CHAPTER-II

DETERMINATION OF PALLADIUM

2.1 INTRODUCTION

In the present investigation it was observed that TAG is comparable with other known reagents for palladium. It is superior to some known reagents which suffer from slow rate of complex formation; whereas TAG forms complex instantaneously.

Palladium is used in stainless steel and high chromium steel from 1 to 10 %. Alloys of palladium with noble metals are used as electrical contacts, resistances, thermoelectrodes, solders etc. In many chemical reactions, surfaces of palladium which are normally deposits of palladium on inert supporting material, function as excellent catalysts. The proportions of the alloys of palladium are strictly governed by the concentration of palladium and hence the estimation of the palladium contact 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. Beamish[1] has reviewed the photometric determination of palladium. Numerous oximes have been proposed for the extractive photometric determination of Pd(II).

Due to low sensitivities, reagents like dimethylglyoxime[2] (0.06 $\mu g/cm^2$), 8-aminoquinoline[3] (0.04 $\mu g/cm^2$) and acenaphthenequinone monoxime[4] (0.084 $\mu g/cm^2$) are not suitable for trace determination of palladium.

Due to low kinetic stability, complex formation in case of 4-methylcyclohexane-1:2-dioxime[5], 5-amino-2-benzimidazole-thiol[6], aluminon[7], phthalimide dioxime[8], procaine[9], chrome azurol S[10] and azurubine[11] takes place after 30 to 90 minutes. Rate of formation of complexes is slow in case of nitroso-R-salt[12], glycine thymol blue[13], 3-nitrosopyridine-2, 6-diol[14], melamine[15] and tropolon[16] and hence requires heating.

Some reagents are not selective though sensitive, Reagents like 2-mercaptoquinoline[17], bismuthol II[18], 2-diethyl-amino ethanethiol hydrochloride,[19] and crystal violet[20] suffer from numerous interfering ions.

In case of N, N'-bis(2-sulphoethyl) dithio-oximide[21] and 2-diethylaminoethanethiol hydrochloride[22] rate of complex formation is slow. Moreover, they are not selective.

Though furylpentadienal thiosemicarbazone[23], 6-methyl picolinaldehyde thiosemicarbazone,[24] phthalimide bisthiosemi-carbazone,[25] bis-acetyl bis-4-phenyl-3-thiosemicarbazone,[26] p-ethylsulphophenyl benzaldehyde thiosemicarbazone[27] and glyoxal bis-thiosemicarbazone[28] are used for colourimetric determination of palladium, most of the reagents suffer from one or the other drawback.

Reagents like 2-mercaptobenzoic acid,[29] o-mercaptobenzoic acid,[30] benzoyl-methylglyoxime,[31] 1-(2-pyridylazo)-2-naphthol,[32] Palladiazo[33] and eriochrome cyanine R[34] are selective and sensitive and hence can be successfully used for the trace determination of palladium.

2.2 EXPERIMENTAL

All the chemicals used were of analytical grade.

2.2.1 Standard Solutions :

Standard Palladium Solution :

A stock solution of palladium (1 mg/ml) was prepared by dissolving A.R. grade palladium chloride in distilled water containing a few mls of concentrated hydrochloric acid. The solution was standardised with DMG[35] gravimetrically. Further dilutions for experimental purposes were done with distilled water.

Reagent Solution :

A stock solution of the reagent, thiophene-2-aldehyde guanylhydrazone (TAG) was prepared by dissolving 168 mg of it in 100 ml distilled ethanol (1.68 mg/ml i.e. 1.0×10^{-2}M).

Buffer Solution :

Buffer solution of pH 11 was prepared by dissolving appropriate amount of sodium carbonate.

2.2.2 Recommended Procedure :

An aliquot of the solution containing 10 µg of palladium(II) was taken in 10 ml volumetric flask. To it was added 3.5 ml of the reagent (TAG) solution of concentration 1.0 x 10^{-2} M. The pH of the solution was adjusted to 10.5 with buffer solution and was diluted upto the mark with distilled ethanol. The absorbance of the palladium(II) - TAG complex was measured at 365 nm against reagent blank. The concentration of palladium in an unknown solution was determined from a calibration curve obtained under identical conditions.

