

# CHAPTER IV

SPECTROPHOTOMETRIC DETERMINATION  
OF PALLADIUM(II) WITH  
N-HYDROXY-N,N-DIPHENYLBENZAMIDINE  
AND 1-(2-PYRIDYLAZO)-2-NAPHTHOL

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NAPHTHOL

SUMMARY

A simple and sensitive spectrophotometric method for the determination of palladium(II) has been described. The method is based on the extraction of palladium(II) with seven different hydroxyamidines(HOAs) in the pH range of 3.5 to 6.0. To enhance the sensitivity of the complex the extracted complex is reacted with 1-(2-pyridylazo)-2-naphthol(PAN) in hydrochloric acid medium. The molar absorptivity of these complexes lie in the range of  $(0.76 - 1.58) \times 10^4 \text{ l mol}^{-1} \text{ cm}^{-1}$  at  $\lambda_{\text{max}}$  610-620 nm. Among the various hydroxyamidines examined, N-hydroxy-N,N'-diphenylbenzamidine(HDPBA) showed the maximum colour intensity and is therefore selected for detailed studies. The molar absorptivity of Pd(II)-HDPBA-PAN complex is  $1.58 \times 10^4 \text{ l mol}^{-1} \text{ cm}^{-1}$  at  $\lambda_{\text{max}}$  620 nm. The detection limit of the method is 0.1  $\mu\text{g/ml}$  aqueous solution.

The system obeys Beer's law upto 4.5  $\mu\text{g/ml}$  of Pd(II) in organic solution. The precision of the method is checked by taking ten replicate measurements, each containing 3.5  $\mu\text{g/ml}$  palladium(II). The relative standard deviation of the method is found to be  $\pm 1.2\%$ . Various analytical parameters have been studied to obtain optimum experimental condition. Most of the common metal ions which are associated with palladium do not

interfere. Only the serious interference of Cu(II) and V(V) are observed. However, they could effectively be masked by adding EDTA to the test solution prior to the extraction. The method has been applied successfully for the recovery of palladium(II) from synthetic mixtures.

Palladium is one of the major constituents of both naturally occurring and industrially prepared platinum metal products.<sup>1</sup> It is obtained by the reduction of its salts with hydrogen, or by deposition of its solution in the presence of zinc.<sup>2</sup> Palladium is found in ores, concentrates, mattes, jewellery and in a variety of miscellaneous industrial products.<sup>3</sup> The main uses of palladium are in low current electrical contacts and as a catalysts for hydrogenation in liquid and gas phase reaction.<sup>4,5</sup> The use of palladium in different fields has stimulated the development of new method for the determination of trace amount of palladium.

A large number of reagents have been employed for the spectrophotometric determination of palladium. Reagents such as tin(II) chloride + rhodamine 6G,<sup>6</sup> o-hydroxy hydroquinone-naphthalein + methylcellulose + cetyltrimethyl ammonium bromide,<sup>7</sup> potassium thiocyanate + rhodamine B,<sup>8</sup> 4-(3,5-dichloro-2-pyridylazo)-1,3-diaminobenzene + trichloroacetate II,<sup>9</sup> 2-(5-bromo-2-pyridylazo)-5-diethylaminophenol,<sup>10</sup> Meso-tetrakis (4-acetoxyphenyl) porphyrin + sodium dodecyl sulphate,<sup>11</sup>  $\alpha, \beta, \tau, \delta$  (2-chlorophenyl) porphine + surfactant OP,<sup>12</sup> meso-tetrakis (p-hydroxyphenyl) porphyrin + sodium lauryl sulfate,<sup>13</sup> chrome azurol B + cetyldimethylammonium acetate + triton X -100,<sup>14</sup> o-chlorophenylfluorone + cetyltrimethylammonium bromide<sup>15</sup> gives highly sensitive colour reactions with palladium(II). The sensitivity of these complexes lie in the range of  $10^5$  to  $10^6$  l mol<sup>-1</sup> cm<sup>-1</sup> but selectivity is poor as many metal ions interfere seriously in all these methods.<sup>6-11</sup> Moreover, they

suffer from many drawbacks like narrow range of acidity, critical pH, time consuming, etc.<sup>9-12,14</sup> In some of these methods<sup>11,12,15</sup> heating of the reaction mixture on water bath at 50-60°C is required for obtaining the maximum and constant absorbance, and complete formation of the complex.

Various other reagents have been employed for the spectrophotometric determination of palladium like 2-( $\alpha$ -pyridyl) thiopicolinamide,<sup>16</sup> diethylenetriaminepentaacetic acid,<sup>17</sup> N-naphthylaminothioformyl-N'-phenylhydroxylamine,<sup>18</sup> tetrabutylammonium iodide,<sup>19</sup> picoline amidoxime,<sup>20</sup> 2-allylthiourea + thiocyanate + EDTA,<sup>21</sup> 2-mercapto- $\beta$ -naphthothiazole,<sup>22</sup> benzyl-dimethylphenylammonium chloride,<sup>23</sup> 2-thiobarbituric acid,<sup>24</sup> and others.<sup>25-30</sup> The sensitivity of all these methods are low and even the final colour of the complex is measured inconveniently at lower wavelengths or UV-region.

Many chromogenic reagents have been used for the spectrophotometric determination of palladium such as 1(2-pyridylazo) resarcinol,<sup>31</sup> 1-(2-pyridylazo)-2-naphthol<sup>1,32</sup> alone and with N-m-chlorophenyl-p-methoxybenzohydroxamic acid,<sup>33</sup> 4-(2-triazolylazo) resarcinol,<sup>34</sup> 4-(2-pyridylazo) resarcinol + mesityl oxide<sup>35</sup> solochrome Red B,<sup>36</sup> various other azo compounds,<sup>37-46</sup> sulphur containing reagents,<sup>47-53</sup> and many other<sup>54-58</sup> reagents. But most of them require a prolonged heating,<sup>31</sup> careful control of pH and acidity<sup>40-43,48,51,53</sup> or suffer from a large number of interference from cations and anions.<sup>1,32-36,42-44,53-58</sup> Many of them also have the drawback of low sensitivity<sup>34,36,38,46-53</sup> and some of them are unstable<sup>32,49</sup> too.

In the present investigation, N-hydroxy-N,N'-diphenylbenzamidline(HDPBA) is used as an extracting reagent alongwith PAN to improve the sensitivity as well as selectivity of the method. It has been applied satisfactorily for the recovery of palladium(II) in synthetic mixtures. Thus, the present method is sensitive, selective and precise than the previously reported methods.

## EXPERIMENTAL

**APPARATUS** - A Carl Zeiss Jena 'Spekol' with EK-5 attachment and matched quartz cells of 1-cm path length, was used for all absorbance measurements. A Systronic digital pH-meter type 335 was employed for pH measurement.

**STANDARD SOLUTION OF PALLADIUM(II)**- A stock solution of palladium(II) was prepared by dissolving weighed amount of palladium chloride in 10 ml of hydrochloric acid (10M) solution and diluted to 100 ml with distilled water. The stock solution was standardized gravimetrically using dimethylglyoxime.<sup>59</sup> Working standard solution was prepared by appropriate dilution of the stock solution.

**CHLOROFORM** - AR Grade chloroform was used for all experimental work.

**HYDROXYAMIDINES(HOAs)** - These were synthesized as described in the literature<sup>60</sup> and their 0.3% (w/v) or  $\approx 1.0 \times 10^{-2}$  M solution in chloroform was used for extraction purpose.

**1-(2-PYRIDYLAZO)-2-NAPHTHOL(PAN)** - A 0.1% (w/v) or  $4.0 \times 10^{-3}$  M solution of PAN in 1-propanol was used.

**BUFFER SOLUTION** - Acetic acid - sodium acetate buffer solution of pH 5.0 was prepared as described in the literature.<sup>61</sup>

**HYDROCHLORIC ACID** - A 10 M hydrochloric acid solution was employed for all acidity adjustment.

**SOLUTION OF DIVERSE IONS** - The solution of desired diverse ions were prepared as in the literature.<sup>62</sup> A 1 mg/ml solution of the ions were prepared.

All chemicals used were of Analytical Reagent grade (S D Fine Chem./E. Merck).

#### PROCEDURE

##### [A] EXTRACTION OF PALLADIUM(II) WITH HDPBA

An aliquot of the test solution containing upto 70.0  $\mu\text{g}$  of palladium(II) is transferred to a 125-ml separatory funnel. The pH of the aqueous solution is maintained at  $5.0 \pm 0.2$  by adding acetate buffer solution, in a total volume of 10 ml. This solution is equilibrated by shaking for 2 min with 5 ml of HDPBA solution in chloroform. The organic phase is separated and the aqueous phase is washed with 1 x 2 ml of fresh portion of chloroform. All the extracts are collected, dried over anhydrous sodium sulphate ( $\approx 2\text{g}$ ) and transferred to a 10-ml volumetric flask. The combined extract is made upto the mark with chloroform. The absorbance of the complex is measured against reagent blank at  $\lambda_{\text{max}}$  400 nm.

##### [B] SPECTROPHOTOMETRIC DETERMINATION OF PALLADIUM(II) WITH PAN

The chloroform extract of Pd(II)-HDPBA complex obtained as above, containing upto 45.0  $\mu\text{g}$  of palladium(II) is placed in a 125-ml separatory funnel. To this, 2.5 ml of PAN solution and 1 ml of HCl are added. The mixture is shaken vigorously for 2 min. The organic layer is separated and dried over anhydrous sodium sulphate ( $\approx 2\text{g}$ ). The organic solution is transferred to a 10-ml volumetric flask and filled upto the mark with 1-propanol. The absorbance of the complex is measured against reagent blank at absorption maxima 620 nm.



## RESULTS AND DISCUSSION

[A] EXTRACTION OF PALLADIUM(II) WITH N-HYDROXY-N, N'-  
DIPHENYLBENZAMIDINE(HDPBA)

## ABSORPTION SPECTRA

The Pd(II)-HDPBA complex in chloroform exhibits maximum absorbance at absorption maxima 400 nm against reagent blank. The reagent blank of the above complex shows negligible absorbance at absorption maxima. The position of  $\lambda_{\max}$  remained constant on variation of metal concentration, as shown in Figure 4.1.

## EFFECT OF SOLVENTS

Various organic solvents such as chloroform, benzene, toluene, xylene, carbon tetrachloride, ethyl acetate and isobutyl methyl ketone were tried for the extraction of metal complex (Table 4.1, Figure 4.2). No extraction of the metal complex was seen with isobutyl methyl ketone whereas other solvents extract the complex quantitatively but the sensitivity of the metal complex in chloroform is high. Therefore, chloroform was selected as the best extracting solvent.

## EFFECT OF pH

The maximum extraction of the Pd(II)-HDPBA complex was obtained in the pH range of 3.5 - 6.0 (Table 4.2, Figure 4.3). Therefore, subsequent determinations were performed at pH  $5.0 \pm 0.2$  using acetate buffer.

