
CHAPTER - III
DETERMINATION OF PALLADIUM (II)

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3.1 INTRODUCTION

Palladium is a silver white metal. Palladium and its alloys find variable applications in chemical industry and in instrument making. 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. Alloys of palladium with noble and rare metals are used as electrical contacts, resistances, thermoelectrodes solders etc. Alloys of palladium with other precious metals have found uses in dentistry and jewellery. Palladium is capable of taking high polish. In many chemical reactions, surfaces of palladium which are normally deposits of palladium on inert supporting material, function as excellent catalysts. In organic synthesis, oxidation, hydrogenation and dehydrogenation, it is principally used as a catalyst. 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. Addition of trace amount of palladium increases the resistance of stainless steel, high chromium steel and renders the titanium resistant to the action of boiling solutions of mineral acids^{1,2}. It is used from 1 to 10 % in stainless steel and high chromium steel.

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 the reagent ATG 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 ATG forms complex instantaneously. As far as the interferences are concerned, some of the reported reagents like 6-HNQDT³ and furil- α -dioxime⁴ are more advantageous as compared to ATG.

Beamish⁵ has reviewed the photometric determination of Pd (II). Some reagents are not selective though sensitive. Reagents like 2-mercaptoquinoline⁶, bismuthol-II⁷, 2-diethylaminoethanethiol hydrochloride⁸ and crystal violet⁹ suffer from numerous interfering ions.

Due to low sensitivities, reagents like dimethyl glyoxime¹⁰ ($0.06\mu\text{g}/\text{cm}^2$), 8-aminoquinoline¹¹ ($0.04\mu\text{g}/\text{cm}^2$) and acenaphthene quinone monoxime¹² ($0.084\mu\text{g}/\text{cm}^2$) are not suitable for trace determination of palladium.

In case of N, N'-bis (2-sulphoethyl) dithiooxi-
mide¹³ and 2-diethylamino ethane thiol hydrochloride¹⁴, rate
of complex formation is slow. Moreover, they are not selec-
tive.

Complex formation in case of 4-methyl cyclohexane-
1:2 dioxime¹⁵, 5-amino-2-benzimidazole thiol¹⁶, aluminon¹⁷,
phthalimide dioxime¹⁸, procaine¹⁹, chrome azurol S²⁰,
dimethyl glyoxime²¹ and azorubine²² takes place after 30 to
90 minutes due to low kinetic stability. Rate of formation
of complexes is slow in case of nitroso-R-salt²³, glycine
thymol blue²⁴, 3-nitroso-pyridine-2, 6-diol²⁵, malamine²⁶
and tropolon²⁷, and hence requires heating.

Analytical reagents like 2-mercaptobenzoic acid²⁸,
o-mercaptobenzoic acid²⁹, benzoyl methyl glyoxime³⁰, 1-(2-
pyridylazo)-2-naphthol³¹, palladiaz³² and eriochrome
cyanine R³³ are selective and sensitive and hence can be
successfully used for the trace determination of palladium.

Though furylpentadienal thiosemicarbazone³⁴,
6-methyl picolinaldehyde thiosemicarbazone³⁵, phthalimide-
bis-thiosemicarbazone³⁶, bis-acetyl-bis-4-phenyl-3-thiosemi-
cabrazone³⁷, P-ethyl sulphophenyl benzaldehyde thiosemicar-
bazone³⁸ and glyoxal-bis-thiosemicarbazone³⁹ 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 derivatives⁴⁰, butylene diamine tetramethylene phosphoric acid⁴¹, 2-methyl-1,4-naphthoquinone monoxime⁴², 2-(5-bromo-2-pyridylazo)-5-(diethylamino) phenol⁴³, triethylene tetramino hexamethylene phosphoric acid⁴⁴, o,o'-diamino azobenzene⁴⁵, indane-1,2,3-trione trioxime⁴⁶, mandelazo I⁴⁷, 1,5-diphenyl-carbazide⁴⁸, 2-(4,5-dimethyl-2-triazolylazo) 5-dimethylamino phenol⁴⁹, chlorophosphonazo II⁵⁰, 1,8-dihydroxy-2-[(4-chloro-2-phosphonophenyl)azo]-7-[(6,8-disulphonaphthyl)azo] naphthalene⁵¹, 4-carbamoyl-1-[3-(2-hydroxyiminomethyl-1-pyridino)-oxapropyl] pyridinium dichloride (HI-6)⁵², 2(4',5'-dimethyl-2' thiazolylazo)-5-dimethyl amino aniline⁵³, 2-(2'-benzothiazolylazo)-5-dimethylamino-4-tolylarsonic acid⁵⁴, 5-phenylazo-8-aminoquinoline⁵⁵, 5-(2'-benzothiazolylazo)-8-aminoquinoline⁵⁶, semixylenol orange⁵⁷, 5-(4'-amino-2'-hydroxy-benzeneazo) tetrazole⁵⁸, 2-(2'-benzothiazolylazo)-5-dimethylamino-4-tolylarsonic acid⁵⁹, 1-(5-bromo-2-pyridylazo)-2-naphthol-6-sulfonic acid⁶⁰, 7-(2-pyridylazo)-5-chloro-8-hydroxyquinoline⁶¹ and o-hydroxy acetophenone thiosemicarbazone⁶².