2.3 RESULTS AND DISCUSSION

2.3.1 Spectral Characteristics :

The absorption spectrum of Pd(II)-TAG complex containing 0.9396 x 10^{-4}M palladium (II) and 1.0 x 10^{-2}M reagent (TAG) was recorded at pH 10.5 against reagent blank. The complex has absorption maximum at 365 nm and molar extinction coefficient of the complex is 1.5441 x 10^{4} l mole^{-1} cm^{-1} at 365 nm. The molar extinction coefficient of the reagent at 365 nm is 0.0105 x 10^{4} l mole^{-1} cm^{-1} (Fig. 2.1). The observations for the spectra are given in table 2.1.

Table 2.1 : Molar extinction coefficients of the Pd(II)-TAG complex and the reagent (TAG).

Wavelength λ, nm	Molar extinction coefficients, ϵ	
	Pd(II)-TAG complex $\epsilon \times 10^4$ l mole^{-1} cm^{-1}	Reagent, TAG $\epsilon \times 10^4$ l mole^{-1} cm^{-1}
340	0.9052	0.0280
350	1.3312	0.0180
360	1.5236	0.0120
365	1.5441	0.0105
370	1.2779	0.0086
380	0.8519	0.0068
390	0.5750	0.0055
400	0.4153	0.0045
410	0.3514	0.0038
420	0.3088	0.0030
430	0.2875	0.0028
440	0.2715	0.0028
450	0.2449	0.0025
460	0.2236	0.0023
470	0.1916	0.0020
480	0.1703	0.0016
490	0.1597	0.0016
500	0.1384	0.0015
510	0.1171	0.0012
520	0.1064	0.0010
540	0.0958	0.0006
560	0.0745	0.0005
580	0.0638	0.0005
600	0.0585	0.0003

2.3.2 Effect of pH :

A series of solutions varying in pH were prepared as per the recommended procedure. The complex has maximum and constant absorbance over the pH range 10.0 to 11.0. It falls below pH 10.0 and above pH 11.0. Hence, the pH value 10.5 was selected for the study of Pd(II) - TAG complex. In acidic medium the complex shows comparatively less absorbance. The observations are given in table 2.2. The plot of observations is shown in fig. 2.2.

Table 2.2 : Effect of pH on the absorbance of Pd(II)-TAG complex
[Pd(II)] = 10 ppm; [TAG] = 1.0×10^{-2} M

pH	Absorbance at 365 nm
2.0	0.04
4.0	0.12
6.0	0.75
7.0	0.85
8.0	0.93
9.0	1.10
10.0	1.20
10.5	1.20
11.0	1.20
12.0	1.00
13.0	0.90