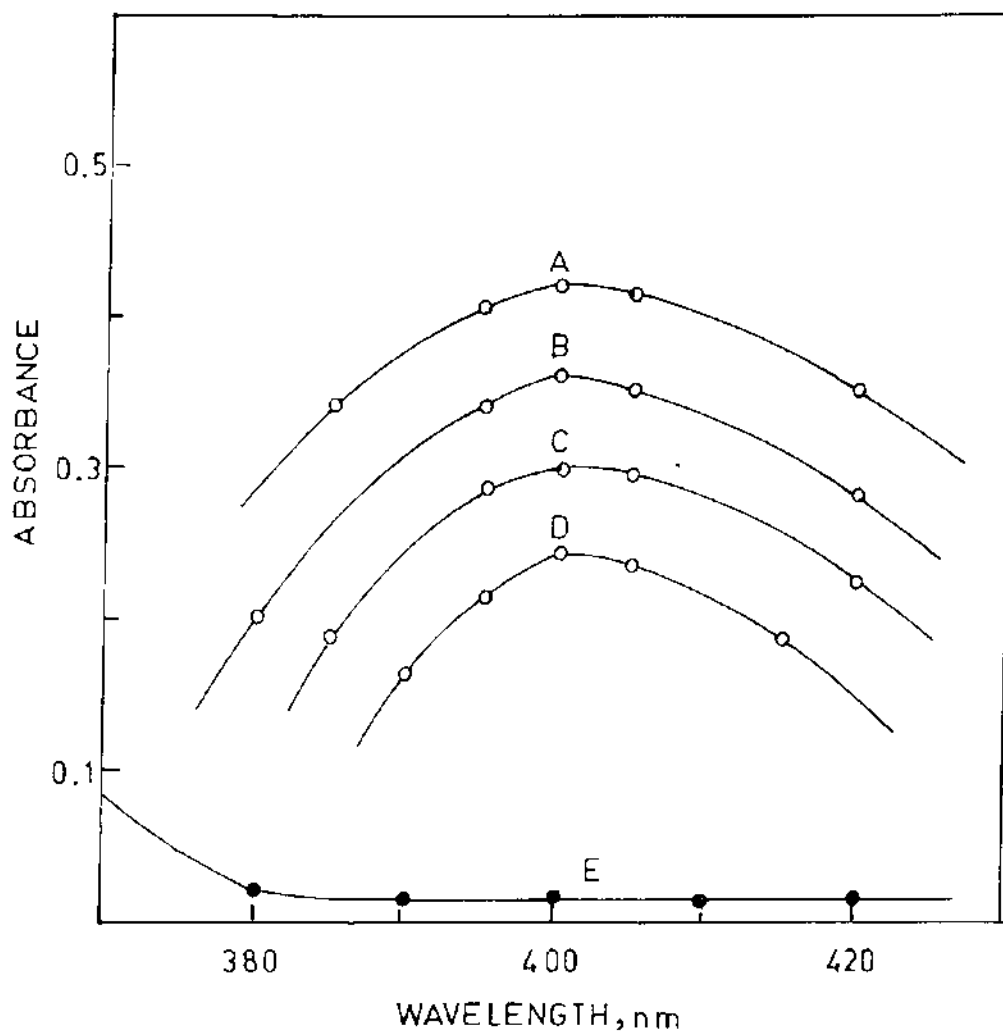


FIG. 4.1 EFFECT OF METAL CONCENTRATION ON THE POSITION OF  $\lambda_{\max}$  OF THE Pd(II)-HDPBA COMPLEX IN CHLOROFORM

[A]  $C_{\text{Pd(II)}} \simeq 6.58 \times 10^{-5} \text{ M}$  (70.0  $\mu\text{g}/10 \text{ ml}$  organic phase)

[B]  $C_{\text{Pd(II)}} \simeq 5.64 \times 10^{-5} \text{ M}$  (60.0  $\mu\text{g}/10 \text{ ml}$  organic phase)

[C]  $C_{\text{Pd(II)}} \simeq 4.70 \times 10^{-5} \text{ M}$  (50.0  $\mu\text{g}/10 \text{ ml}$  organic phase)

[D]  $C_{\text{Pd(II)}} \simeq 3.76 \times 10^{-5} \text{ M}$  (40.0  $\mu\text{g}/10 \text{ ml}$  organic phase)

[E] REAGENT BLANK

TABLE 4.1 EFFECT OF SOLVENTS ON THE EXTRACTION OF Pd(II)-HDPBA COMPLEX

$$C_{\text{Pd(II)}} = 6.58 \times 10^{-5} \text{ M (70.0 } \mu\text{g/10 ml organic phase)}$$

$$\text{pH} = 5.0 \pm 0.2$$

$$C_{\text{HDPBA}} = 1.0 \times 10^{-2} \text{ M}$$

Solvent	$\lambda_{\text{max}}$ nm	Molar absorptivity $1 \text{ mol}^{-1} \text{ cm}^{-1}$ $\times 10^3$
Chloroform	400	6.4
Benzene	400	6.0
Toluene	400	5.8
Xylene	390	5.0
Carbon tetrachloride	400	3.0
Ethyl acetate	400	2.4
Isobutyl methyl acetate	-	No extraction

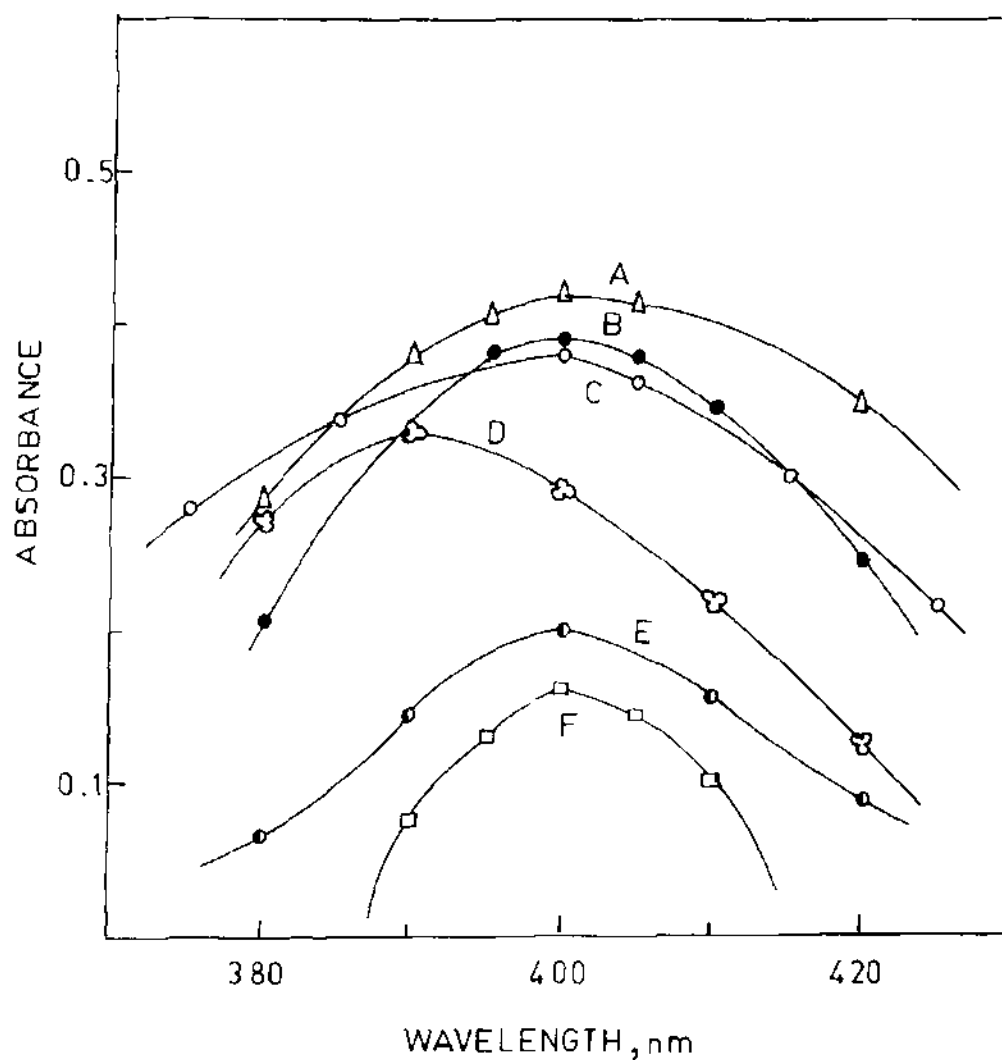


FIG. 4.2 EFFECT OF SOLVENTS ON THE ABSORBANCE AND  $\lambda_{\max}$  OF THE Pd(II)-HDPBA COMPLEX

$$C_{\text{Pd(II)}} = 6.58 \times 10^{-5} \text{ M};$$

$$\text{pH} = 5.0 \pm 0.2;$$

$$C_{\text{HDPBA}} = 1.0 \times 10^{-2} \text{ M}.$$

[A] CHLOROFORM [B] BENZENE [C] TOLUENE [D] XYLENE  
 [E] CARBON TETRACHLORIDE [F] ETHYL ACETATE

#### EFFECT OF N-HYDROXY-N,N'-DIPHENYLBENZAMIDINE(HDPBA)

The extraction of metal with HDPBA was studied. It was found that a minimum of  $0.69 \times 10^{-2}$  M solution of HDPBA is essential for complete extraction and maximum absorbance of the complex, and an excess of upto  $1.73 \times 10^{-2}$  M HDPBA had no adverse effect on the absorbance of the extracted complex. Thus, all extractions were carried out with  $1.0 \times 10^{-2}$  M HDPBA in chloroform (Table 4.3, Figure 4.4).

#### EFFECT OF DILUTION, TEMPERATURE AND ELECTROLYTES

The effect of dilution on the extraction of metal complex was examined. The result shows that the minimum and constant absorbance was found, when the volume ratio of organic to aqueous phase was varied from 2:1 to 1:5 (Table 4.4, Figure 4.5). The complex is quantitatively extracted in the temperature range of  $15-30^{\circ}\text{C}$  (Table 4.5). Hence, 1:2 volume ratio of organic to aqueous phase was maintained throughout the experiment and all extractions were performed at room temperature  $25 \pm 2^{\circ}\text{C}$ .

The extraction efficiency of the metal complex was unaffected in the presence of upto 1 M electrolytes viz.  $\text{KCl}/\text{NH}_4\text{Cl}/(\text{NH}_4)_2\text{SO}_4$ .

#### EFFECT OF EXTRACTION TIME, STABILITY OF THE COMPLEX, BEER'S LAW AND MOLAR ABSORPTIVITY

A shaking time of 2-3 min was sufficient for the maximum extraction of the Pd(II)-HDPBA complex. Prolonged extraction

TABLE 4.2 EFFECT OF pH OF THE AQUEOUS PHASE ON THE ABSORBANCE OF Pd(II)-HDPBA COMPLEX IN CHLOROFORM

$$C_{\text{Pd(II)}} = 5.64 \times 10^{-5} \text{ M (60.0 } \mu\text{g/10 ml aqueous phase)}$$

$$C_{\text{HDPBA}} = 1.0 \times 10^{-2} \text{ M}$$

pH of the aqueous phase	Absorbance at 400 nm
2.0	0.23
3.0	0.32
3.5	0.36
4.0	0.36
5.0	0.36
6.0	0.36
6.5	0.33
7.5	0.24

TABLE 4.3 EFFECT OF HDPBA CONCENTRATION ON THE EXTRACTION OF Pd(II)-HDPBA COMPLEX IN CHLOROFORM

$$C_{\text{Pd(II)}} = 5.64 \times 10^{-5} \text{ M (60.0 } \mu\text{g/10 ml aqueous phase)}$$

$$\text{pH} = 5.0 \pm 0.2$$

Concentration of HDPBA, M $\times 10^{-2}$	Absorbance at 400 nm
0.30	0.28
0.50	0.32
0.69	0.36
1.04	0.36
1.38	0.36
1.73	0.36
2.00	0.29
2.20	0.24