By extractive spectrophotometric method, palladium(II) was determined with the reagents such as pyronine B⁶³, 5,5-methylene-bis-thiosalicylic acid⁶⁴, N-N'-diphenyl propane dithioamide⁶⁵, 4-(2-pyridylazo)-resorcinol and

tetraphenyl arsonium⁶⁶, 2-hydroxynaphthalene-4-phenyl-3-thiosemicarbazone⁶⁷, pyridine-2-acetaldehyde salicyloylhydrazone⁶⁸, 5-chlorosalicylaldoxime⁶⁹, 2-allylthiourea⁷⁰, furilacrolein oxime⁷¹, 2-mercaptobenzamide⁷², diphenyl thiovioluric acid⁷³, cetyltrimethyl ammonium bromide⁷⁴, 2-N-(2-mercaptophenyl)-1,2,3-benzothiadiazoline⁷⁵, 2,2'-dipyridyl-1-phthalazinohydrazone⁷⁶, 2-N-(2, mercapto-4-chlorophenyl)-6-chloro, 1,2,3-benzothiadiazoline⁷⁷ and isonitrosomalondianilide⁷⁸.

Palladium(II) was also determined spectrophotometrically as Pd(II)-KI-rhodamine 6G-PVA⁷⁹ system, Pd(II)-tin(II) chloride-crystal violet⁸⁰ system, Pd(II)-Picoline amidoxime⁸¹ system, Pd(II)-5-Br-PADAP-triton-x-100⁸² system, Pd(II)-CPA-MA-CTMAN⁸³ system and Pd(II)-1,10-phenanthroline cation A-peregal-O⁸⁴ system.

Pd(II) was also determined by spectrophotometric extraction as Pd(II)-thiocyanate-tetrabutyl ammonium⁸⁵ ion pair and Pd(II)-PAR-xylometazoline hydrochloride⁸⁶ ion pair.

3.2 EXPERIMENTAL

3.2.1 Standard Solutions:

Standard palladium solution:

A stock solution of palladium (1 mg/ml i.e. $9.397 \times 10^{-3} \text{M}$) was prepared by dissolving 0.169 g of A.R. grade palladium(II) chloride in 100.0 ml distilled water

containing a few mls. of concentrated hydrochloric acid. The solution was standardised with dimethyl glyoxime gravimetrically^{B7}. Further dilutions for experimental purposes were done with distilled water.

Reagent (ATG) solution:

A stock solution of the reagent 2-acetyl thiophene guanylhydrazone (ATG) was prepared by dissolving 182 mg of it in 100.0 ml 50% ethanol (1.82 mg/ml i.e. 0.01 M).

Buffer solution:

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

All chemicals used were of analytical grade.

3.2.2 Recommended Procedure:

An aliquot of the solution containing 50 µg of palladium(II) was taken in a 10 ml volumetric flask. Then 0.9 ml of 1.0×10^{-2} M reagent (ATG) solution was added which provides desired excess quantity to complete the complex formation. The pH of the solution was adjusted to 12.6 by adding 1.0 ml buffer solution and was adjusted to the mark with distilled water. The absorbances of the complex was measured at 375 nm against reagent blank. The concentration of palladium was read out from a calibration curve.

3.3 RESULTS AND DISCUSSION

3.3.1 Spectral Characteristics:

The absorption spectrum of Pd(II)-ATG complex of the solution of the concentration 4.6983×10^{-5} M was recorded at pH 12.6 against reagent blank. The complex shows absorption maximum at 375 nm. The molar extinction coefficient at 375 nm is 0.7492×10^4 l mole⁻¹ cm⁻¹. The reagent does not absorb in this region. The observations of absorbances and molar extinction coefficients of the complex and the reagent are given in table 3.1 (Figure 3.1).