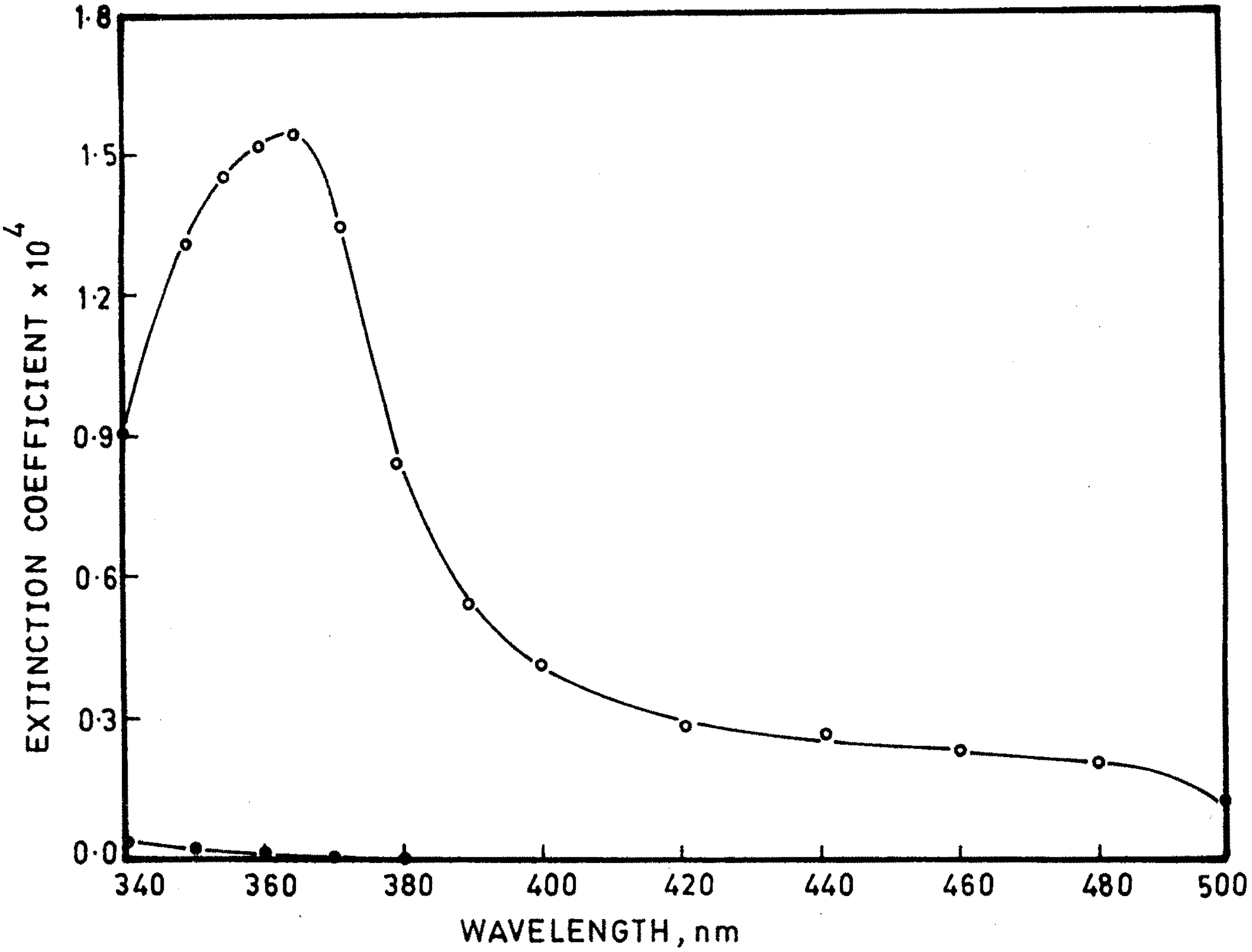

FIG. 2·1 – ○—○ ABSORPTION SPECTRUM OF PALLADIUM-TAG COMPLEX.
●—● ABSORPTION SPECTRUM OF REAGENT (TAG).