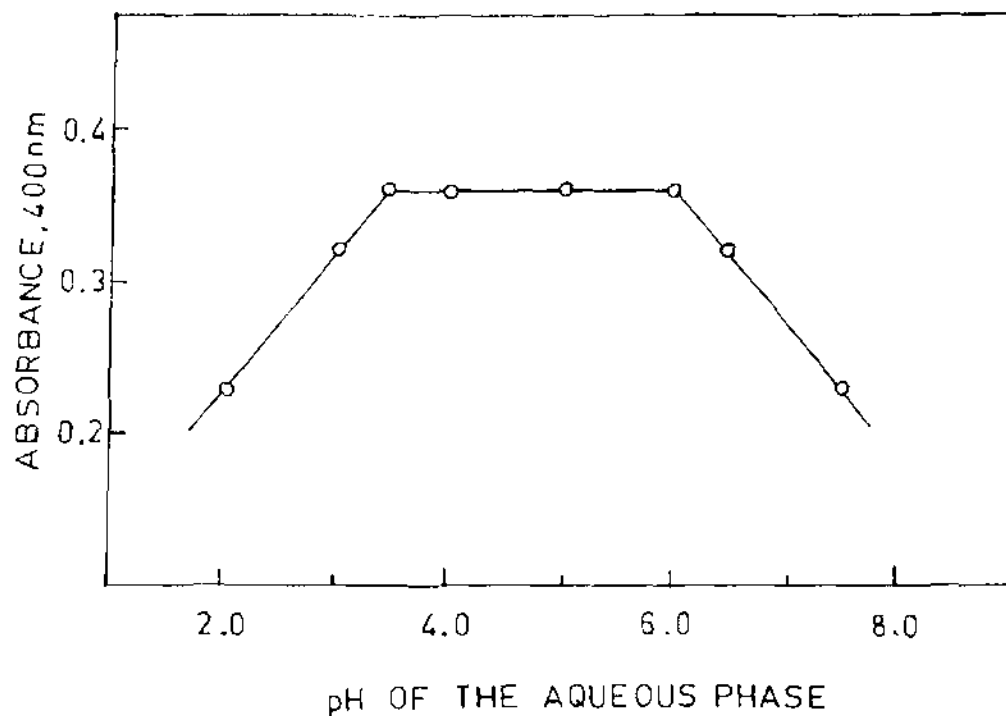


FIG. 4.3 EFFECT OF pH OF THE AQUEOUS PHASE ON THE EXTRACTION AND ABSORBANCE OF THE Pd(II)-HDPBA COMPLEX IN CHLOROFORM

$$C_{\text{Pd(II)}} = 5.64 \times 10^{-5} \text{ M}; C_{\text{HDPBA}} = 1.0 \times 10^{-2} \text{ M.}$$

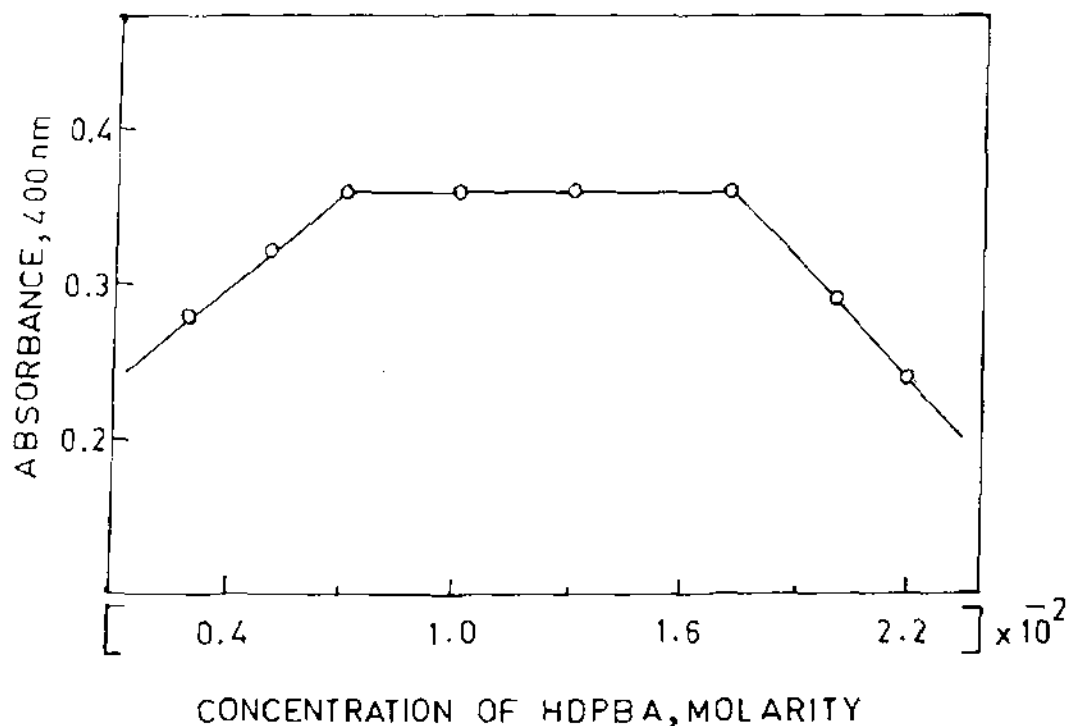


FIG. 4.4 EFFECT OF HDPBA CONCENTRATION ON THE EXTRACTION OF Pd(II)-HDPBA COMPLEX IN CHLOROFORM

$$C_{\text{Pd(II)}} = 5.64 \times 10^{-5} \text{ M}; \text{pH} = 5.0 \pm 0.2.$$



TABLE 4.4 EFFECT OF VOLUME RATIO OF ORGANIC TO AQUEOUS PHASE ON THE EXTRACTION OF Pd(II)-HDPBA COMPLEX IN CHLOROFORM

$$C_{\text{Pd(II)}} = 60.0 \mu\text{g}$$

$$\text{pH} = 5.0 \pm 0.2$$

$$C_{\text{HDPBA}} = 1.0 \times 10^{-2} \text{ M}$$

Volume ratio of organic to aqueous phase	Absorbance at 400 nm
2 : 1	0.36
1 : 1	0.36
1 : 2	0.36
1 : 3	0.36
1 : 4	0.36
1 : 5	0.36
1 : 6	0.31
1 : 7	0.27

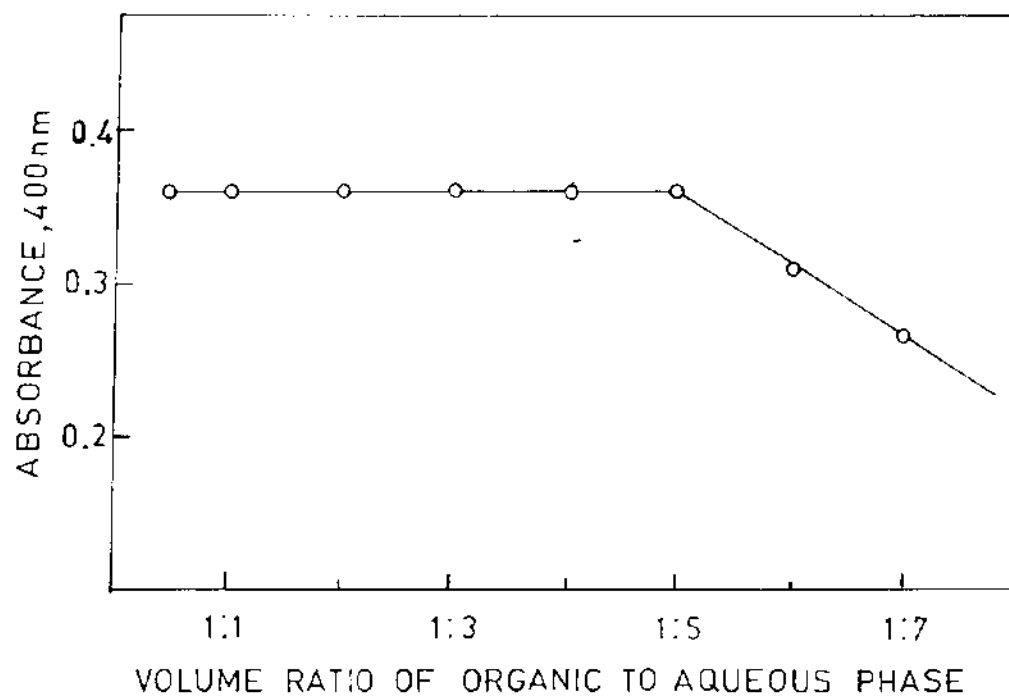


FIG. 4.5 EFFECT OF VOLUME RATIO OF ORGANIC TO AQUEOUS PHASE ON THE EXTRACTION OF Pd(II)-HDPBA COMPLEX IN CHLOROFORM

$C_{Pd(II)} = 60.0 \mu\text{g}$ ;  $\text{pH} = 5.0 \pm 0.2$ ;  $C_{HDPBA} = 1.0 \times 10^{-2} \text{ M}$ .

TABLE 4.5 EFFECT OF TEMPERATURE OF THE AQUEOUS PHASE ON THE EXTRACTION OF Pd(II)-HDPBA COMPLEX IN CHLOROFORM

$$C_{\text{Pd(II)}} = 5.64 \times 10^{-5} \text{ M (60.0 } \mu\text{g/10 ml aqueous phase)}$$

$$\text{pH} = 5.0 \pm 0.2$$

$$C_{\text{HDPBA}} = 1.0 \times 10^{-2} \text{ M}$$

Temperature of the aqueous phase, °C	Absorbance at 400 nm
10	0.25
12	0.30
15	0.36
20	0.36
25	0.36
30	0.36
35	0.32
40	0.22

time had no adverse effect on the complete formation of the metal complex. The stability of the complex was found to be 12 hr. The Pd(II)-HDPBA complex obeys Beer's law upto 7.0 ppm (70.0  $\mu\text{g}/10$  ml organic solution). The molar absorptivity of this complex in chloroform is found to be  $6.4 \times 10^3 \text{ l mol}^{-1} \text{ cm}^{-1}$  at  $\lambda_{\text{max}}$  400 nm.

#### [B] SPECTROPHOTOMETRIC DETERMINATION OF PALLADIUM(II) WITH 1-(2-PYRIDYLAZO)-2-NAPHTHOL(PAN)

The Pd(II)-HDPBA extract, after reacting with PAN in acidic medium forms a green coloured Pd(II)-HDPBA-PAN complex.

#### ABSORPTION SPECTRA

The absorption spectra of the metal complex formed with seven different hydroxyamidines(HOAs) and 1-(2-pyridylazo)-2-naphthol(PAN) in chloroform + 1-propanol mixture shows maximum absorbance at  $\lambda_{\text{max}}$  610-620 nm against their respective reagent blanks. The reagent blank of N-hydroxy-N,N'-diphenylbenzamidine (HDPBA) alongwith PAN against chloroform + 1-propanol mixture shows some absorbance at absorption maxima of the metal complex. Hence, it was used as reference for all absorbance measurements. The Pd(II)-HDPBA complex alongwith PAN exhibits maximum absorbance than the metal complexes of seven different hydroxyamidines(HOAs) (Table 4.6, Figure 4.6). Therefore, HDPBA is selected for all experimental work. The position of  $\lambda_{\text{max}}$  is unchanged at different metal concentrations, shown in Figure 4.7.