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

Wavelength λ , nm	Absorbance		Molar extinction coefficient, ϵ	
	Pd(II) -ATG 4.6983×10^{-5} M	ATG, reagent 6.0×10^{-4} M	Pd(II) -ATG complex $\epsilon \times 10^4$ l mole $^{-1}$ cm $^{-1}$	ATG, reagent $\epsilon \times 10^4$ l mole $^{-1}$ cm $^{-1}$
350	0.086	0.443	0.1830	0.0738
360	0.128	0.237	0.2724	0.0395
370	0.345	0.152	0.7343	0.0253
375	0.352	0.142	0.7492	0.0236
380	0.328	0.133	0.6981	0.0221
390	0.249	0.062	0.5299	0.0103
400	0.162	0.033	0.3448	0.0055
410	0.106	0.025	0.2256	0.0041
420	0.087	0.022	0.1851	0.0036
440	0.068	0.016	0.1447	0.0026
460	0.057	0.010	0.1213	0.0016
480	0.043	0.005	0.0915	0.0008
500	0.034	-	0.0723	-
520	0.026	-	0.0553	-
540	0.020	-	0.0425	-

3.3.2 Effect of pH:

To study the effect of pH of the solution on the absorbance of complex, a series of solutions containing 0.5ml of 9.397×10^{-4} M of Pd(II) and 0.6 ml of 1.0×10^{-2} M reagent (ATG) were prepared as per recommended procedure.

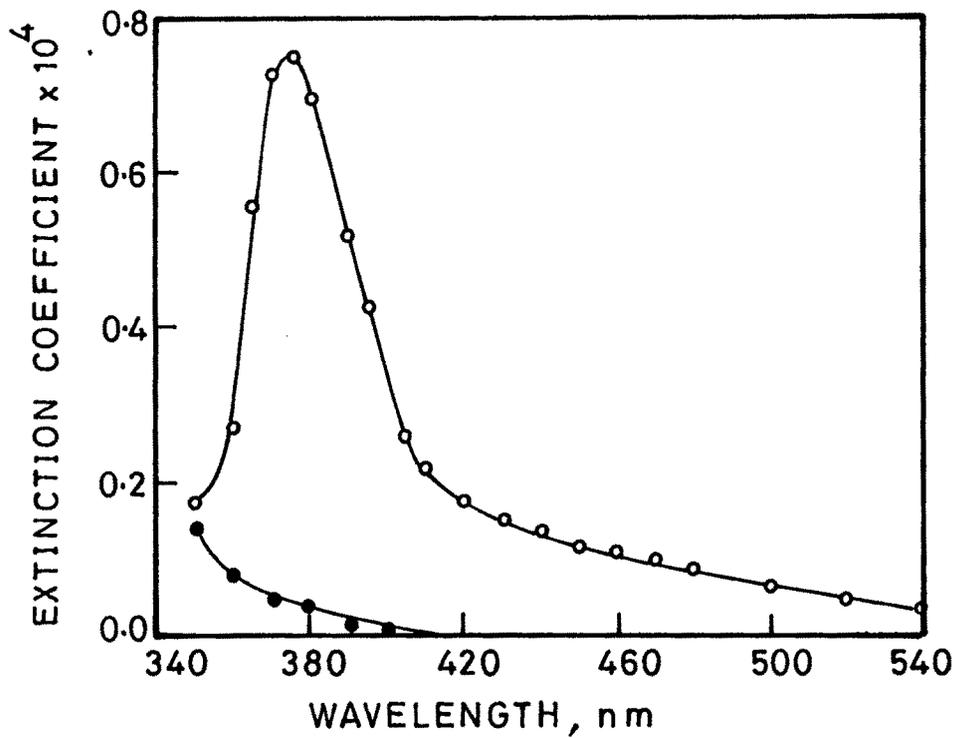


FIG. 3.1 - ○-○ ABSORPTION SPECTRUM OF PALLADIUM (II)-ATG COMPLEX.
●-● ABSORPTION SPECTRUM OF REAGENT (ATG).