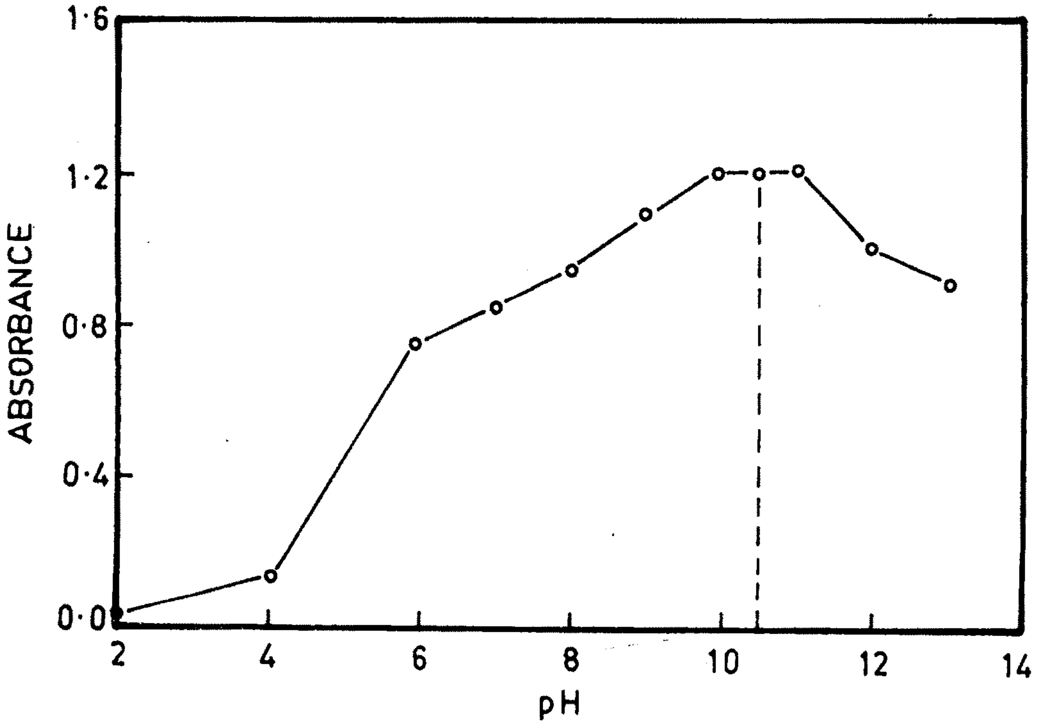

FIG. 2·2 – EFFECT OF pH

2.3.3 Effect of reagent concentration :

It was observed that the amount of excess of reagent was the least critical. About a three fold excess 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 5.0×10^{-3} M to 4.0×10^{-2} M, while the concentration of palladium was kept constant at 0.9396×10^{-4} M. The pH value was adjusted and the solution was made upto the mark in 10 ml volumetric flask. The absorbance was measured at 365 nm wavelength against reagent blank. The results are given in table 2.3 show that, three fold molar excess of the reagent is sufficient for full colour development of 10 ppm palladium.

Table 2.3 : Effect of reagent concentration on the absorbance of Pd(II)-TAG complex
[Pd(II)] = 10 ppm; [TAG] = 1.0×10^{-2} M

Amount of TAG added ml	Absorbance at 365 nm
0.5	0.80
1.0	0.95
1.5	1.00
2.0	1.20
2.5	1.25
3.0	1.35
3.5	1.40
4.0	1.40

2.3.4 Stability and reaction rate :

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

2.3.5 Validity of Beer's Law :

The solutions containing different amounts of palladium and the same amount of reagent (TAG) 3.5 ml of 1.0×10^{-2}M at pH 10.5 were used to study the validity of Beer's Law. It was found that the Beer's law is valid up to 15 ppm of palladium at 365 nm (Table 2.4; Fig. 2.3).

The optimum concentration range for the determination of palladium was calculated from the Ringbom plot[36] and was found to be 3.0 to 7.4 ppm at 365 nm (Fig. 2.4).

Table 2.4 : Validity of Beer's Law

$[Pd(II)] = 0.9396 \times 10^{-4}M, [TAG] = 1.0 \times 10^{-2}M$

Amount of Palladium(II) ppm	Absorbance at 365 nm
3.0	0.25
6.0	0.50
9.0	0.76
12.0	1.00
15.0	1.25
18.0	1.40