TABLE 4.6 EFFECT OF NATURE OF HYDROXYAMIDINES ON THE ABSORBANCE OF THE Pd(II)-HOA-PAN COMPLEXES IN CHLOROFORM + 1-PROPANOL MIXTURE

$$C_{Pd(II)} = 2.35 \times 10^{-5} \text{ M (25.0 } \mu\text{g/10 ml organic phase)}$$

$$C_{HOAs} \approx 1.0 \times 10^{-2} \text{ M}$$

$$C_{HCl} = 1.0 \text{ M}$$

$$C_{PAN} = 1.0 \times 10^{-3} \text{ M}$$

Hydroxyamidines (HOAs)	$\begin{bmatrix} \text{Ph} - \text{C} = \text{N} - \text{Ph}' \\   \\ \text{Ph}'' - \text{N} - \text{OH} \end{bmatrix}$	Ph''	Ph'	Ph	$\lambda_{\text{max}}$ nm	Molar absorptivity
						$\text{l mol}^{-1} \text{ cm}^{-1} \times 10^4$
N-Hydroxy-N, N'-diphenylbenzamide		-C <sub>6</sub> H <sub>5</sub>	-C <sub>6</sub> H <sub>5</sub>	-C <sub>6</sub> H <sub>5</sub>	620	1.58
N-Hydroxy-N-(3-chlorophenyl)-N'-(2-methylphenyl) benzamide		3-Cl-C <sub>6</sub> H <sub>4</sub>	2-CH <sub>3</sub> -C <sub>6</sub> H <sub>4</sub>	-C <sub>6</sub> H <sub>5</sub>	615	1.37
N-Hydroxy-N-phenyl-N'-(3-chlorophenyl) benzamide		-C <sub>6</sub> H <sub>5</sub>	3-Cl-C <sub>6</sub> H <sub>4</sub>	-C <sub>6</sub> H <sub>5</sub>	620	1.28
N-Hydroxy-N-(4-chlorophenyl)-N'-(2-methylphenyl)-2-chlorobenzamide		4-Cl-C <sub>6</sub> H <sub>4</sub>	2-CH <sub>3</sub> -C <sub>6</sub> H <sub>4</sub>	2-Cl-C <sub>6</sub> H <sub>4</sub>	620	1.19
N-Hydroxy-N-(2-chlorophenyl)-N'-(3-chlorophenyl)-2-chlorobenzamide		2-Cl-C <sub>6</sub> H <sub>4</sub>	3-Cl-C <sub>6</sub> H <sub>4</sub>	2-Cl-C <sub>6</sub> H <sub>4</sub>	610	1.06
N-Hydroxy-N-(4-chlorophenyl)-N'-(3-chlorophenyl)-2-chlorobenzamide		4-Cl-C <sub>6</sub> H <sub>4</sub>	3-Cl-C <sub>6</sub> H <sub>4</sub>	2-Cl-C <sub>6</sub> H <sub>4</sub>	620	1.02
N-Hydroxy-N-(2-chlorophenyl)-N'-(4-chlorophenyl)-2-chlorobenzamide		2-Cl-C <sub>6</sub> H <sub>4</sub>	4-Cl-C <sub>6</sub> H <sub>4</sub>	2-Cl-C <sub>6</sub> H <sub>4</sub>	615	0.76

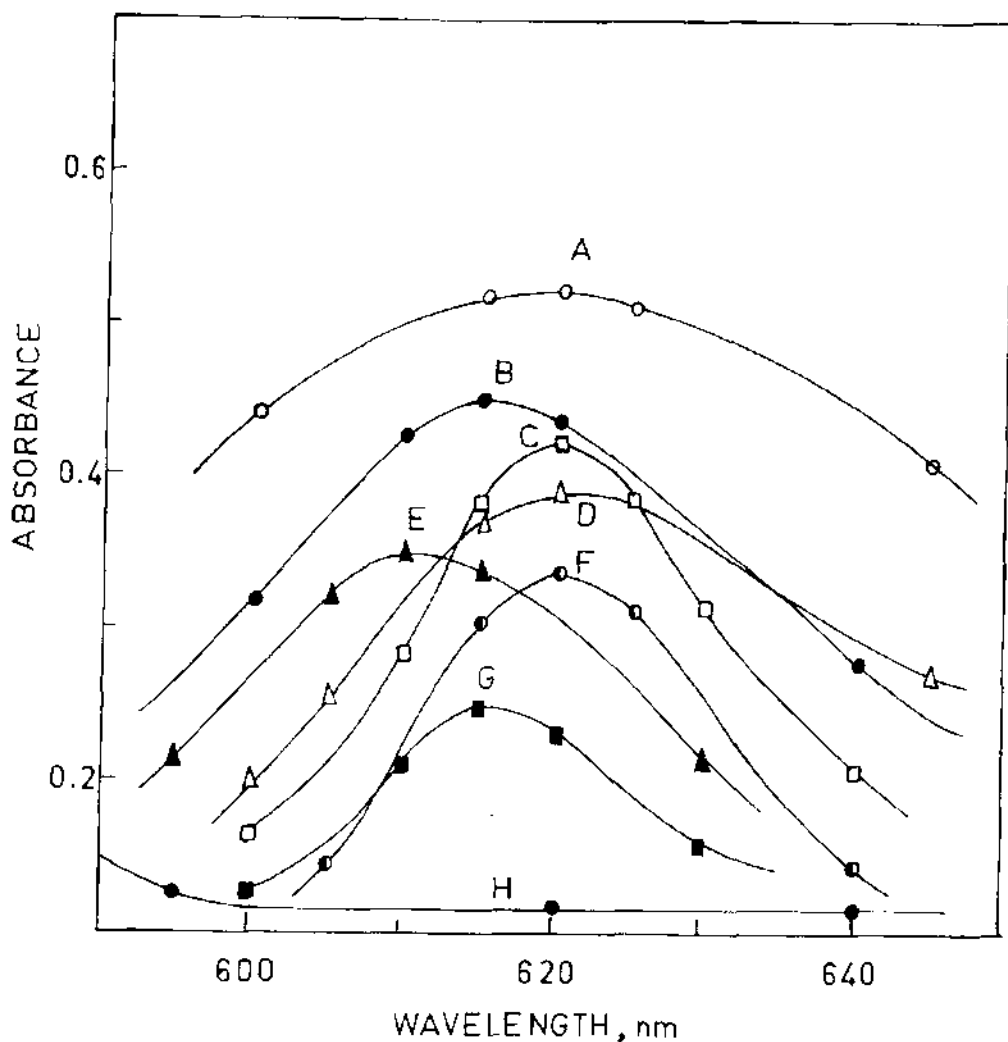


FIG. 4.6 ABSORPTION SPECTRA OF PALLADIUM(II) COMPLEX WITH DIFFERENT HYDROXYAMIDINES(HOAs) AND PAN AGAINST THEIR RESPECTIVE REAGENT BLANKS IN CHLOROFORM + 1-PROPANOL MIXTURE

$$C_{Pd(II)} = 3.29 \times 10^{-5} \text{ M}; C_{HOAs} \approx 1.0 \times 10^{-2} \text{ M};$$

$$C_{HCl} = 1.0 \text{ M}; C_{PAN} = 1.2 \times 10^{-3} \text{ M}.$$

- [A] N-HYDROXY-N,N'-DIPHENYLBENZAMIDINE
- [B] N-HYDROXY-N-(3-CHLOROPHENYL)-N'-(2-METHYLPHENYL)-BENZAMIDINE
- [C] N-HYDROXY-N-PHENYL-N'-(3-CHLOROPHENYL)-BENZAMIDINE
- [D] N-HYDROXY-N-(4-CHLOROPHENYL)-N'-(2-METHYLPHENYL)-2-CHLOROBENZAMIDINE
- [E] N-HYDROXY-N-(2-CHLOROPHENYL)-N'-(3-CHLOROPHENYL)-2-CHLOROBENZAMIDINE
- [F] N-HYDROXY-N-(4-CHLOROPHENYL)-N'-(3-CHLOROPHENYL)-2-CHLOROBENZAMIDINE
- [G] N-HYDROXY-N-(2-CHLOROPHENYL)-N'-(4-CHLOROPHENYL)-2-CHLOROBENZAMIDINE
- [H] REAGENT BLANK OF N-HYDROXY-N,N'-DIPHENYLBENZAMIDINE

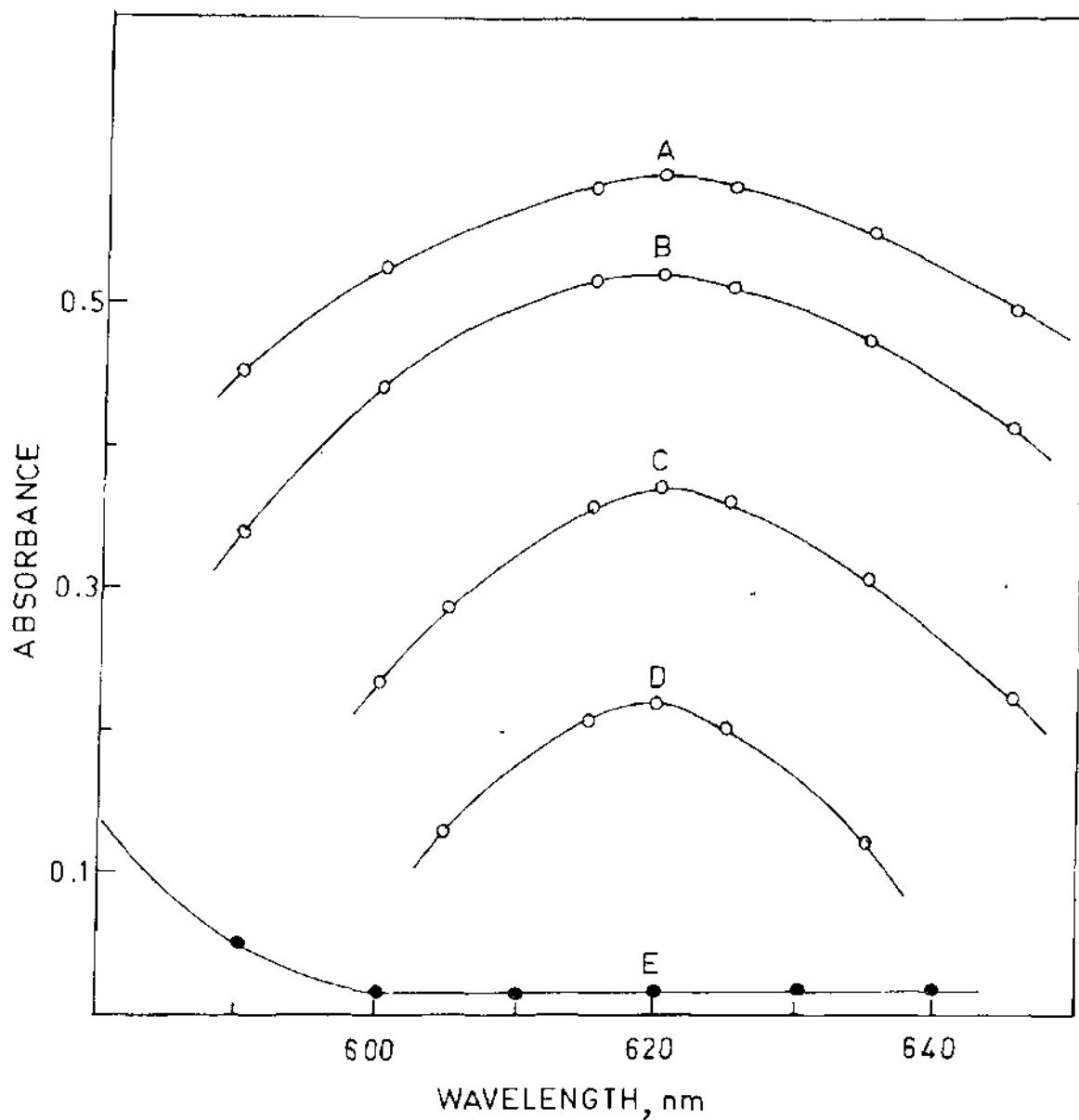


FIG. 4.7 EFFECT OF METAL CONCENTRATION ON THE POSITION OF  $\lambda_{\max}$  OF THE Pd(II)-HDPBA-PAN COMPLEX IN CHLOROFORM + 1-PROPANOL MIXTURE

[A]  $C_{Pd(II)} \simeq 3.76 \times 10^{-5}$  M (40.0  $\mu\text{g}/10$  ml organic phase)

[B]  $C_{Pd(II)} \simeq 3.29 \times 10^{-5}$  M (35.0  $\mu\text{g}/10$  ml organic phase)

[C]  $C_{Pd(II)} \simeq 2.35 \times 10^{-5}$  M (25.0  $\mu\text{g}/10$  ml organic phase)

[D]  $C_{Pd(II)} \simeq 1.40 \times 10^{-5}$  M (15.0  $\mu\text{g}/10$  ml organic phase)

[E] REAGENT BLANK

#### EFFECT OF DILUENT

Various diluents such as ethanol, methanol, acetone and 1-propanol alongwith chloroform have been tested to increase the sensitivity of the complex. It was found that the sensitivity of the complex is high in 1-propanol alongwith chloroform (Table 4.7). Hence, 1-propanol was used for all absorbance measurements.

