CHAPTER - V

DETERMINATION OF PALLADIUM

5.1 INTRODUCTION

Palladium is a silver white metal and is capable of taking high polish. It is both malleable and ductile. Palladium melts at 1556° and hence is the most fusible of all the platinum metals.

The ability of palladium to take up large volumes of hydrogen makes it a useful catalyst in hydrogenation reactions and in some analytical operations. In many chemical reactions, surfaces of palladium which are normally deposits of palladium on inert supporting material, function as excellent catalysts. Its permanence in the air and its high reflecting power makes it useful for optical mirrors. 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 metals are used as electrical contacts, resistances, thermoelectrodes, solders, etc. 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.

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

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.

Some reagents are not selective though sensitive. Reagents like 2-mercaptoquinoline[5], bismuthol II[6], 2-diethylamino ethanethiol hydrochloride[7] and crystal violet[8] suffer from numerous interfering ions.

Due to low kinetic stability, complex formation in case of 4-methylcyclohexane-1:2-dioxime[9], 5-amino-2-benzimidazolethiol[10], aluminon[11], phthalimide dioxime[12] procaine[13], chrome azurol S[14] and azurubine[15] takes place after 30 to 90 minutes. Rate of formation of complexes is slow in case of nitroso-R-salt[16], glycine thymol blue[17], 3-nitrosopyridine-2,6-diol[18], melamine[19] and tropolone[20] and hence requires heating.

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

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

Reagents like 2-mercaptobenzoic acid[29], o-mercaptobenzoic acid[30], benzoylmethylglyoxime[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.

Recently, reagents such as bidentate pyrimidine-2-thiols[35], diphenylthiovioluric acid[36] and p-nitroso-dimethylaniline[37] are used for the spectrophotometric determination of palladium.

5.2 EXPERIMENTAL

All the chemicals used were of analytical grade.

5.2.1 Standard Solutions :

Standard Palladium Solution ;

A stock solution of palladium (1mg/ml) was prepared by dissolving 0.166 g of A.R. grade palladium chloride in 100 ml distilled water containing a few mls of concentrated hydrochloric acid. The solution was standardised with dimethylglyoxime[38] gravimetrically. Further dilutions for experimental purposes were done with distilled water.

Reagent Solution :

A stock solution of the reagent, cinnamaldehyde guanulhydrazone (CAG) was prepared by dissolving 188 mg of it in 100 ml ethanol (1.88 mg/ml i.e. 0.01 M).

Buffer Solution :

Buffer solution of pH 10 was prepared by dissolving appropriate amount of sodium hydroxide and boric acid.

5.2.2 Recommended Procedure

An aliquot of the solution containing 10 µg of palladium (II) was taken in 10 ml volumetric flask. To it was added 2 ml of the reagent (CAG) solution of concentration 0.001 M. The pH of the solution was adjusted to 10.5 with buffer solution and was diluted upto the mark with ethanol. The absorbance of the palladium (II)-CAG complex was measured at 370 nm against reagent blank. The concentration of palladium in an unknown solution was determined from a calibration curve obtained under identical conditions.

5.3 RESULTS AND DISCUSSION

5.3.1 Spectral Characteristics

The absorption spectrum of Pd(II)-CAG complex contianing 0.9398 x 10^{-4} M palladium (II) and 0.001 M reagent (CAG) was recorded at pH 10.5 against reagent blank. The complex has absorption maximum at 370 nm and molar extinction coefficient of the complex is

0.7455×10^4 l $mole^{-1}$ cm^{-1} at 370 nm. The molar extinction coefficient of reagent at 370 nm is 0.015×10^4 l $mole^{-1}$ cm^{-1} (Fig 5.1). The observations for the spectra are given in table 5.1.

5.3.2 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 9.5 to 11. It falls below pH 9.5 and above 11. Hence, the pH value 10.5 was selected for the study of Pd(II)-CAG complex. In acidic medium the complex shows comparatively less absorbance. The observations are given in table 5.2. The plot of observations is shown in fig 5.2.

Table 5.1 : Molar extinction coefficient of the Pd(II)-CAG complex and the reagent (CAG).