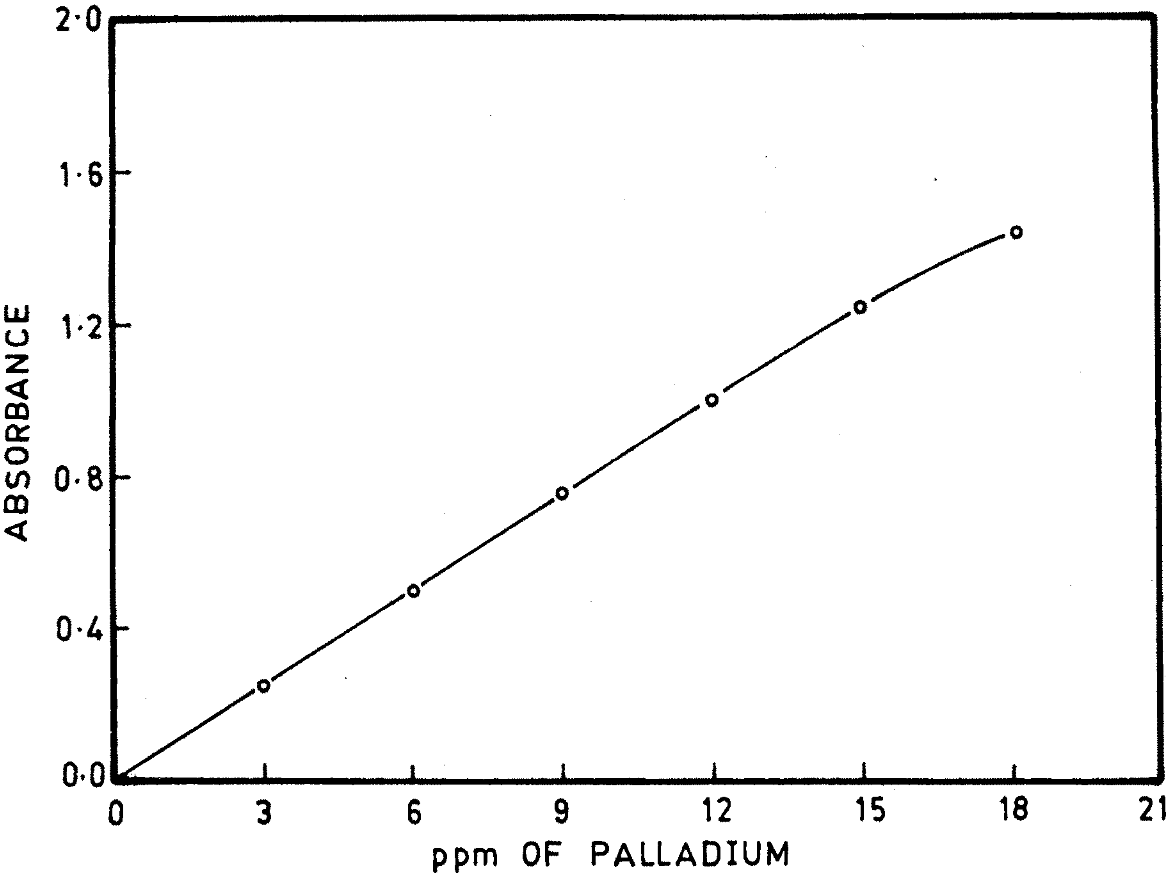

FIG. 2·3 – VALIDITY OF BEER'S LAW.

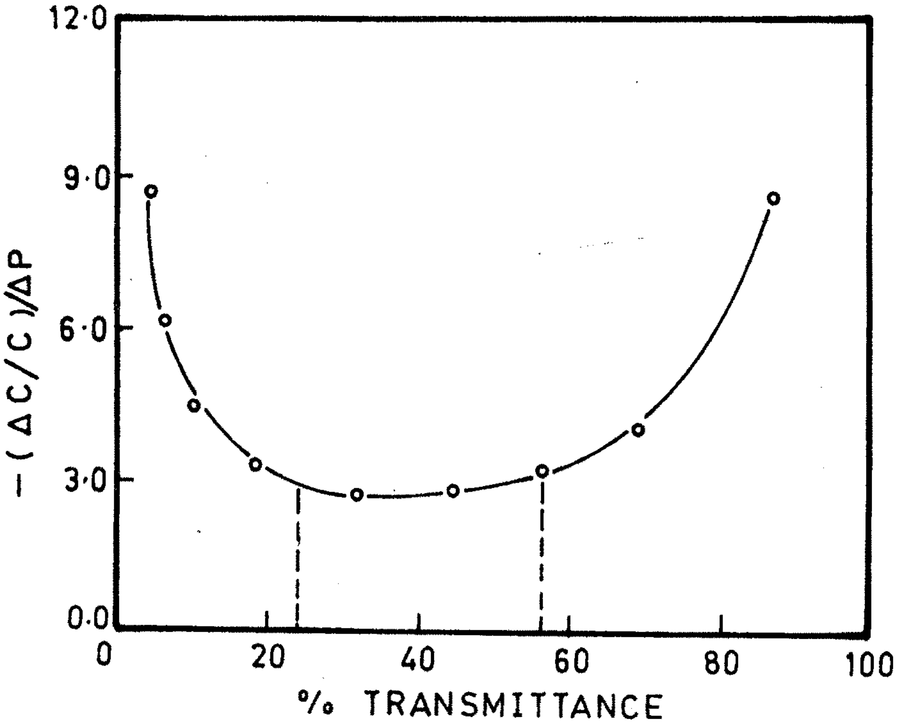

FIG. 2·4 – RINGBOM PLOT.

2.3.6 Composition of the Complex :

The empirical formula for Pd(II)-TAG complex was determined by Job's method[37] of continuous variation, molar ratio method[38] and slope ratio method.[39] For Job's method of continuous variation, a series of solutions were prepared by keeping the sum of molar concentrations of palladium and ligand constant, while their ratio varied in different solutions. For this purpose, equimolar solutions of palladium and ligand were used (Table 2.5).

The plots of absorbances at 350 nm, 365 nm, 380 nm and 405 nm wavelengths against mole fraction of the reagent indicate that ligand forms 1:2 complex (Fig. 2.5).

In a molar ratio method, ligand concentration (0.9396×10^{-4}M) was maintained constant and different concentrations of palladium ion ranging from 1.88×10^{-5}M to 1.88×10^{-4}M were used. (Table 2.6). The absorbances were measured at 365 nm and 390 nm wavelengths.

Molar ratio plot indicates and confirms the formation of 1:2 complex at pH 10.5 (Fig. 2.6).

In slope ratio method, a series of solutions were prepared by keeping the metal concentration variable and a very large excess of ligand concentration and vice versa. Slope ratio method also confirms the 1:2 complex.