#### EFFECT OF ACIDITY

The effect of acidity on the colour intensity of the Pd(II)-HDPBA-PAN complex was studied. It was found that 0.5-2.0 M hydrochloric acid is essential for constant and maximum absorbance of the complex (Table 4.8, Figure 4.8). Therefore, a 1.0 M hydrochloric acid was used for full colour development of the complex.

#### EFFECT OF 1-(2-PYRIDYLAZO)-2-NAPHTHOL(PAN)

For constant and maximum absorbance of the metal complex,  $(0.8-1.4) \times 10^{-3}$  M PAN solutions were necessary (Table 4.9, Figure 4.9). Hence,  $1.0 \times 10^{-3}$  M PAN solution was selected for full colour development.

#### STANDING TIME, STABILITY OF THE COMPLEX AND ORDER OF ADDITION OF REAGENTS

The colour development of the complex was found to be instantaneous and the absorbance of the complex was constant upto 24 hr at room temperature  $25 \pm 2^\circ\text{C}$ . The order in which the reagents were added was found to be immaterial.



TABLE 4.7 EFFECT OF DILUENTS ON THE COLOUR INTENSITY OF THE Pd(II)-HDPBA-PAN COMPLEX IN CHLOROFORM + DILUENT MIXTURE

$$C_{Pd(II)} = 3.29 \times 10^{-5} \text{ M (35.0 } \mu\text{g/10 ml organic phase)}$$

$$C_{HDPBA} = 1.0 \times 10^{-2} \text{ M}$$

$$C_{HCl} = 1.0 \text{ M}$$

$$C_{PAN} = 1.0 \times 10^{-3} \text{ M}$$

Diluent	$\lambda_{\text{max}}$ nm	Molar absorptivity $1 \text{ mol}^{-1} \text{ cm}^{-1}$ $\times 10^4$
1-Propanol	620	1.58
Acetone	620	1.04
Ethanol	620	1.02
Methanol	620	1.02

TABLE 4.8 EFFECT OF ACIDITY ON THE COLOUR DEVELOPMENT OF THE Pd(II)-HDPBA-PAN COMPLEX IN CHLOROFORM + 1-PROPANOL MIXTURE

$$C_{\text{Pd(II)}} = 3.29 \times 10^{-5} \text{ M (35.0 } \mu\text{g/10 ml aqueous phase)}$$

$$C_{\text{HDPBA}} = 1.0 \times 10^{-2} \text{ M}$$

$$C_{\text{PAN}} = 1.0 \times 10^{-3} \text{ M}$$

Concentration of HCl, M	Absorbance at 620 nm
0.1	0.39
0.2	0.42
0.3	0.46
0.5	0.52
1.0	0.52
1.5	0.52
2.0	0.52
2.2	0.48
2.5	0.43
3.0	0.33

TABLE 4.9 EFFECT OF PAN CONCENTRATION ON THE COMPLEX FORMATION AND COLOUR DEVELOPMENT OF THE Pd(II)-HDPBA-PAN COMPLEX IN CHLOROFORM + 1-PROPANOL MIXTURE

$$C_{Pd(II)} = 3.29 \times 10^{-5} \text{ M (35.0 } \mu\text{g/10 ml aqueous phase)}$$

$$C_{HDPBA} = 1.0 \times 10^{-2} \text{ M}$$

$$C_{HCl} = 1.0 \text{ M}$$

Concentration of PAN, M $\times 10^{-3}$	Absorbance at 620 nm
0.4	0.43
0.6	0.47
0.8	0.52
1.0	0.52
1.2	0.52
1.4	0.52
1.5	0.48
1.6	0.45
1.8	0.38

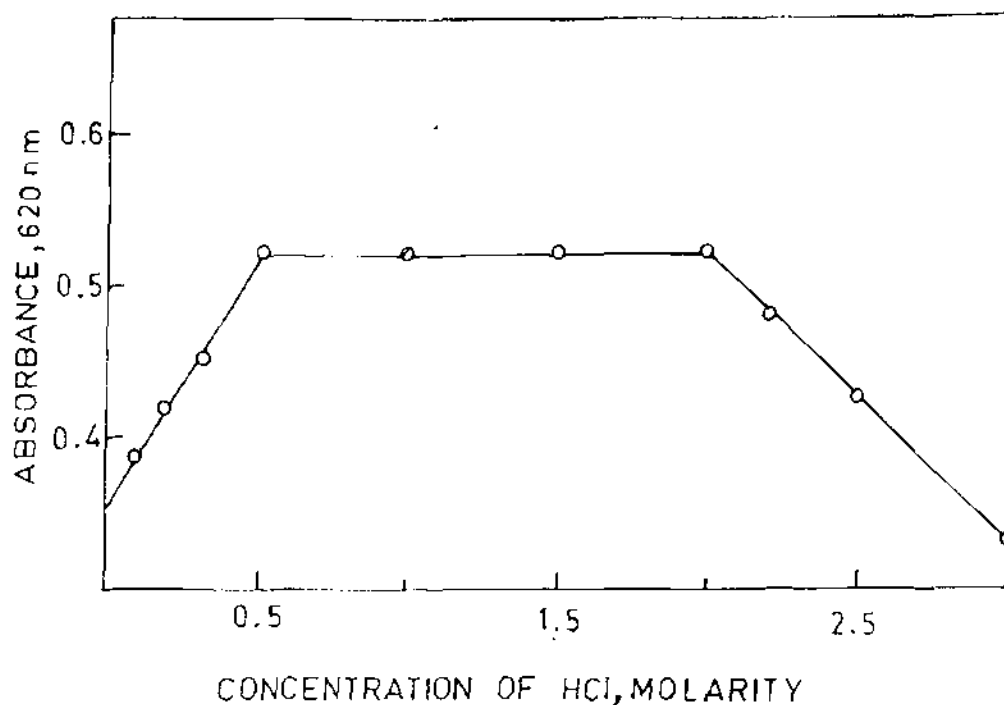


FIG. 4.8 EFFECT OF HYDROCHLORIC ACID ON THE ABSORBANCE OF THE COMPLEX CHLOROFORM + 1-PROPANOL MIXTURE

$$C_{Pd(II)} = 3.29 \times 10^{-5} \text{ M}; \quad C_{HDPBA} = 1.0 \times 10^{-2} \text{ M};$$

$$C_{PAN} = 1.0 \times 10^{-3} \text{ M}.$$

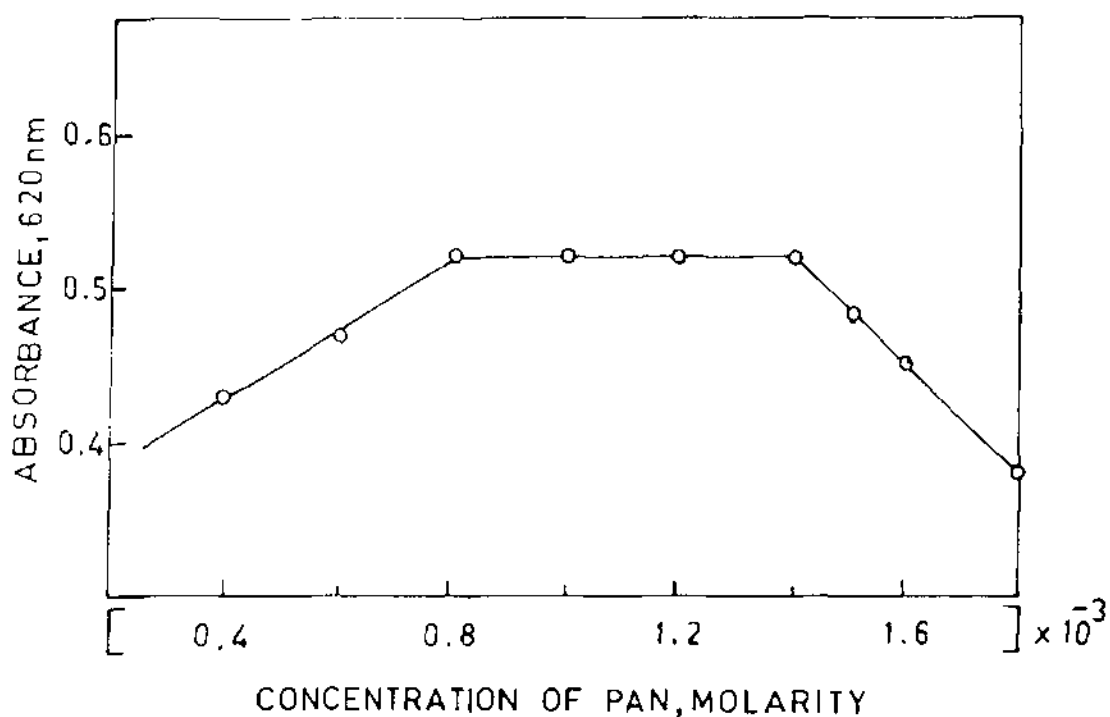


FIG. 4.9 EFFECT OF PAN CONCENTRATION ON THE ABSORBANCE OF Pd(II)-HDPBA-PAN COMPLEX IN CHLOROFORM + 1-PROPANOL MIXTURE

$$C_{Pd(II)} = 3.29 \times 10^{-5} \text{ M}; \quad C_{HDPBA} = 1.0 \times 10^{-2} \text{ M}; \quad C_{HCl} = 1.0 \text{ M}.$$

### BEER'S LAW, CORRELATION COEFFICIENT AND OPTIMUM CONCENTRATION RANGE

The Pd(II)-HDPBA-PAN complex obeys Beer's law upto 4.5 ppm (45.0  $\mu\text{g}/10\text{ ml}$  organic solution) with a correlation coefficient<sup>63</sup> value of 0.98. The optimum concentration range evaluated from calibration curve is found to be 1.5-4.0 ppm (15.0-40.0  $\mu\text{g}/10\text{ ml}$  organic solution) (Table 4.10, Figure 4.10).

### MOLAR ABSORPTIVITY, SENSITIVITY AND DETECTION LIMIT

The molar absorptivity of the ternary complexes of seven different hydroxyamidines (HOAs) and PAN lie in the range of  $(0.76-1.58) \times 10^4\text{ l mol}^{-1}\text{ cm}^{-1}$  at  $\lambda_{\text{max}}$  610-620 nm. The molar absorptivity of the Pd(II)-HDPBA-PAN complex, calculated in terms of palladium(II), is found to be  $1.58 \times 10^4\text{ l mol}^{-1}\text{ cm}^{-1}$ . The Sandell's sensitivity<sup>64</sup> of the method is  $0.0067\text{ }\mu\text{g}/\text{cm}^2$  for 0.001 absorbance unit. The limit of detection for the metal ion is  $0.1\text{ }\mu\text{g}/\text{ml}$  aqueous solution.

### PRECISION OF THE METHOD AND CONFIDENCE LIMIT

Statistical studies have been carried out in order to check the precision of the method. Ten replicate measurements each containing  $35\text{ }\mu\text{g}/10\text{ ml}$  of palladium(II) were performed. A calculated value of mean absorbance and standard deviation were found to be 0.52 and  $\pm 0.0063$ . The relative standard deviation of the method was found to be  $\pm 1.2\%$ . The confidence limit<sup>63</sup> of the method in terms of mean absorbance and molar absorptivity were found to be  $(0.52 \pm 0.0045)$  and  $(1.58 \pm 0.01) \times 10^4\text{ l mol}^{-1}\text{ cm}^{-1}$ , respectively at 95% probability (Table 4.11).