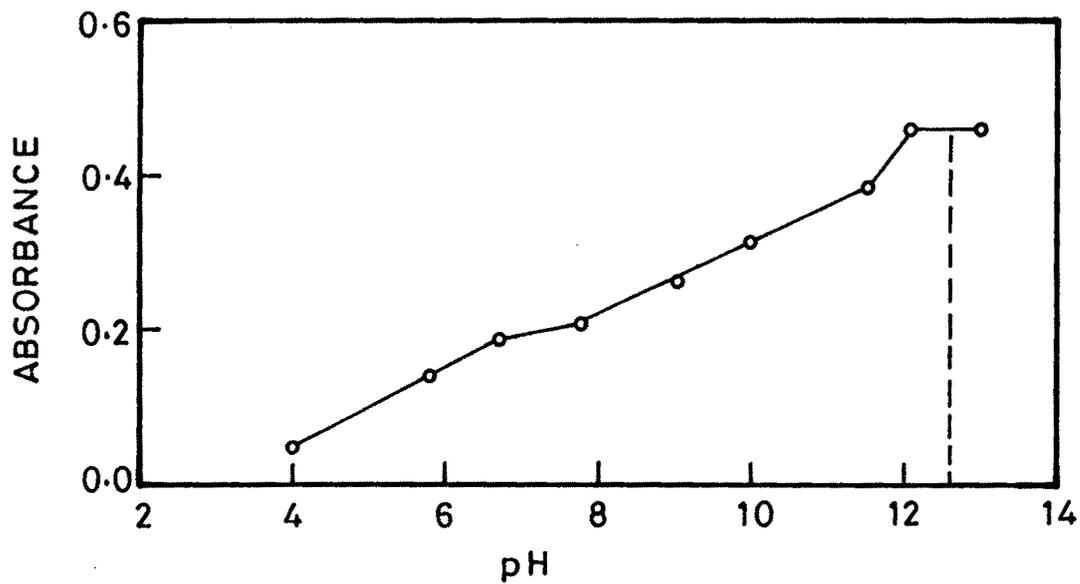


FIG. 3.2 - EFFECT OF pH.

The absorbances were measured against corresponding reagent blank. It was found that the complex has maximum and constant absorbance over the pH range 12.0 to 13.0. Therefore pH 12.6 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
 $[Pd(II)] = 4.6983 \times 10^{-5} \text{ M}$; $[ATG] = 6.0 \times 10^{-4} \text{ M}$

pH	Absorbance at 375 nm
4.00	0.046
5.85	0.143
6.80	0.190
7.78	0.211
9.10	0.266
10.00	0.313
11.45	0.381
12.00	0.455
13.04	0.455

3.3.3 Effect of Reagent Concentration:

The effect of reagent concentration on the colour intensity of Pd(II)-ATG complex at pH 12.6 was studied by varying the volume of $1.0 \times 10^{-2} \text{ M}$ reagent from 0.2 to 1.0 ml for constant concentration of palladium (50.0 μg). The

determination of the metal complex was carried out as per recommended procedure. The results in table 3.3 show that about thirteen-fold molar excess of the reagent was sufficient to ensure the full complexation of palladium(II).

Table 3.3: Effect of reagent concentration
 $[Pd(II)] = 5.0 \text{ ppm}$; $[ATG] = 1.0 \times 10^{-2} \text{ M}$

Amount of reagent, ml	Absorbance at 375 nm
0.2	0.283
0.4	0.358
0.5	0.363
0.6	0.370
0.7	0.356
0.8	0.323
1.0	0.313

3.3.4 Stability and Reaction Rate:

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

3.3.5 Validity of Beer's Law:

The solutions containing different amounts of palladium(II) in the range 2.0 to 24.0 ppm, were used for the study of the validity of Beer's law. The complex was measured at 375 nm against reagent blank. The absorbance was

plotted versus the concentration of palladium taken (Table 3.4; Figure 3.3). The curve indicates that there is a rectilinear relationship between the absorbance and the concentration of palladium (II) in the range 0.0 to 12.0 ppm. The Beer's law is valid upto 12.0 ppm of Pd(II).

The optimum concentration range for the determination of palladium was studied from Ringbom plot^{BB} and was found to be 8.0 to 19.0 ppm at the conditions chosen for the experiment (Figure 3.4).

Table 3.4: Validity of Beer's law
[ATG] = 1.4094×10^{-4} M

Amount of Palladium(II), ppm	Absorbance at 375 nm	Transmittance, %	$-(\Delta c/c)/\Delta p$
2.0	0.076	98.2	50.50
4.0	0.154	70.2	4.01
6.0	0.230	58.9	3.26
8.0	0.302	49.9	2.89
10.0	0.376	42.1	2.73
12.0	0.450	35.5	2.72
14.0	0.482	33.0	2.72
16.0	0.521	30.1	2.77
18.0	0.578	26.4	2.89
20.0	0.638	23.0	2.89
24.0	0.682	20.8	3.11