Table 2.5 : Job's continuous variation method

$[Pd(II)] = [TAG] = 0.9396 \times 10^{-4} M$

Palladium(II) ml	Reagent (TAG) ml	Molar Ratio M:L	Absorbances at λ			
			350 nm	365nm	380 nm	405 nm
0.0	1.8	-	-	-	-	-
0.2	1.6	1:8	0.115	0.170	0.100	0.070
0.4	1.4	2:7	0.295	0.370	0.235	0.160
0.6	1.2	1:2	0.465	0.635	0.370	0.225
0.8	1.0	4:5	0.370	0.535	0.270	0.150
1.0	0.8	5:4	0.215	0.370	0.170	0.090
1.2	0.6	2:1	0.130	0.200	0.090	0.040
1.4	0.4	7:2	0.080	0.135	0.040	0.020
1.6	0.2	8:1	0.350	0.070	0.020	0.010
1.8	0.0	-	-	-	-	-

Table 2.6 : Molar ratio method

$[Pd(II)] = [TAG] = 0.9396 \times 10^{-4}$ M

Palladium(II) ml	Reagent(TAG) ml	Molar Ratio M:L	Absorbances at λ	
			365 nm	390 nm
0.0	2.0	-	-	-
0.2	2.0	1:10	0.080	0.055
0.4	2.0	1:5	0.155	0.105
0.6	2.0	3:10	0.215	0.155
0.66	2.0	1:3	0.295	0.200
0.8	2.0	2:5	0.345	0.235
1.0	2.0	1:2	0.380	0.270
1.2	2.0	3:5	0.405	0.290
1.33	2.0	2:3	0.420	0.300
1.4	2.0	7:10	0.420	0.305
1.6	2.0	4:5	0.425	0.305
1.8	2.0	9:10	0.425	0.305
2.0	2.0	1:1	0.425	0.305