TABLE 4.10 CALIBRATION CURVE DATA AND CORRELATION COEFFICIENT FOR THE DETERMINATION OF PALLADIUM(II) AS Pd(II)-HDPBA-PAN COMPLEX IN CHLOROFORM + 1-PROPANOL MIXTURE

$$C_{\text{HDPBA}} = 1.0 \times 10^{-2} \text{ M}$$

$$C_{\text{PAN}} = 1.0 \times 10^{-3} \text{ M}$$

$$C_{\text{HCl}} = 1.0 \text{ M}$$

No. of obser- vation	Concentration of Pd(II) in organic solution X <sub>i</sub> = $\mu\text{g}/10 \text{ ml}$	Absorbance at 620 nm Y <sub>i</sub>	Correlation coefficient r
	10.0	0.15	
	15.0	0.22	
	20.0	0.31	
	25.0	0.37	
8	30.0	0.45	0.98
	35.0	0.52	
	40.0	0.59	
	45.0	0.67	

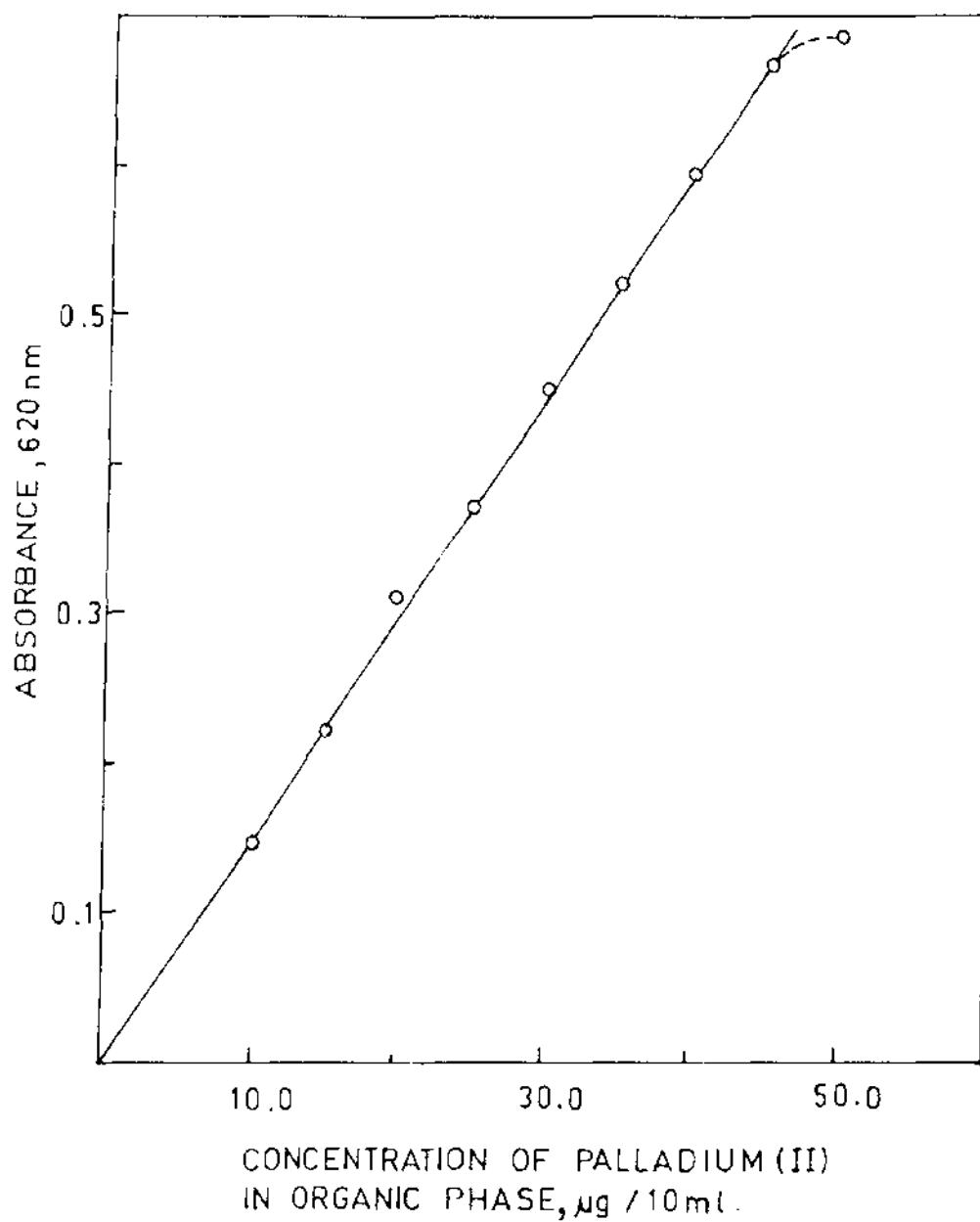


FIG. 4.10 CALIBRATION CURVE FOR THE DETERMINATION OF PALLADIUM(II) AS Pd(II)-HDPBA-PAN COMPLEX IN CHLOROFORM + 1-PROPANOL MIXTURE

TABLE 4.11 DETERMINATION OF PRECISION OF THE METHOD

$$C_{Pd(II)} = 3.29 \times 10^{-5} \text{ M (35.0 } \mu\text{g/10 ml aqueous phase)}$$

$$C_{HDFBA} = 1.0 \times 10^{-2} \text{ M}$$

$$C_{HCl} = 1.0 \text{ M}$$

$$C_{PAN} = 1.0 \times 10^{-3} \text{ M}$$

No. of obser- vation	Absorbance at 620 nm	Mean absorbance	Standard deviation	Relative standard deviation	Value of 't' at 95% confi- dence level	Confidence limit	$\left[ \bar{x} \pm \frac{ts}{\sqrt{N}} \right]$
N		$\bar{x}$	$\pm S$	$\pm, \%$			
	0.52						
	0.52						
	0.51						
	0.53						
10	0.52	0.52	0.0063	1.2	2.262	(0.52±0.0045)	(1.58±0.01)
	0.52						
	0.51						
	0.52						
	0.51						
	0.52						



#### EFFECT OF DIVERSE IONS

To study the effect of diverse ions, variable amounts of foreign ions were introduced to a fixed amount of palladium(II) and the absorbance was measured as above described procedure. The method is free from the interferences of common metal ions except Cu(II) and V(V) which were effectively masked by the addition of EDTA prior to extraction. The tolerance limit of various diverse ions in the determination of 3.5  $\mu\text{g/ml}$  are summarised in Table 4.12.

TABLE 4.12 EFFECT OF DIVERSE IONS ON THE DETERMINATION OF 35.0  
 $\mu\text{g}$  PALLADIUM(II)

Ion	Added as	Tolerance limit <sup>#</sup> mg
Cu(II)	$\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$	0.05 <sup>a</sup>
V(V)	$\text{NH}_4\text{VO}_3$	0.05 <sup>a</sup>
Au(III)	$\text{AuCl}_3 \cdot 2\text{H}_2\text{O}$	0.1
Ru(III)	$\text{RuCl}_3$	0.4
Rh(III)	$\text{RhCl}_3$	0.4
Pt(IV)	$\text{PtCl}_4$	0.5
Os(VI)	$\text{Na}_2\text{OsO}_4$	0.5
Co(II)	$\text{CoSO}_4 \cdot 6\text{H}_2\text{O}$	0.8
Ni(II)	$\text{NiSO}_4 \cdot 6\text{H}_2\text{O}$	0.8
Fe(III)	$\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$	0.8
As(III)	$\text{As}_2\text{O}_3$	2.0
Thiocyanate	KSCN	2.0
Iodide	KI	2.0
Fluoride	NaF	2.0
Cr(III)	$\text{Cr}_2(\text{SO}_4)_3 \cdot \text{Al}_2(\text{SO}_4)_3 \cdot 24\text{H}_2\text{O}$	3.0
Ti(IV)	$\text{K}_2\text{TiO}(\text{C}_2\text{O}_4)_2 \cdot \frac{1}{2}\text{H}_2\text{O}$	3.0
Mo(VI)	$(\text{NH}_4)_6\text{Mo}_7\text{O}_{24} \cdot 4\text{H}_2\text{O}$	4.0
U(VI)	$\text{Na}_2\text{WO}_4 \cdot 2\text{H}_2\text{O}$	4.0

Contd..

TABLE 4.12 (Contd.)

Ion	Added as	Tolerance limit <sup>#</sup> mg
Citrate	$\text{Na}_3\text{C}_6\text{H}_5\text{O}_7 \cdot 2\text{H}_2\text{O}$	5.0
Oxalate	$\text{Na}_2\text{C}_2\text{O}_4$	5.0
Persulphate	$\text{Na}_2\text{S}_2\text{O}_8$	5.0
Cd(II)	$3\text{CdSO}_4 \cdot 8\text{H}_2\text{O}$	6.0
Pb(II)	$\text{Pb}(\text{NO}_3)_2$	6.0
Zr(II)	$\text{ZrO}_2\text{Cl}_2 \cdot 8\text{H}_2\text{O}$	6.0
Mg(II)	$\text{MgSO}_4 \cdot 7\text{H}_2\text{O}$	10
Ca(II)	$\text{CaCl}_2 \cdot \text{H}_2\text{O}$	10
Sr(II)	$\text{SrSO}_4$	10
Ba(II)	$\text{BaCl}_2$	10
EDTA	$\text{Na}_2\text{-EDTA}$	20
Tartrate	$\text{Na}_2\text{C}_4\text{H}_4\text{O}_6 \cdot 2\text{H}_2\text{O}$	20

<sup>#</sup> Causing error in absorbance less than  $\pm 2\%$ .

a Masked by 1 ml of 0.2% (w/v) EDTA solution.

## COMPOSITION AND REACTION MECHANISM

The stoichiometry of the complex was determined by curve-fitting method. The results obtained indicate that the metal to ligand ratio in Pd(II)-HDPBA and Pd(II)-HDPBA-PAN complexes are 1:2 and 1:1:1, respectively. This is in support with the formation of a similar kind of complex, reported by Agrawal et al.<sup>32</sup>

## PROCEDURE

## [A] DETERMINATION OF THE RATIO OF HDPBA

The test solution containing 60.0  $\mu\text{g}$  Pd(II) was placed in a 125-ml separatory funnel. The buffer solution was added so that the pH of the aqueous phase is maintained around  $5.0 \pm 0.2$  in a final volume of 10 ml. The metal ion was extracted with varying known concentration of HDPBA solution in chloroform as in the procedure describe above. The absorbance of the complex was measured against reagent blank. The distribution ratio of the metal ion was computed as in chapter II.

The graph was plotted between logarithmic value of distribution ratio ( $D = A_{\text{eq}} / A_{\text{max}} - A_{\text{eq}}$ ) of the metal versus log molar concentration of the reagent. The slope of the curve was found to be 2.0 (Table 4.13, Figure 4.11). Thus, molar ratio of palladium(II) to HDPBA is 1:2 in Pd(II)-HDPBA complex.

