd(II) is dissolved in dilute HCl and diulted with distilled water. An aliquot of this solution containing about 100 µg of Pd was treated with reagent BPG and colour is developed as per recommended procedure. Absorbance was measured at 415 nm and concentration of palladium on catalyst was determined. Results are given in table 3.10. The solution was standardised using QDT[93]. Results obtained with QDT and BPG are found to be quite consistent.

Table 3.10 : Determination of palladium chloride on carbon catalyst

Sample	Determination of $PdCl_2$		Standard deviation
	Using BPG*	Using QDT	
5.0 % $PdCl_2$	4.94	4.91	0.006
3.0 % $PdCl_2$	2.89	2.92	0.009

* Triplicate analyses.

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