Wavelength λ, nm	Molar extinction coefficients, ϵ	
	Pd(II)-CAG complex $\epsilon \times 10^4$ l mole^{-1} cm^{-1}	Reagent, CAG $\epsilon \times 10^4$ l mole^{-1} cm^{-1}
360	0.6596	0.025
365	0.7021	0.020
370	0.7455	0.015
375	0.6915	0.015
380	0.6596	0.010
385	0.6383	0.010
390	0.5745	0.006
400	0.4260	0.0025
410	0.3404	0.0020
420	0.2556	0.001
430	0.1915	-
440	0.1489	-
450	0.1171	-
460	0.0957	-
470	0.0745	-
480	0.0638	-
490	0.0532	-
500	0.0425	-
510	0.0319	-

Table 5.2 : Effect of pH on the absorbance of Pd(II)-CAG complex.

[Pd (II)] = 10 ppm; [CAG] = 0.001 M

pH	Absorbance at 370 nm
2.0	-
4.0	0.01
6.0	0.09
7.0	0.30
8.0	0.50
9.0	0.52
9.5	0.70
10.0	0.70
10.5	0.70
11.0	0.70
11.5	0.53
12.0	0.50

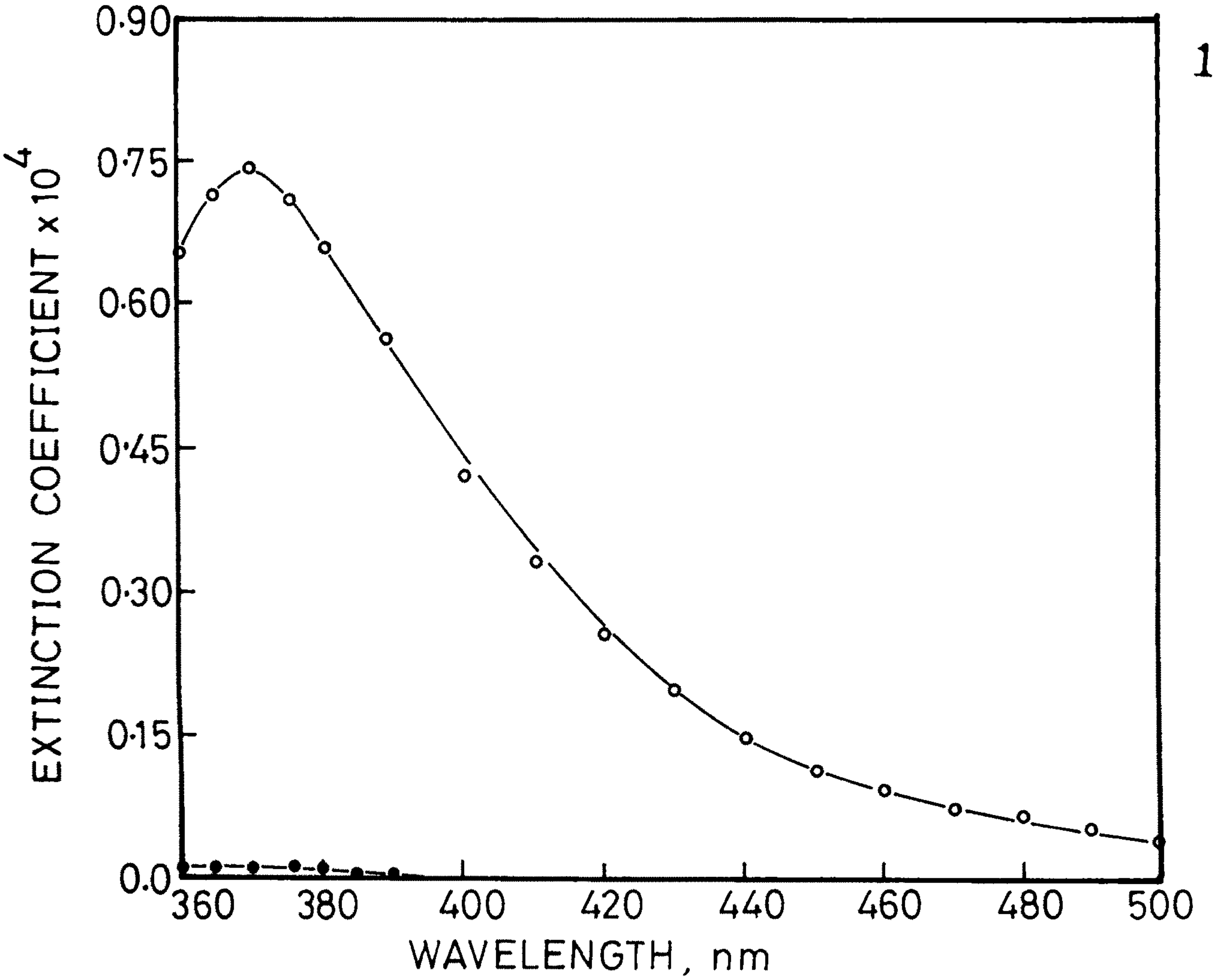


FIG.5·1 — ○——○ ABSORPTION SPECTRUM OF PALLADIUM-CAG COMPLEX.
●——● ABSORPTION SPECTRUM OF REAGENT (CAG).