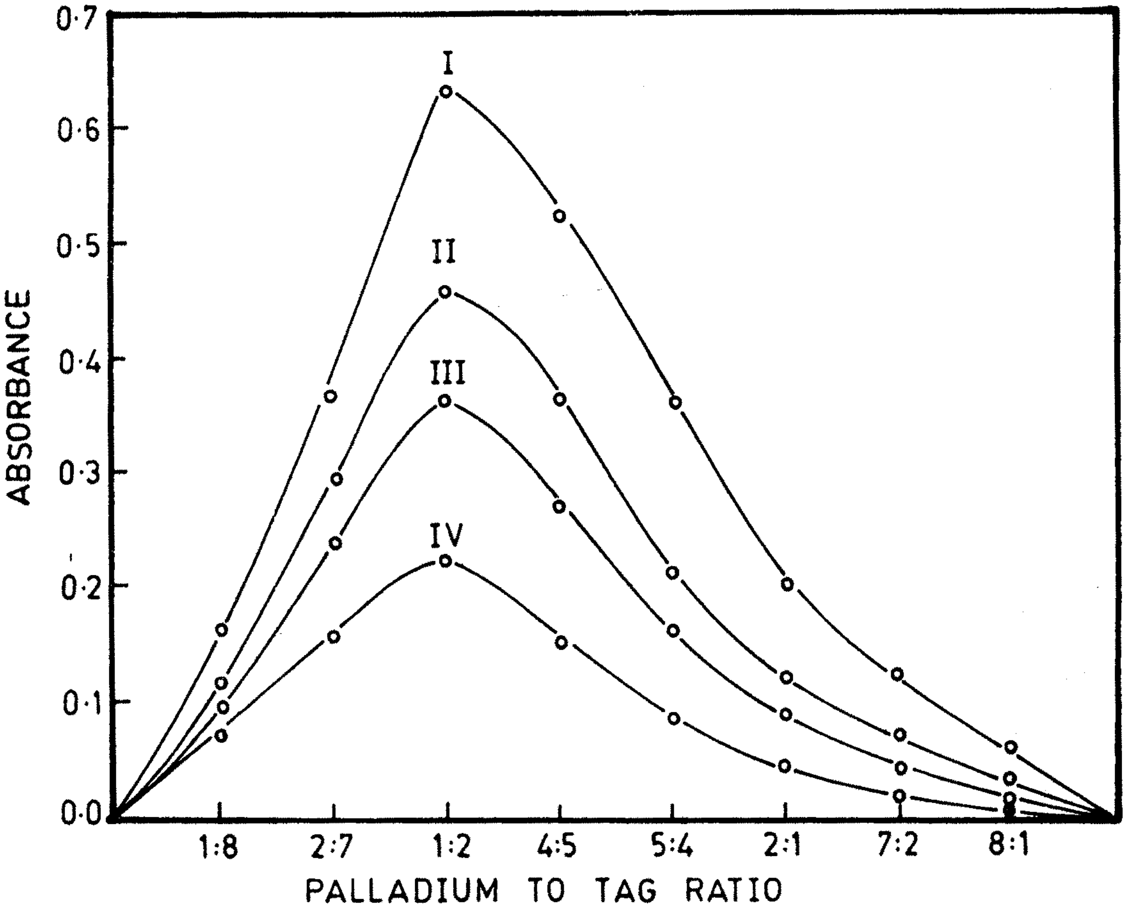

FIG. 2·5 – JOB'S CONTINUOUS VARIATION METHOD.
I – 365 nm, II – 350 nm, III – 380 nm, IV – 405 nm.

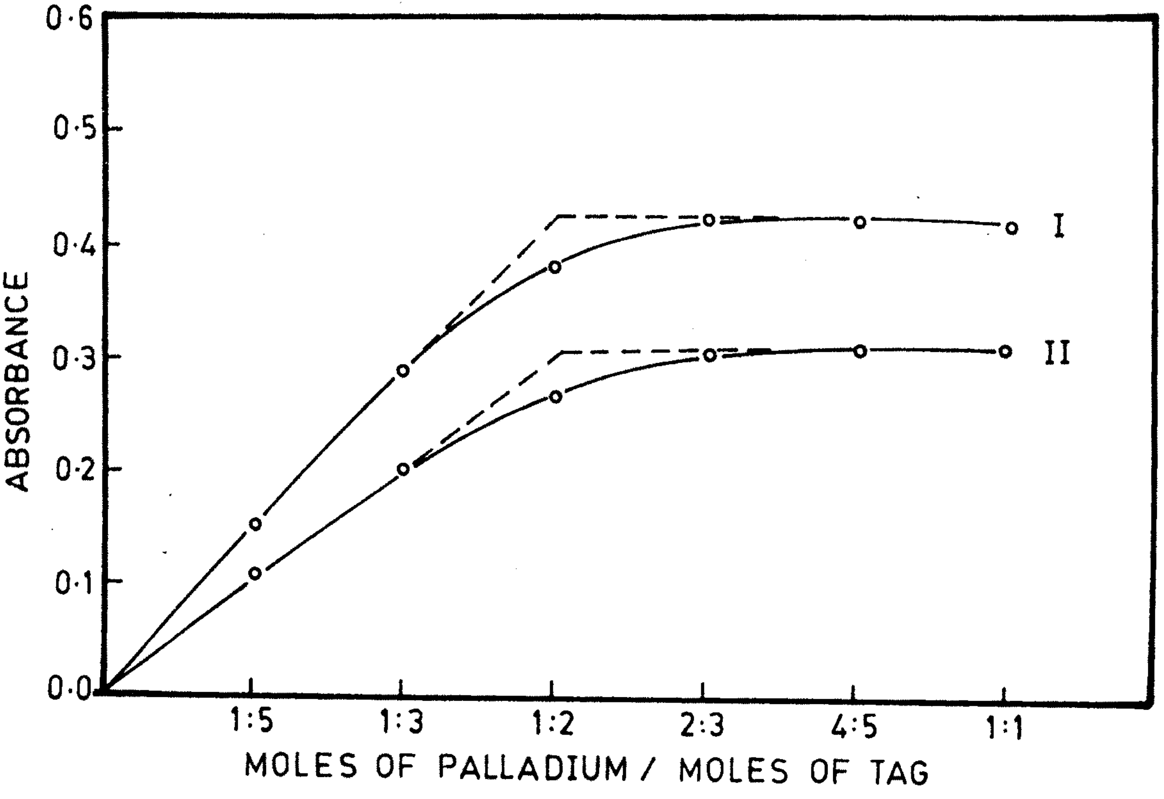

FIG. 2·6 – MOLE RATIO METHOD.
I – 365 nm, II – 390 nm.