## [B] DETERMINATION OF THE RATIO OF PAN

An aliquot of the test solution containing 35.0  $\mu\text{g}$

TABLE 4.13 CURVE - FITTING METHOD FOR THE DETERMINATION OF RATIO OF PALLADIUM(II) TO HDPBA IN Pd(II)-HDPBA COMPLEX IN CHLOROFORM

$$C_{Pd(II)} = 5.64 \times 10^{-5} \text{ M (60.0 } \mu\text{g/10 ml aqueous phase)}$$

$$\text{pH} = 5.0 \pm 0.2$$

Concentration of HDPBA in organic phase, M $\times 10^{-2}$	Log M	$D = \frac{A_{eq}}{A_{max} - A_{eq}}$	Log D
0.6	-2.22	11.0	1.04
0.5	-2.30	8.0	0.90
0.4	-2.40	5.0	0.70
0.3	-2.52	3.5	0.54

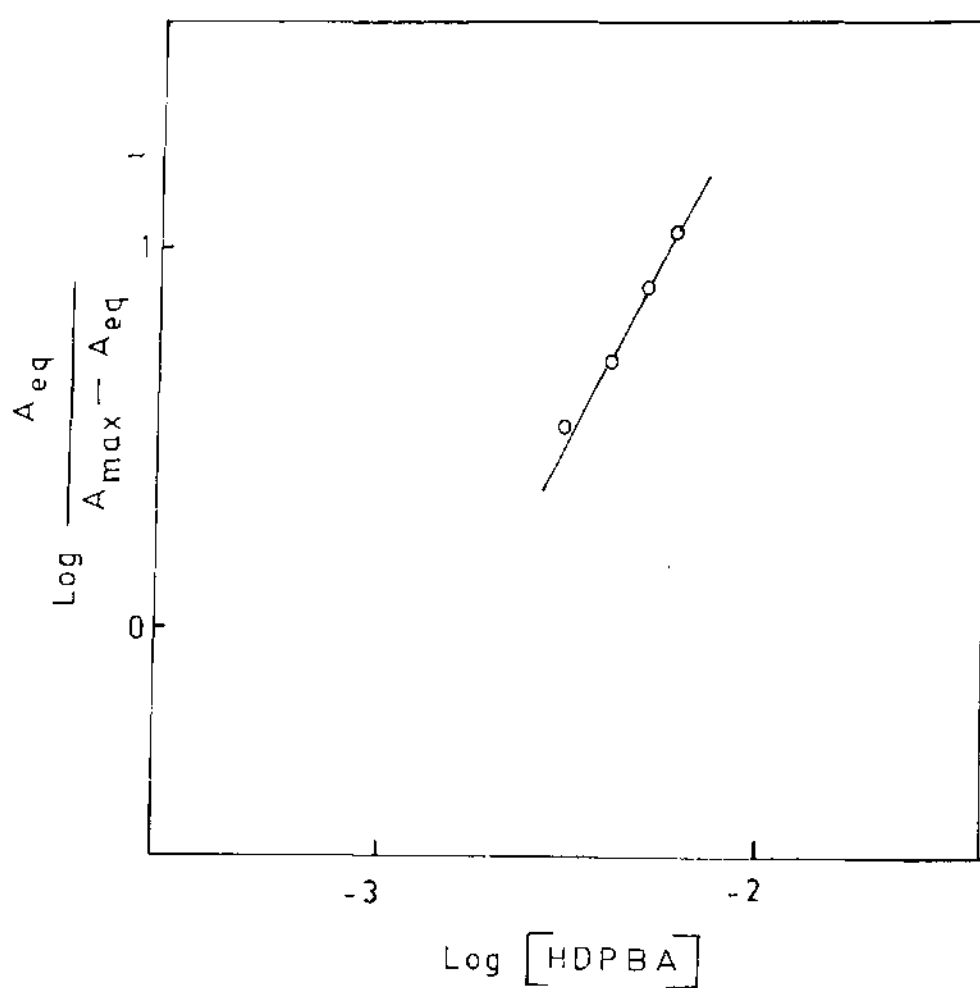


FIG. 4.11 CURVE-FITTING METHOD FOR THE DETERMINATION OF PALLADIUM(II) TO HDPBA RATIO IN Pd(II)-HDPBA COMPLEX, FORMED IN CHLOROFORM

$$C_{\text{Pd(II)}} = 5.64 \times 10^{-5} \text{ M};$$

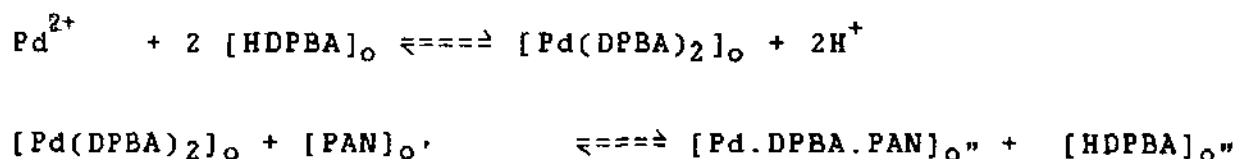
$$\text{pH} = 5.0 \pm 0.2;$$

$$\lambda_{\text{max}} = 400 \text{ nm.}$$

Pd(II) was transferred to a 125-ml separatory funnel. The pH of the aqueous phase was adjusted around  $5.0 \pm 0.2$  in a total volume of 10 ml using acetate buffer and the metal was extracted with HDPBA solution in chloroform. The extract was reacted with a varying known concentration of PAN solution in 1.0 M HCl medium. The absorbance of the ternary complex was measured at 620 nm against reagent blank.

The logarithmic value of the distribution ratio of metal was plotted versus log molar concentration of the reagents (Table 4.14, Figure 4.12). The slope of the curve was found to be 1.0. Hence, the ratio of metal to PAN is found to be 1:1 in Pd(II)-HDPBA-PAN complex. Thus the result shows that on addition of PAN to the chloroform extract of Pd(II)-HDPBA complex, one molecule of HDPBA is replaced by one molecule of PAN.

The overall reaction mechanism for the extraction and colour reaction with PAN can be written as :



Where abbreviations HDPBA and PAN, and subscripts  $o, o'$  and  $o''$  denote N-hydroxy-N,N'-diphenylbenzamidine, 1-(2-pyridyl-azo)-2-naphthol, and chloroform, 1-propanol and chloroform + 1-propanol mixture, respectively.

TABLE 4.14 CURVE - FITTING METHOD FOR THE DETERMINATION OF PALLADIUM(II) TO PAN RATIO IN Pd(II)-HDPBA-PAN COMPLEX IN CHLOROFORM + 1-PROPANOL MIXTURE

$$C_{Pd(II)} = 3.29 \times 10^{-5} \text{ M (35.0 } \mu\text{g/10 ml aqueous phase)}$$

$$C_{HDPBA} = 1.0 \times 10^{-2} \text{ M}$$

$$C_{HCl} = 1.0 \text{ M}$$

Concentration of PAN in organic phase, M $\times 10^{-3}$	Log M	D = $\frac{A_{eq}}{A_{max} - A_{eq}}$	Log D
0.6	-3.22	8.45	0.93
0.5	-3.30	6.43	0.80
0.4	-3.40	4.78	0.68
0.3	-3.52	3.73	0.57



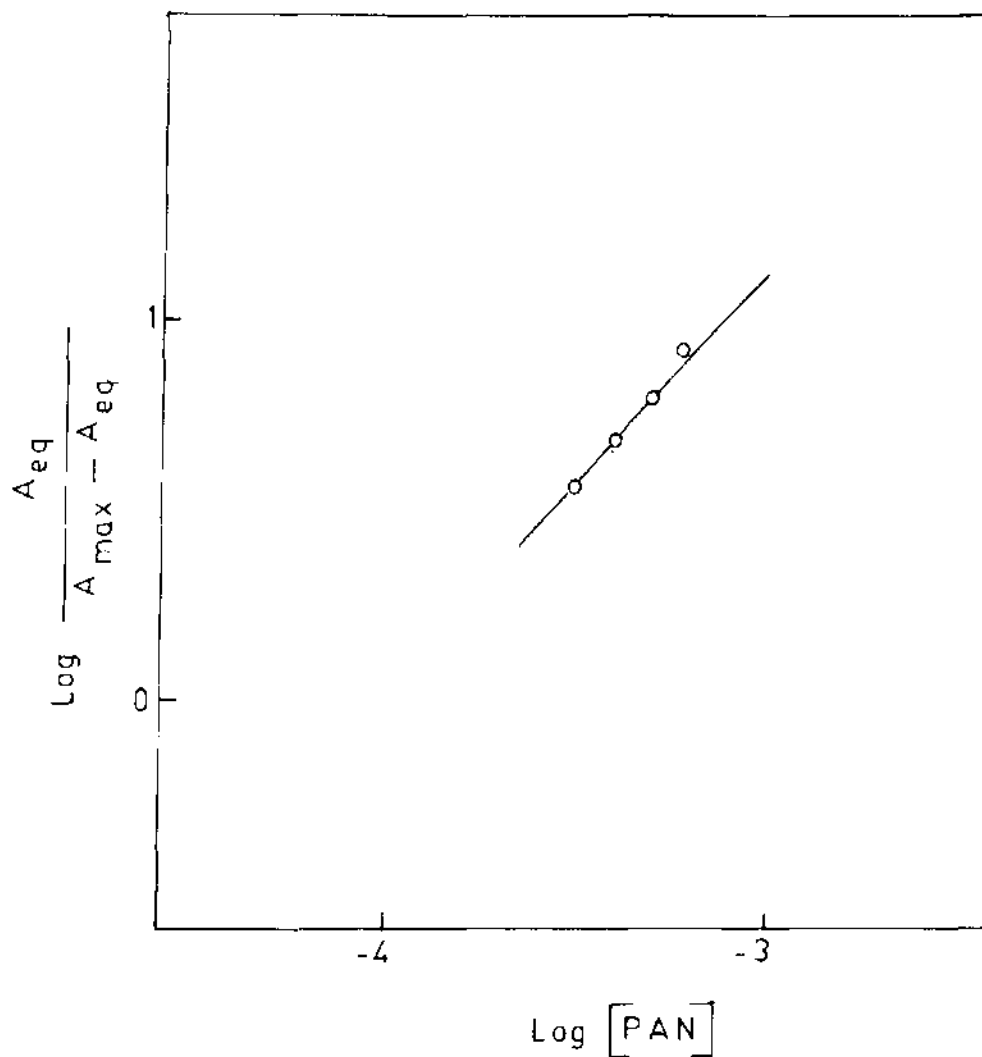


FIG. 4.12 CURVE-FITTING METHOD FOR THE DETERMINATION OF PALLADIUM(II) TO PAN RATIO IN Pd(II)-HDPBA-PAN COMPLEX, FORMED IN CHLOROFORM + 1-PROPANOL MIXTURE

$$C_{Pd(II)} = 3.29 \times 10^{-5} \text{ M};$$

$$C_{HDPBA} = 1.0 \times 10^{-2} \text{ M};$$

$$C_{HCl} = 1.0 \text{ M};$$

$$\lambda_{max} = 620 \text{ nm.}$$

## APPLICATION OF THE METHOD

The application of the present method has been tried for the analysis of the metal in synthetic mixtures (Table 4.15).

The synthetic mixtures were prepared by mixing a various known concentration of platinum metals in a fixed amount of palladium(II) and the palladium(II) content are determined as in the previously described procedure.

TABLE 4.15 RECOVERY OF PALLADIUM(II) FROM SYNTHETIC MIXTURES

Solution No.	Composition of the Synthetic mixtures	Pd(II) found	Recovery	Relative standard deviation <sup>a</sup>
		$\mu\text{g}$	%	$\pm$ , %
1.	Pd(35)+Rh(400)+Ru(400)	35.0	100.0	1.2
2.	Pd(35)+Pt(500)+Os(400) Au(100)	34.0	97.1	1.2
3.	Pd(35)+Os(500)+Pt(500)	35.0	100.0	1.1
4.	Pd(35)+Rh(400)+Ru(400) +Pt(500)+Os(500)	33.0	94.3	1.3
5.	Pd(35)+Au(100)+Pt(400)	35.0	100.0	1.1

<sup>a</sup> Average of six determinations

Figures in parentheses show concentration of metal ions in  $\mu\text{g}$  per 10 ml aqueous phase.

#### COMPARISON WITH OTHER METHODS

The spectral characteristics of the various spectrophotometric methods are shown in Table 4.16 and compared with present method. The comparison reveals that the present method is superior to other reported methods in terms of selectivity.