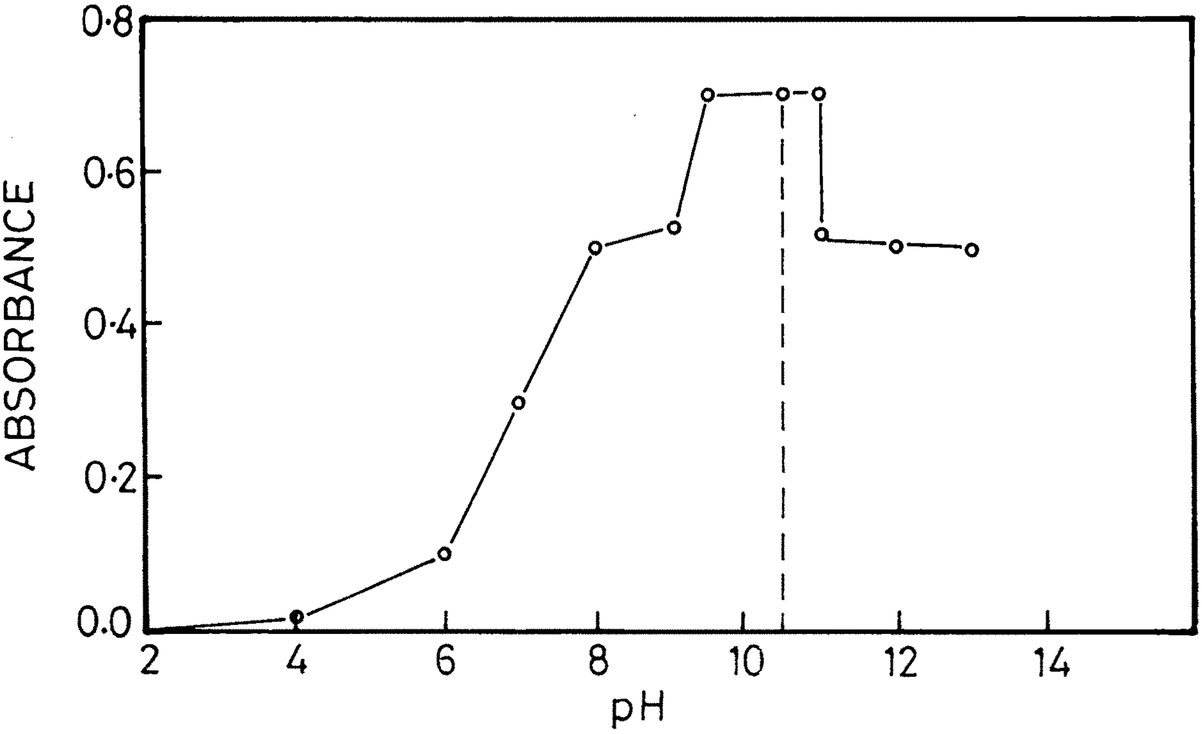


FIG. 5·2 — EFFECT OF pH.

5.3.3 **Effect of reagent concentration :**

A series of solutions containing constant concentration of palladium (10 ppm) and different amounts of CAG ranging in concentrations from 0.5×10^{-3} M to 3.0×10^{-3} M were prepared. Complex was developed as per recommended procedure and its absorbance was measured. Results in table 5.3 show that 2.5 fold molar excess of the reagent was sufficient for full colour development of 10 ppm of palladium.

Table 5.3 : Effect of reagent concentration

[Pd (II)] = 10 ppm; [CAG] = 0.001 M

ml of CAG	Absorbance at 370 nm
0.5	0.42
1.0	0.47
1.5	0.63
2.0	0.70
2.2	0.70
2.5	0.70
3.0	0.70

5.3.4 Stability :

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

5.3.5 Validity of Beer's law :

The measurement of absorbance of Pd(II)-CAG complex at pH 10.5 containing varying amounts of palladium showed that Beer's law is valid upto 8.0 ppm of Pd (II) (Fig 5.3; Table 5.4)

The optimum concentration range for the determination of palladium was studied from Ringbom plot[39] and was found to be 3.8 to 7.5 ppm at the conditions chosen for the experiment (Fig. 5.4).