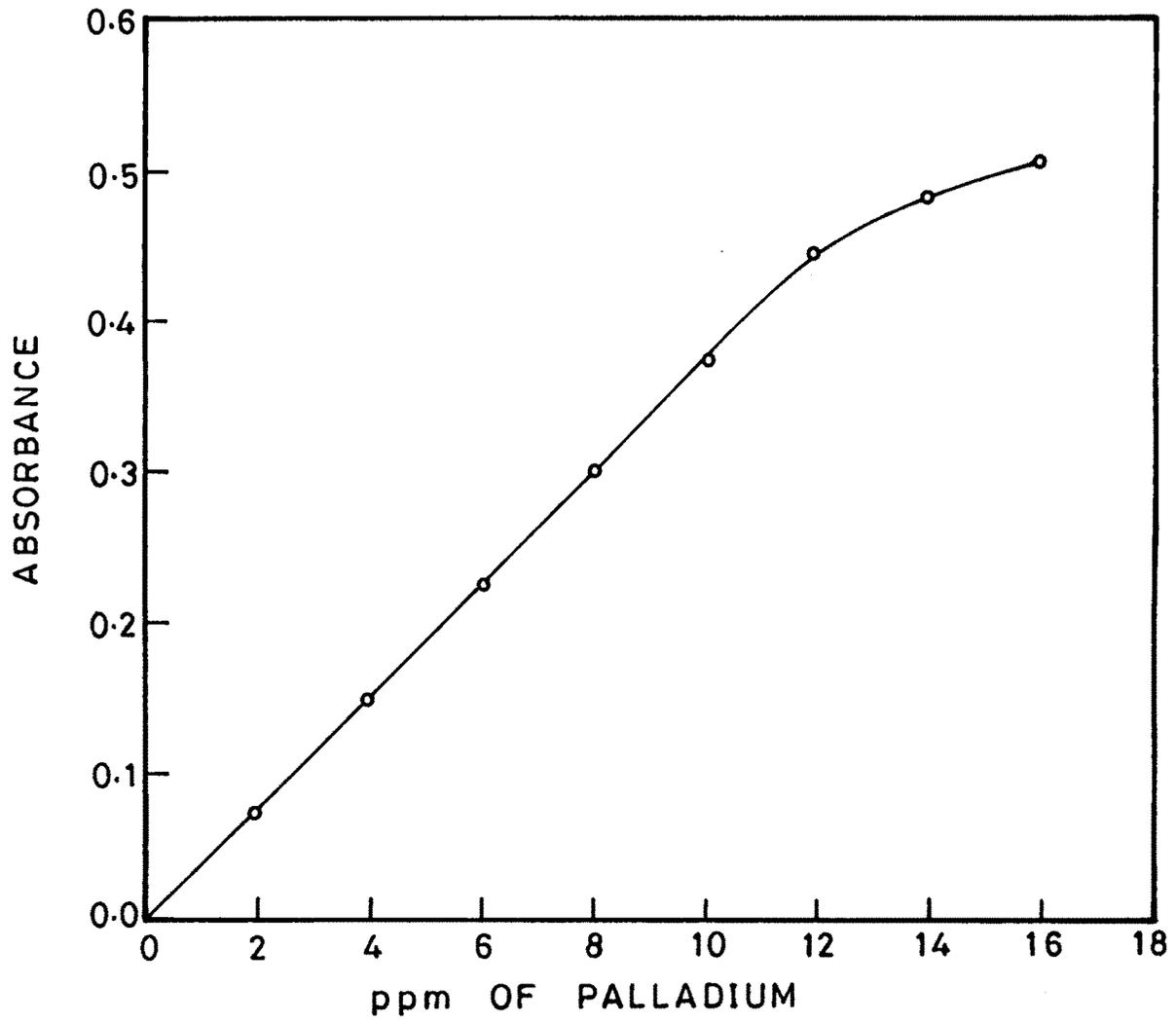


FIG. 3.3 - VALIDITY OF BEER'S LAW .