2.3.7 Sensitivity :

The complex of palladium is not sensitive to the light. The photometric sensitivity of the method was calculated by the method of Sandell[40] and found to be 0.01148 $\mu g/cm^2$

2.3.8 Degree of dissociation and instability constant :

The instability constant is calculated from the mole ratio plot (Fig. 2.6). The equation is

$$K = \frac{(\,m\alpha c\,)^m \, (n\alpha c)^n}{c(1-\alpha)}$$

where,

K = Instability constant

α = Degree of dissociation

c = Concentration of the complex in moles per litre

m & n = 1 and 2 respectively.

The degree of dissociation α, is calculated from the relationship,

$$\alpha = \frac{d_E - d_O}{d_E}$$

where,

d_E = Optical density when complex is completely formed, (extrapolated value of O.D.)

d_O = Optical density observed actually at Stoichiometric molar ratio.

The degree of dissociation of the complex at 365 nm was found to be 0.1059.

The apparent instability constant[41] was calculated as 4.690×10^{-13}.

From this value, the change in free energy[42] can be calculated by using the relation.

$$\Delta F = - RT \ln K \quad \text{at } 25^{\circ}C$$

where,

R = Gas constant

T = Absolute temperature

and K = Instability constant.

The change in free energy of the system is -16.920 K cals/mole.

2.3.9 Reproducibility of the method :

The reproducibility of the method was studied by determining palladium in sets of six observations for each concentration. The table 2.7 summarises the results and shows that the results are reproducible.

Table 2.7 : Standard deviation of the method at pH 10.5 and at 365 nm

Palladium ppm	Mean absorbance of six observations	Standard deviation	Coefficient of variation %
2.0	0.17	0.0032	1.8823
4.0	0.35	0.0060	1.7142
6.0	0.50	0.0088	1.7600

2.3.10 Effect of diverse ions :

The effect of diverse ions was studied using fixed amount of Palladium (1.00 ppm) and developing and measuring the colour intensity as per recommended procedure. An error upto 2 % in absorbance was considered to be tolerable.

It is found that citrate ion, tartrate ion and thiourea interfere seriously; while the tolerance limit of urea is 80.0 ppm. For various foreign ions, the tolerance limits are given in table 2.8.

Table 2.8 : Effect of diverse ions

[Pd(II)] = 1.0 ppm; [TAG] = 1.0×10^{-3}M

Foreign ions	Added as	Tolerance limit ppm
Cations		
Cr(III)	$CrCl_3 \cdot 6H_2O$	1.0
V(IV)	$VOSO_4 \cdot H_2O$	4.0
Ba(II)	$BaCl_2 \cdot 2H_2O$	3.0
Cu(II)	$CuSO_4 \cdot 5H_2O$	3.0
Ca(II)	$Ca(NO_3)_2 \cdot 4H_2O$	2.0
Zn(II)	$ZnSO_4 \cdot 7H_2O$	2.0
Mn(II)	$MnSO_4 \cdot H_2O$	0.8
Co(II)	$Co(NO_3)_2 \cdot 6H_2O$	1.0
Fe(III)	$FeCl_3 \cdot 6H_2O$	0.8
Ni(II)	$NiSO_4 \cdot 6H_2O$	1.0
Cd(II)	$CdSO_4 \cdot 8/3\ H_2O$	1.0
Cr(VI)	$K_2Cr_2O_7$	1.0
Anions :		
Citrate	Citric acid	none
Thiourea	Thiourea	none
Oxalate	Potassium oxalate	2.0
$EDTA^{-4}$	Disodium salt	0.1
Acetate	Sodium acetate	2.0
Tartrate	Tartaric acid	none
Urea	Urea	80.0

2.4 APPLICATIONS :

Determination of palladium chloride in palladium (II) carbon catalyst :

Palladium(II) carbon catalyst was prepared by standard method.[43] This catalyst was roasted to convert into fine powdered form. Adsorbed palladium (II) was dissolved in 1:1 hydrochloric acid and diluted with distilled water. An aliquot of this solution containing about 250 µg of Pd was treated with reagent TAG and colour was developed as per recommended procedure. Absorbance was measured at 365 nm and concentration of palladium in catalyst was determined. Results are given in table 2.9. The solution was standardised using QDT[44] (quinoxaline 2,3 dithiol). Results obtained with QDT and TAG are found to be consistent.

Table 2.9 : Determination of palladium chloride on carbon catalyst

Sample	Determination of palladium chloride	
	Using TAG	Using QDT
Approximately 6 % $PdCl_2$	5.88 %	5.90 %
Approximately 4 % $PdCl_2$	3.93 %	3.91 %

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