Table 5.4 : Validity of Beer's law

Palladium (II), ppm	Absorbance at 370 nm
1	0.075
2	0.15
3	0.22
4	0.30
5	0.37
6	0.46
7	0.52
8	0.64
9	0.67
10	0.72
11	0.77
12	0.80

5.3.6 Composition of the complex :

The composition of the Pd(II)-CAG complex was ascertained by Job's method of continuous variation[40] (Table 5.5), mole ratio method[41] (Table 5.6) and slope ratio method[42]. Complex was developed by using equimolar solutions of palladium (II) and the reagent (CAG). Job's plot (Fig 5.5) indicated the formation of 1:2 complex of Pd(II) : CAG and this composition was confirmed by the mole ratio method (Fig 5.6) and slope ratio method.

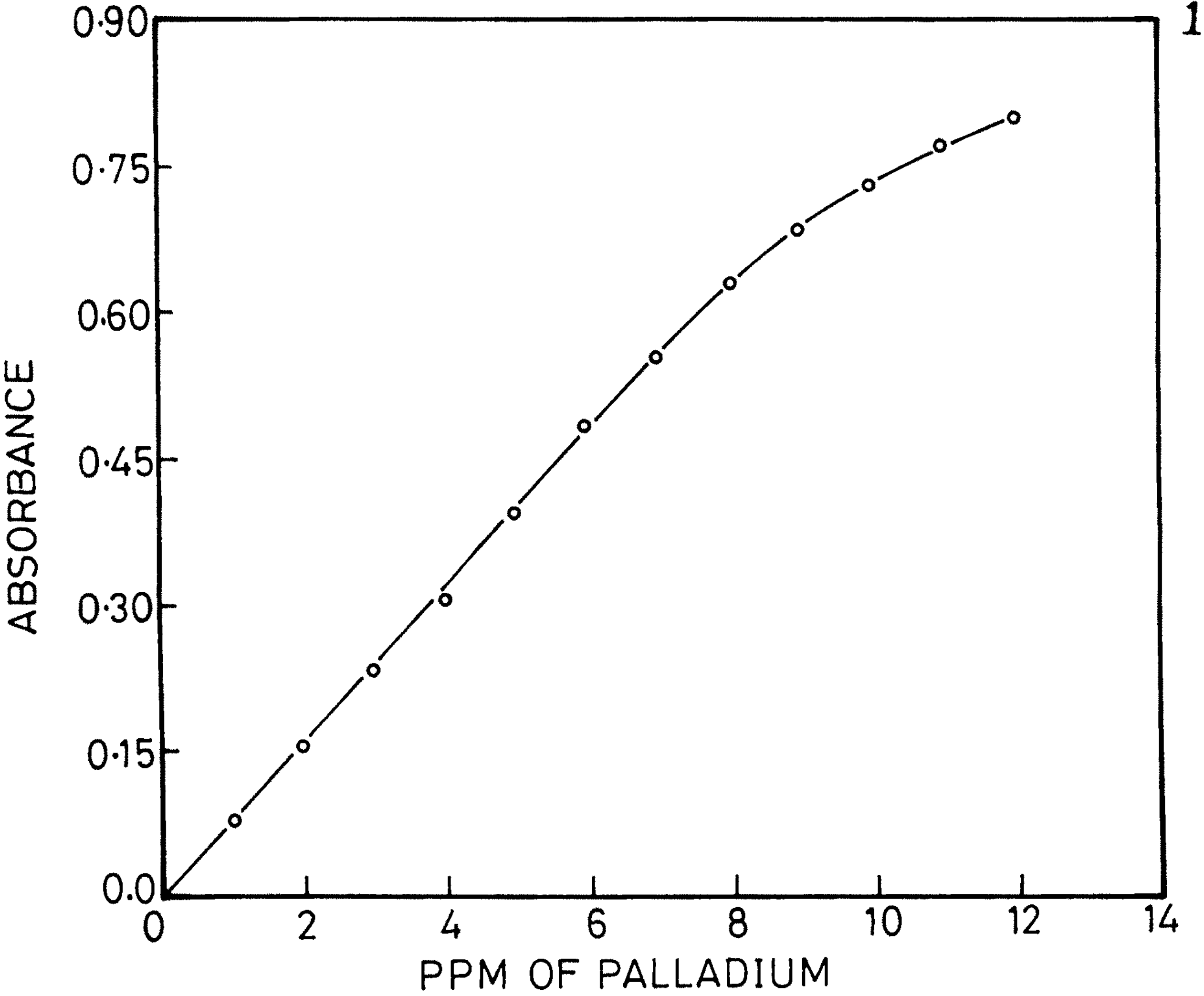


FIG. 5·3 — VALIDITY OF BEER'S LAW.