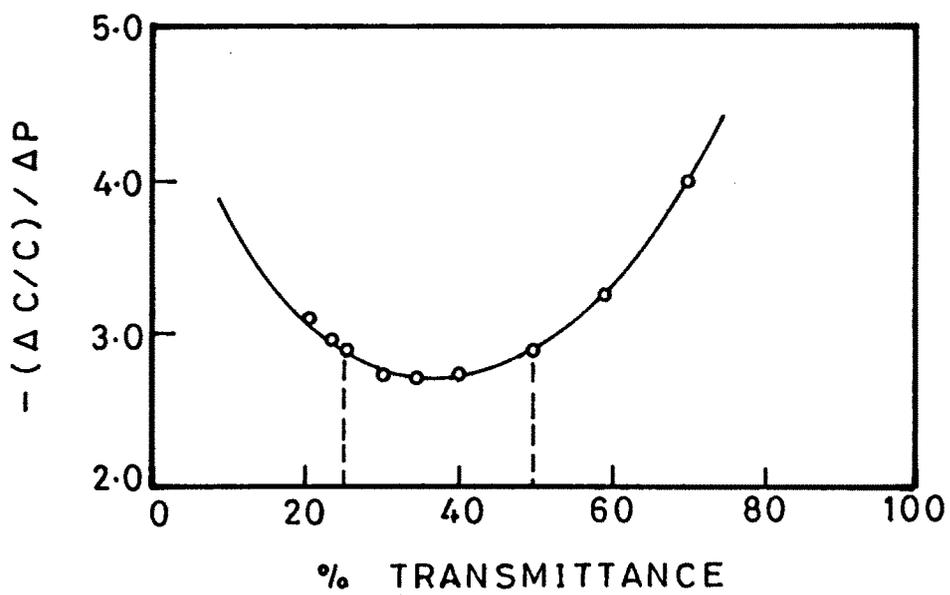


FIG. 3.4 - RINGBOM PLOT .

3.3.6 Composition of the Complex:

The composition of Pd(II)-ATG complex was ascertained by Job's method of continuous variation⁸⁹ (Table 3.5), mole ratio method⁹⁰ (Table 3.6) and slope ratio method⁹¹. Complex was developed by using equimolar solutions of palladium and reagent (ATG). Job's plot (Figure 3.5) indicated the formation of 1:2 complex of Pd(II) -ATG and this composition was confirmed by mole ratio (Figure 3.6) and slope ratio methods.

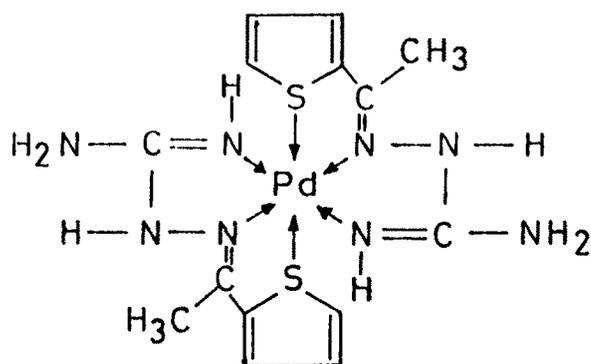
Table 3.5: Job's continuous variation method
 $[\text{Pd(II)}] = [\text{ATG}] = 4.6983 \times 10^{-4} \text{ M}$

[Pd(II)], ml	[ATG], ml	$\frac{[\text{ATG}]}{[\text{Pd(II)}] + [\text{ATG}]}$	Absorbance at λ	
			375 nm	415 nm
4.0	0.0	0.0	-	-
3.6	0.4	0.1	0.020	0.010
3.2	0.8	0.2	0.055	0.031
2.8	1.2	0.3	0.171	0.101
2.4	1.6	0.4	0.312	0.196
2.0	2.0	0.5	0.409	0.285
1.6	2.4	0.6	0.454	0.350
1.33	2.66	0.66	0.462	0.365
1.2	2.8	0.7	0.455	0.355
1.0	3.0	0.75	0.450	0.325
0.8	3.2	0.8	0.391	0.286
0.4	3.6	0.9	0.270	0.187
0.0	4.0	1.0	-	-

Table 3.6: Mole ratio method
 $[Pd(II)] = [ATG] = 4.6983 \times 10^{-4} M$

[Pd(II)], ml	[ATG], ml	$\frac{[ATG]}{[Pd(II)]}$	Absorbance at λ	
			375 nm	395nm
1.2	0.0	0.0	-	-
1.2	0.6	0.5	0.122	0.083
1.2	1.2	1.0	0.226	0.162
1.2	1.8	1.5	0.307	0.219
1.2	2.4	2.0	0.373	0.256
1.2	3.0	2.5	0.414	0.285
1.2	3.6	3.0	0.443	0.304
1.2	4.0	3.5	0.458	0.310

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



3.3.7 Sensitivity:

The reagent or palladium complex do not show any effect due to light. The photometric sensitivity of the

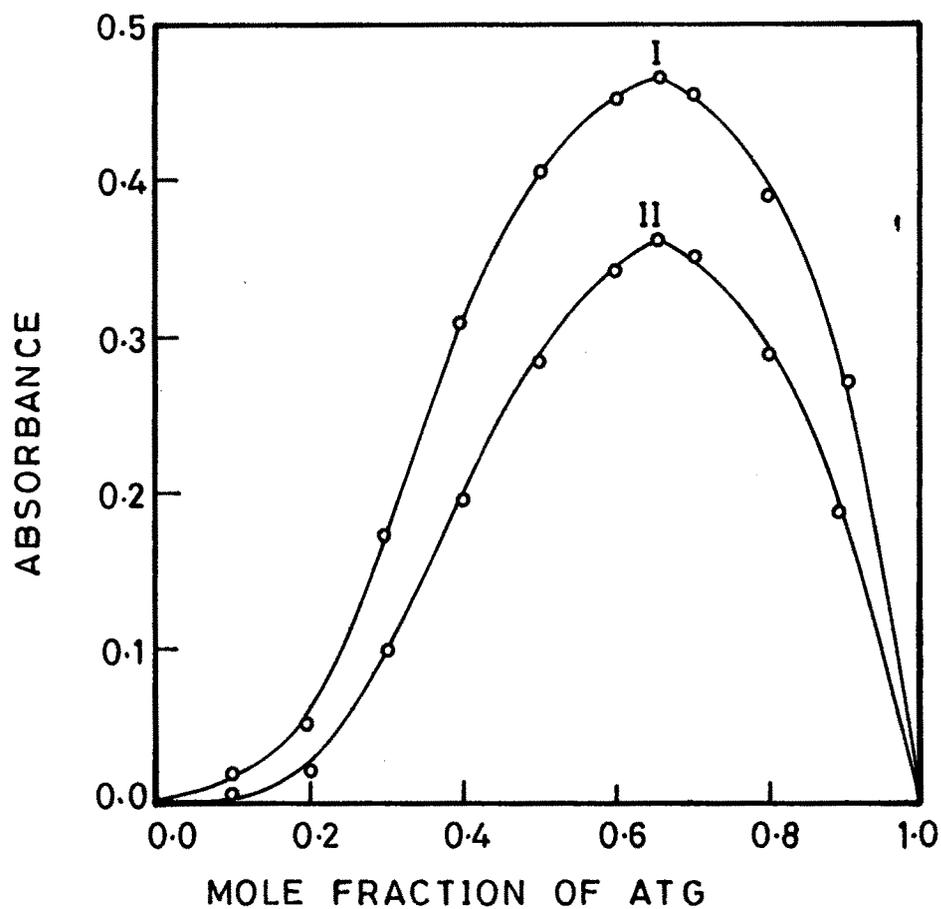


FIG.3.5 - JOB'S CONTINUOUS VARIATION METHOD.

I - 375 nm ; II - 415 nm

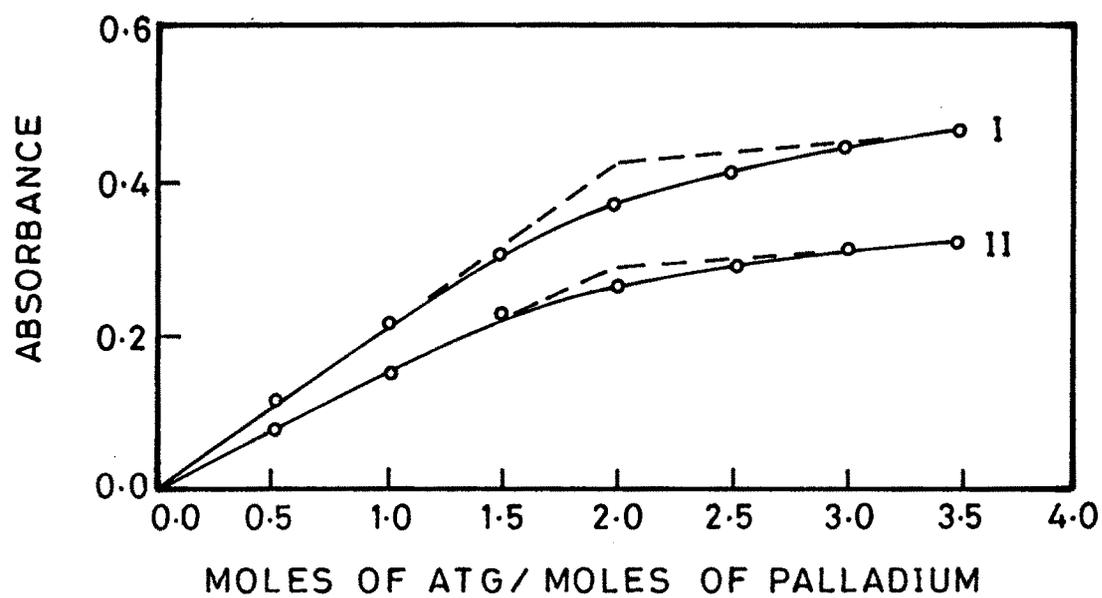


FIG.3.6 - MOLE RATIO METHOD.

I - 375 nm ; II - 395 nm

method was calculated by Sandell's method⁹² and was found to be 0.0627 $\mu\text{g}/\text{cm}^2$.