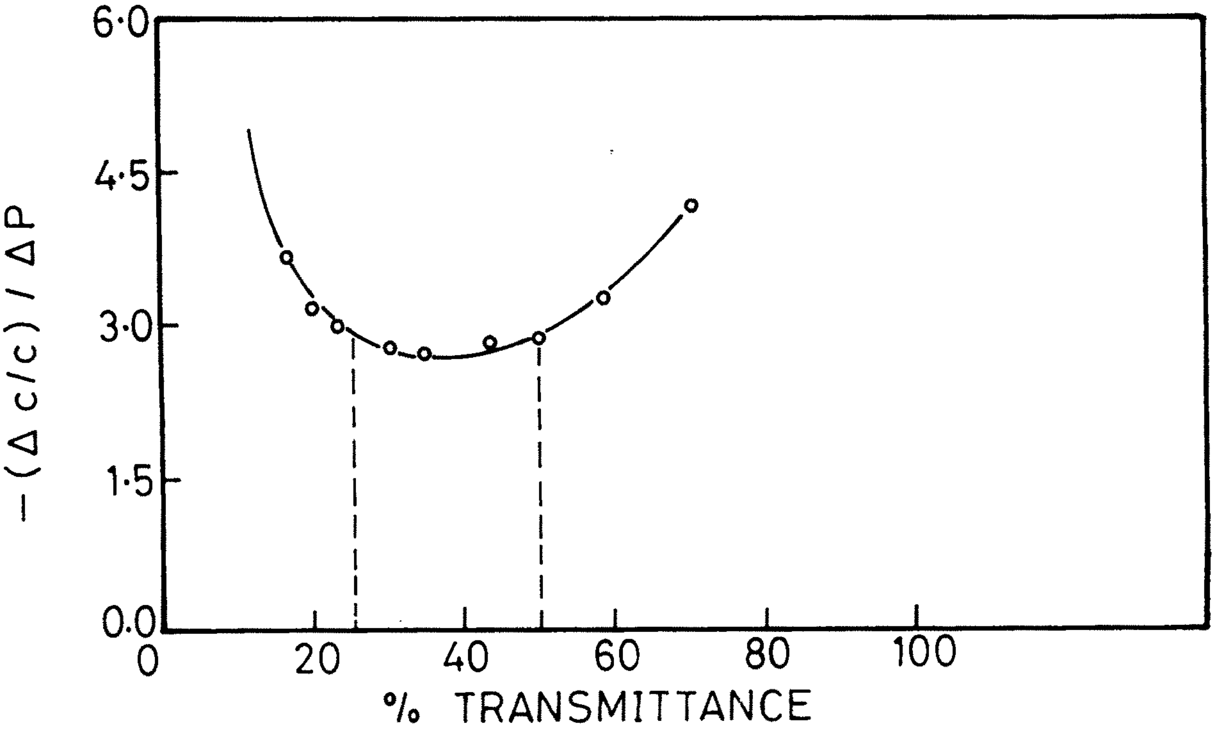


FIG. 5·4 — RINGBOM PLOT.

Table 5.5 : Job's continuous variation method

$[Pd(II)] = [CAG] = 0.9398 \times 10^{-4}$ M.

Palladium(II) ml	Ragent (CAG),ml	Molar Ratio M:L	Absorbances at λ		
			370 nm	390 nm	410 nm
0.0	1.8	-	-	-	-
0.2	1.6	1:8	0.08	0.055	0.03
0.4	1.4	2:7	0.12	0.09	0.05
0.6	1.2	1:2	0.14	0.10	0.06
0.8	1.0	4:5	0.095	0.07	0.045
1.0	0.8	5:4	0.07	0.05	0.03
1.2	0.6	2:1	0.06	0.04	0.02
1.4	0.4	7:2	0.04	0.03	0.01
1.6	0.2	8:1	0.025	0.01	-
1.8	0.0	-	-	-	-