3.3.8 Degree of Dissociation and Instability Constant:

The degree of dissociation, α , was calculated from the mole ratio plot (Figure 3.6). The value of α , was found to be 0.1395.

The apparent instability constant⁹³ was found to be 0.4011×10^{-10} for Pd(II)-ATG complex.

3.3.9 precision and Accuracy of the Method:

In order to test the accuracy and precision of the method, different amounts of palladium were determined in six identical samples. The results in table 3.7 show that there is a good agreement in the experimental values. The coefficient of variation and standard deviations of the method are also given.

Table 3.7: Precision and accuracy of the method

Palladium(II), ppm	Mean absorbance of six observations	Standard deviation	Coefficient of variation, %
3.0	0.118	0.0018	1.607
5.0	0.195	0.0014	0.760
7.0	0.265	0.0029	1.106
9.0	0.340	0.0025	0.755

3.3.10 Effect of Diverse Ions:

To study the effect of diverse ions of palladium(II) -ATG complex, various cations and anions were added to the solution containing 5.0 ppm of palladium. Colour was developed at pH 12.6 and measured at 375 nm.

It is observed that Cd(II), thiourea and EDTA^{4-} ions interfere seriously, while the tolerance limit of borate ion and urea are 2500.0 and 950.0 ppm respectively. Tolerance limits of other ions are listed in table 3.8.

Table 3.8: Effect of diverse ions
[Pd(II)] = 5.0 ppm, [ATG] = 6.0×10^{-4} M

Foreign ions	Added as	Tolerance limit, ppm
Cations:		
Al(III)	$\text{AlCl}_3 \cdot 6\text{H}_2\text{O}$	75.0
Pb(II)	$\text{Pb}(\text{NO}_3)_2$	5.0
Ba(II)	$\text{BaCl}_2 \cdot 2\text{H}_2\text{O}$	15.0
Zn(II)	$\text{ZnSO}_4 \cdot 7\text{H}_2\text{O}$	7.0
Mg(II)	$\text{MgSO}_4 \cdot 7\text{H}_2\text{O}$	25.0
Cd(II)	$\text{CdSO}_4 \cdot 8/3 \text{H}_2\text{O}$	None
Tl(I)	TlNO_3	65.0
Y (III)	$\text{Y}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$	15.0
Be(II)	$\text{BeSO}_4 \cdot 4\text{H}_2\text{O}$	2.0
Sn(II)	$\text{SnCl}_2 \cdot 2\text{H}_2\text{O}$	1.0
Bi(III)	$\text{Bi}(\text{NO}_3)_3 \cdot 5\text{H}_2\text{O}$	15.0
Mo(VI)	$(\text{NH}_4)_2\text{MoO}_4$	20.0
Pt(IV)	H_2PtCl_6	1.0

Foreign ions	Added as	Tolerance limit, ppm
Anions:		
Thiosulphate	Sodium thiosulphate	56.0
Citrate	Citric Acid	19.0
Thiourea	Thiourea	None
Tartrate	Tartaric acid	22.0
EDTA ⁻⁴	Disodium salt	None
Acetate	Sodium acetate	35.0
Thiocyanate	Potassium thiocyanate	8.0
Phosphate	Sodium phosphate	23.0
Oxalate	Potassium oxalate	17.0
Urea	Urea	950.0
Bromate	Potassium bromate	25.0
Persulphate	Potassium persulphate	9.0
Borate	Boric acid	2500.0

3.4 APPLICATION:

In order to confirm the usefulness of the reagent, the proposed method was applied for the determination of Pd(II) in Ni-Al catalyst.

Determination of Palladium(II) in Ni-Al Catalyst:

The sample of Ni-Al catalyst, 40.0 mg was dissolved in a mixture of nitric acid and hydrochloric acid.

Concentrated sulphuric acid, 10.0 ml was added in it. The mixture was heated until fuming. For complete oxidation of organic matter in the sample the addition of a few ml of concentrated nitric acid may be necessary during the fuming. The solution was cooled. The salts were taken up in water and after cooling, the solution was transferred to a 50 ml volumetric flask and was diluted upto the mark with distilled water.

An appropriate aliquot was analysed as described in the general procedure. The results are given in table 3.9. The results obtained are consistent with those obtained by 1-nitroso-2-naphthol⁹⁴ photometric method.

Table 3.9: Determination of Palladiu(II) in Ni-Al Catalyst.

Sample	Proposed method using ATG			1-nitroso-2-naphthol	
	Pd(II) %	- X %	Standard deviation	Pd(II) %	- X %
Ni-Al Catalyst	0.121 0.125 0.123 0.120 0.126	0.123	0.0025	0.124 0.121 0.126 0.129 0.125	0.125

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