Table 5.6 : Molar ratio method

$[Pd(II)] = [CAG] = 0.9398 \times 10^{-4}$ M

Palladium (II) ml	Reagent (CAG) ml	Molar Ratio M:L	Absorbances at λ	
			370 nm	390 nm
0.0	2.0	-	-	-
0.2	2.0	1:10	0.05	0.03
0.4	2.0	1:5	0.09	0.06
0.6	2.0	3:10	0.14	0.09
0.66	2.0	1:3	0.175	0.125
0.8	2.0	2:5	0.21	0.15
1.0	2.0	1:2	0.24	0.16
1.2	2.0	3:5	0.26	0.18
1.33	2.0	2:3	0.27	0.19
1.4	2.0	7:10	0.275	0.20
1.6	2.0	4:5	0.275	0.20
1.8	2.0	9:10	0.28	0.20
2.0	2.0	1:1	0.28	0.21

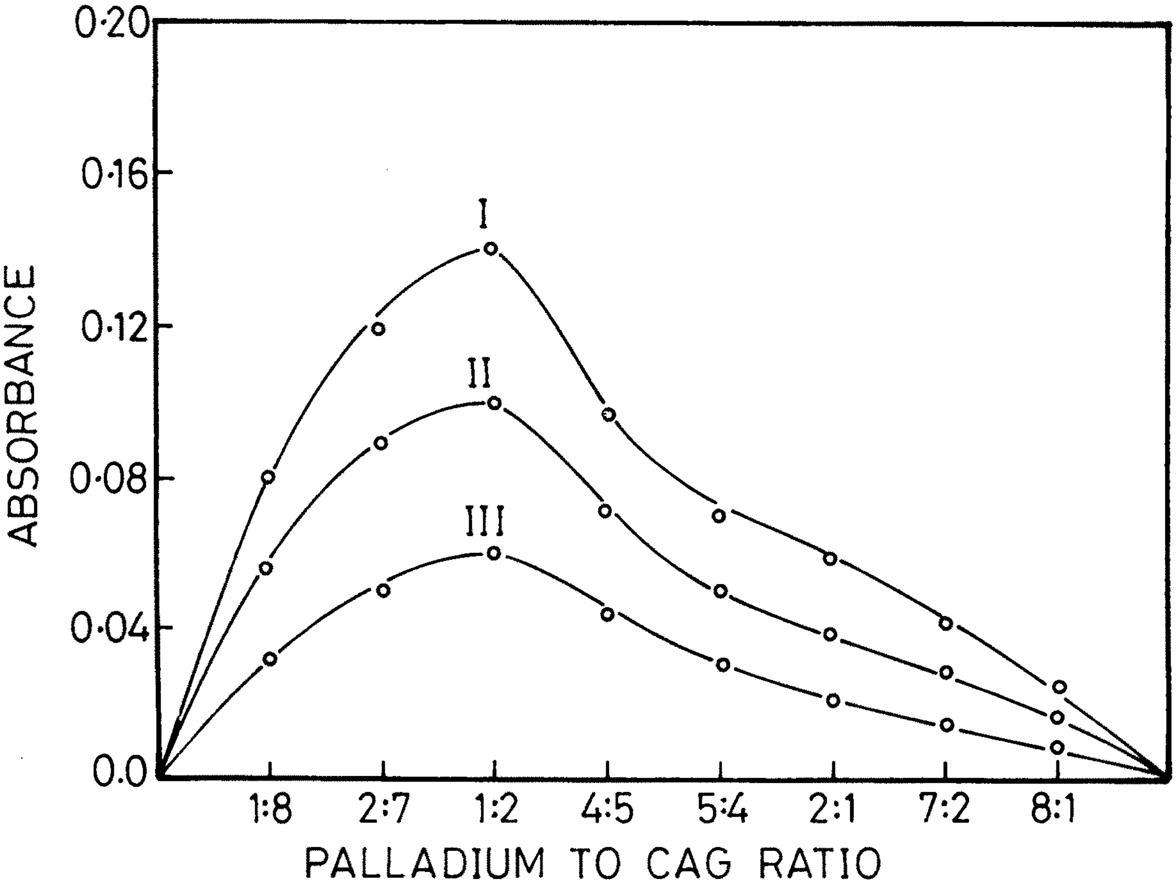


FIG. 5·5 – JOB'S CONTINUOUS VARIATION METHOD.
I – 370 nm, II – 390 nm, III – 410 nm.

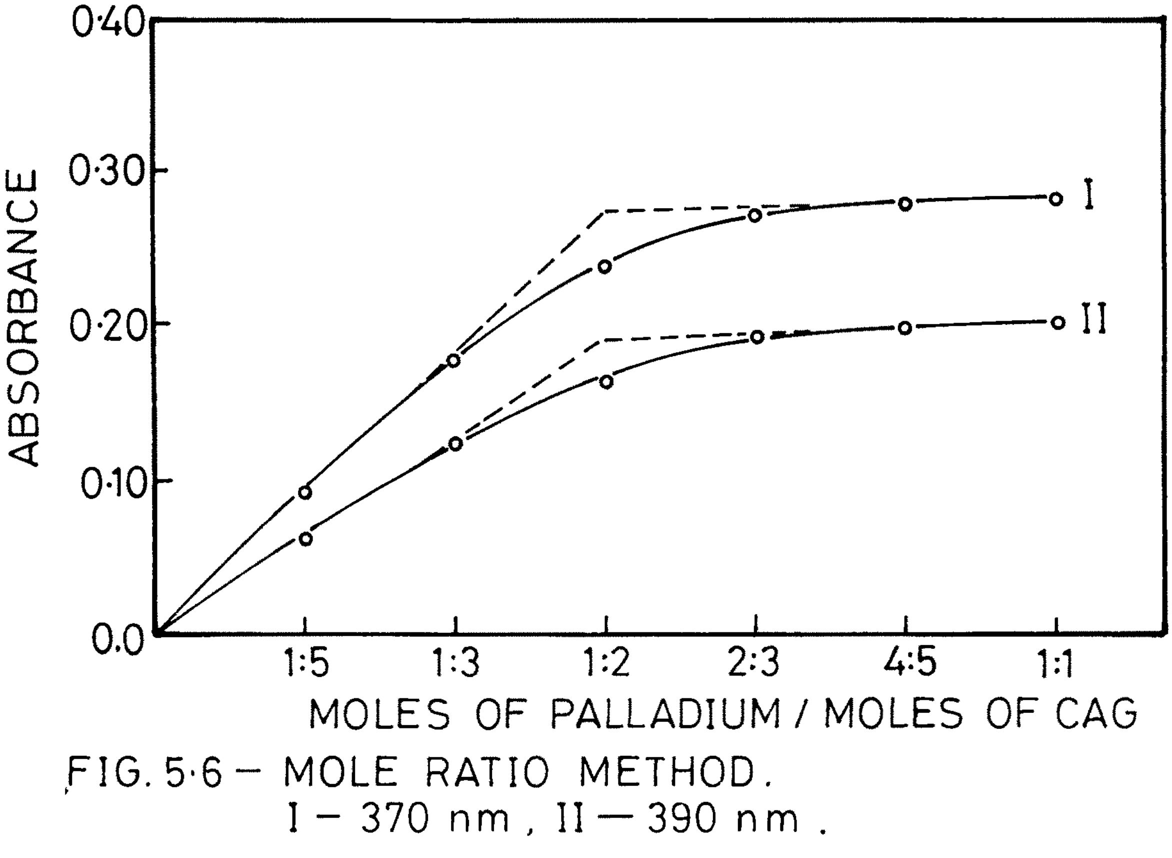
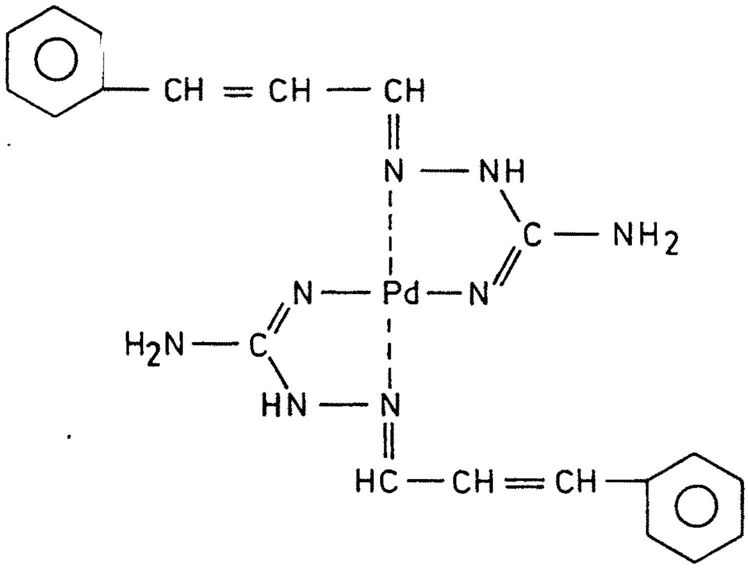


FIG. 5·6 – MOLE RATIO METHOD.
I – 370 nm, II – 390 nm.

The probable structure for Pd(II)-CAG complex may be presented as



5.3.7 Sensitivity :

The reagent or palladium complex do not show any effect due to light.

The photometric sensitivity of the system was calculated by the method of Sandell[43] and was found to be 0.06455 µg/cm^2 at pH 10.5. Molar extinction coefficient of the system at 370 nm is 0.7455 x 10^4 l mole^{-1} cm^{-1}

5.3.8 Degree of Dissociation and Instability Constant

The degree of dissociation was calculated by the method by Harvey and Manning[42]. The value of degree of dissociation (α) was found to be 0.1273.

The apparent instability constant[44] was found to be 8.35×10^{-13} for Pd(II)-CAG complex. The change in free energy[45] of the system is -16.454 K cal/mole.

5.3.9 Reproducibility of the Method :

The reproducibility of the method was tested by determining different amounts of palladium (II) as per recommended procedure. The results are tabulated in table 5.7, which show that the method is reproducible. The standard deviations of the method calculated for six observations and the coefficient of variation are also given in table 5.7.

Table 5.7 : Reproducibility of the method

Pd (II) ppm	Mean absorbance of six observations	standard deviation	coefficient of variation, %
1.5	0.11	0.0030	2.727
3.0	0.21	0.0055	2.619
4.5	0.34	0.0092	2.706
6.0	0.45	0.0118	2.622

5.3.10 Effect of Diverse Ions

To study the effect of diverse ions of Palladium (II)-CAG complex, various cations and anions were added to the solution containing 2 ppm of Pd(II) and 2 ml of 0.001 M reagent. The complexes were developed as per the recommended procedure and the absorbances were measured. The results indicate that V(IV), Ni(II), Cr(III), $EDTA^{-4}$ and citrate anion interfere seriously. The tolerance limit of oxalate anion is 360 ppm. The tolerance limits for the ions are listed in table 5.8

Table 5.8 : Effect diverse ions

[Pd(II)] = 2.0 ppm; [CAG] = 1.0×10^{-3} M.

Foreign ions	Added as	Tolerance limit,ppm
Cations :		
Cr(VI)	$K_2Cr_2O_7$	0.8
V(IV)	$VOSO_4.H_2O$	None
Ba(II)	$BaCl_2.2H_2O$	9.0
Zn(II)	$ZnSO_4.7H_2O$	10.0
Mn(II)	$MnSO_4.H_2O$	1.0
Fe(III)	$Fe_2(SO_4)_3(NH_4)_2SO_4.24H_2O$	0.9

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Foreign ions	Added as	Tolerance limit,ppm
Ni(II)	$Ni(NO_3)_2.6H_2O$	None
Cr(III)	$CrCl_3.6H_2O$	None
Mo(VI)	$(NH_4)_6[Mo_7O_{24}].4H_2O$	12.0
Ag(I)	$AgNO_3$	5.0
Ce(IV)	Cerium (IV) ammonium sulphat	5.0
Cd(II)	$3CdSO_4.8H_2O$	1.0
Anions		
Citrate	citric acid	None
Oxalate	sodium oxalate	360.00
Thiourea	Thiourea	170.00
$EDTA^{-4}$	Disodium salt	None
Urea	Urea	18.0
Acetate	Sodium acetate	35.0
Tartrate	Tartaric acid	11.0

5.4 APPLICATIONS

Analysis of Palladium (II) in Pd/charcoal and Pd/carbonate catalysts

A weighed quantity (0.3 g) of the catalyst sample (fluka) was digested with a mixture of perchloric acid and nitric acid and then centrifuged. The filtrate was concentrated by heating and diluted to 100 ml with 0.05 M HCl. An aliquot of this solution was used for extraction of palladium. The method proposed has been applied to the determination of palladium in Pd/ charcoal and Pd/ carbonate catalysts. The results obtained are in good agreement with those quoted and are given in table 5.9.

Table 5.9 : Determination of palladium in catalyst samples.

Catalysts	standard value of Pd %	Experimental value of Pd %	Relative standard deviation for five observations
Pd/Charcoal	10.0	9.93	0.08
Pd/Carbonate	6.0	6.08	0.05

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