TABLE 4.16 COMPARATIVE STUDY OF SOME SPECTROPHOTOMETRIC METHOD FOR THE DETERMINATION OF PALLADIUM

Reagents	pH/Acidity	Solvent	$\lambda_{\max}$ nm	Molar absorp- tivity $l \text{ mol}^{-1} \text{ cm}^{-1}$	Remarks	Refer- ence
N-m-Chlorophenyl-p-methoxybenzohydroxamic acid + 1-(2-Pyridylazo)-2-naphthol	2.8-3.4	Isoamyl alcohol	620	12000	Maximum absorbance is achieved after 20 min, Fe,V,Ti,Co and Ni interfere and can be masked by using different masking agents.	33
1-(2-Pyridylazo)-2-naphthol	3.0-3.5	Chloroform	675	17733.33*	Co,Ag and Fe interfere.	32
4-(2-Pyridylazo)resorcinol+Mesityl oxide	4.5-5.0	Benzene	610	3900	Cu,V,,Th,EDTA and thio-urea interfere severely, sensitivity is poor.	35
2-Thio-barbituric acid	1.5	Water	374	10000	Procedure is time consuming,method require rigid control of experimental conditions.	24
Glyoxal Bis(4-phenyl-3-thiosemicarbazone)	9.6	60% Dimethylformamide	635	3200	Fe,Bi,Hg,V,Ni,Co,Au and Ag interfere and masked by EDTA.	53
Thiosemicarbazone	1.8-4.0	Cyclohexanol	405	6400	Sensitivity is very low.	52
4-(3,5-Dichloro-2-pyridylazo)-1,3-diaminobenzene + Tri-chloroacetate II	1.2 M H <sub>2</sub> SO <sub>4</sub>	Benzene	600	86000	Reaction is completed after 10 min, Hg and Au interfere seriously.	9
2'-Hydroxy-4-methoxy-5'-chlorochalconic oxime	2.5	Isobutyl methyl ketone	380	7300	Au,Cr,Zn and EDTA interfere.	56
2-(2-Pyridyl)thiopicolinamide	5.0-8.0	Ethanol + Dimethylformamide	410	8000	Poor sensitivity.	16

Contd..

TABLE 4.16 (Contd.)

Reagents	pH/Acidity	Solvent	$\lambda_{\max}$ nm	Molar absorp- tivity $l \text{ mol}^{-1} \text{ cm}^{-1}$	Remarks	Refer- ence
<i>o</i> -Chlorophenyfluorone +Cetyltrimethyl ammo- nium bromide	5.5	-	610	10400	Procedure is time con- suming, pH is critical.	15
<i>o</i> -Hydroxyhydroquin- onephthalein + Methyl- cellulose + Cetyltri- methyl ammonium bromide	4.7-5.5	Water	625	127000	Fe, Cu, Al and Cr inter- fere. Cu and Al masked by citric acid.	7
Thiocaprolactam+Chloride	-		400	5200	Au, Bi, Pt, Hg, Ag and Cu	
Thiocaprolactam+Bromide	-	Chloroform	400	6300	interfere.	55
Thiocaprolactam+Iodide	-		400	8700		
Benzyl dimethylphenyl- ammonium chloride	3.4-5.8	1,2-Dichloro- ethane	-	5340	Poor sensitivity	23
N-Hydroxy-N', N'-di- phenylbenzamidine + 1-(2-Pyridylazo)-2- naphthol	3.5-6.0	Chloroform + 1-Propanol	620	15800	Cu, V interfere and masked by EDTA.	Present method

\* Calculated from Sandell's sensitivity.

### CONCLUSION

The proposed method is based on the formation of green coloured complex by the reaction of palladium(II) with HDPBA and PAN. It removes many drawbacks of the classical PAN method as well as other reported methods. The method is sensitive, selective and reproducible. It is free from the interferences of almost all common metal ions associated with palladium. It has been applied successfully for the determination of palladium(II) in synthetic mixtures.

## REFERENCES

1. F.E. Beamish, "The Analytical Chemistry of the Nobel Metals", Pergamon Press, Oxford 1966.
2. N.A. Lange, "Handbook of Chemistry", 10th Ed., McCraw Hill, New York 1967.
3. R.S. Young, "Chemical Analysis in Extractive Metallurgy", Charles Griffin and Company Limited, London 1971.
4. J.C. Bailar, H.J. Emeleus, S.R. Nyholm and A.F. Trotman-Dickenson, "Comprehensive Inorganic Chemistry", Vol. 3, Pergamon Press, Oxford 1973.
5. F.W. Oehme, "Toxicity of Heavy Metals in the Environment", Part II, Marcel Dekker, New York 1979.
6. K. Kalinowski and Z. Marczenko; Anal. Chim. Acta 186, 331, 1986.
7. I. Mori, Y. Fujita and T. Enoki; Bunseki Kagaku 28, 685, 1979; Chem. Abstr. 92, 51352 y, 1980.
8. S. Cheng and Z. Hwang; Sichuan Daxue Xuebao, Ziran Kexueban 27, 332, 1990; Chem. Abstr. 114, 35073 a, 1991.
9. C.A. Fontan, C.B. Marone and R. Olsina; Bull. Chem. Soc. Jpn. 61, 4121, 1988; Chem. Abstr. 110, 107250 y, 1989.
10. V. Michaylova, B. Evtimova and D. Nonova; Anal. Chim. Acta 207, 373, 1988.
11. D. Wang, C. Jin and Z. Huang; He, Shuqiong, Huaxue Shiji 2, 47, 1987; Chem. Abstr. 107, 16874 b, 1987.
12. Y. Li; Chen., Weiping Xiangtan Daxue Ziran Kexue Xuebao 2, 70, 1987; Chem Abstr. 107, 189809 n, 1987.
13. M. Jiang, H. Du and Y. Han; Lihua Jiayan, Huaxue Fence 24, 277, 282, 1988; Chem. Abstr. 113, 70255 n, 1990.
14. D. Yang; Fenxi Shiyanshi 9, 66, 1990; Chem. Abstr. 114, 16758 m, 1991.
15. C. Jiang and S. Liu; Guiginsu 10, 52, 1989; Chem. Abstr. 114, 94253 g, 1991.
16. A.K. Chakrabarti and S.K. Chakraborty; Proc. Natl. Acad. Sci., India, Sect. A 59, 533, 1989; Chem. Abstr. 115, 84380 c, 1991.



17. M.P. Lopez Martinez, J.M. Fernandez Soils, J.M. Castro Romero, M.H. Bollain Rodriguez and F. Bermejo Martinez; Bol. Acad. Galega Cienc. 9, 29, 1990; Chem. Abstr. 115, 197184 k, 1991.
18. B.K. Purohit, M. Chordia, V. Mathur and S.P. Mathur; Afinidad 47, 193, 1990; Chem. Abstr. 113, 164628 p, 1990.
19. S. Dadfarnia and M. Shamsipour; Iran J. Chem. Chem. Eng. 11, 14, 1992; Chem. Abstr. 117, 263841 s, 1992.
20. E. Lorenzo, J. Losada and S. Vicente-Perez; Afinidad 44, 497, 1987; Chem. Abstr. 108, 160492 p, 1988.
21. E. Kavlentis; Microchem. J. 36, 306, 1987; Chem. Abstr. 108, 123599 h, 1988.
22. S. Fan, J. Wang, M. Zhao and H. Wang; Yang, Wenzhong, Gaodeng Xuexiao Huaxue Xuebao 7, 986, 1986; Chem. Abstr. 106, 188048 f, 1987.
23. K.C. Bayan and H.K. Das; Curr. Sci. 53, 915, 1984.
24. Basilio Morelli; Analyst 109, 47, 1984.
25. M. Aggarwal, N. Bhargava, R.K. Jain and R.L. Mital; Acta Cienc. Indica, [Ser] Chem. 9, 75, 1983; Chem. Abstr. 100, 220824 v, 1984.
26. A.G. Asuero, M.J. Navas, J.M. Bautista and D. Rosales; Microchem. J. 28, 183, 1983; Chem. Abstr. 99, 32373 j, 1983.
27. K. Lal and M. Katyal; Curr. Sci. 51, 1115, 1982.
28. E. Fernandez-Gomez, F. Bermejo-Martinez and J.A. Rodriguez-Vazquez; Anal. Quim. Compostelana 4, 32, 1980; Chem. Abstr. 96, 45525 y, 1982.
29. Y.K. Agrawal and S.P. Chudasma; Bull. Soc. Chim. Belg. 90, 1033, 1981; Chem. Abstr. 96, 27857 d, 1982.
30. K. Lal and S.R. Malhotra; Ann. Chim. 71, 479, 1981; Chem. Abstr. 95, 214520 e, 1981.
31. A.I. Busev and B.M. Ivanov; Zh. Anal. Khim. 19, 232, 1964.
32. F.E. Beamish and J.C. Vanloon, "Recent Advances in the Analytical Chemistry of the Nobel Metals", Pergamon Press, Oxford p. 411, 1972.
33. Y.K. Agrawal and P.C. Parekh; J. Indian Chem. Soc. 63, 230, 1986.
34. L.P. Adamovich, A.L. Gershuns, A.A. Oleinik and N.T. Zung; Zh. Anal. Khim. 22, 634, 1973.

35. A.D. Langade and V.M. Shinde; *Analyst* 107, 708, 1982.
36. A.A. Elsirafy; *Analyst* 105, 912, 1980.
37. R. Fang and Q. Xu; *Huaxue Shiji* 10, 218, 236, 1988; *Chem. Abstr.* 110, 68734 n, 1989.
38. F. Garcia Montelongo, V. Gonzalez Diaz and C.R. Tallo Gonzalez; *Microchem. J.* 27, 194, 1982; *Chem. Abstr.* 97, 48806 x, 1982.
39. T. Katami, T. Hayakawa and M. Furukawa; *Shibata Shozo, Bunseki, Kagaku* 33, 676, 1984; *Chem. Abstr.* 102, 142410 g, 1985.
40. Y. Gong, H. Zhou and G. Zhang; *Lanzhou Daxue Xuebao, Ziran Kexueban* 24, 105, 1988; *Chem. Abstr.* 111, 69958 w, 1989.
41. N. Motekov, L. Jancar and L. Sommer; *Scr. Fac. Sci. Nat. Univ. Purkynianae Brun.* 18, 105, 1988; *Chem. Abstr.* 110, 107222 r, 1989.
42. Y.M. Issa, A.F. Shoukry and N.T. Abdel-Ghani; *Proc. Pak. Acad. Sci.* 16, 85, 1979.
43. F. Garcia Montelongo, V. Gonzalez Diaz and C.R. Tallo Gonzalez; *Analisis* 9, 353, 1981.
44. F. Garcia- Montelongo and J.J. Arias Leon; *Perez Pont, Maria L., An. Quim., Ser. B* 76, 392, 1980; *Chem. Abstr.* 94, 113843 m, 1981.
45. G. Zhang and X. Zhang; *Fenxi Shiyanshi* 7, 24, 1988; *Chem. Abstr.* 112, 15663 y, 1990.
46. S. Mukherjee, B.S. Garg and R.P. Singh; *Ann. Chim.* 70, 481, 1980; *Chem. Abstr.* 94, 113881 x, 1981.
47. J. Lopez Penalver and J.A. Munoz Leyva; *Quim. Anal.* 3, 226, 1984; *Chem. Abstr.* 103, 47421 y, 1985.
48. Y.K. Agrawal and S.P. Chudasma; *Bull. Soc. Chim.* 90, 1033, 1981; *Chem. Abstr.* 96, 27857 d, 1982.
49. H. Ishii, M. Minegishi and T. Odashima; *Anal. Sci.* 7, 73, 1991.
50. K. Saraswathi, A.V.S. Lakshmi and V.V. Ramana; *J. Indian Chem. Soc.* 69, 795, 1992.
51. K. Uesugi, T. Nagahiro, K. Tohru, T. Kumagai and H. Nishioka; *Chim. Acta Turc.* 19, 245, 1991; *Chem. Abstr.* 118, 93440 m, 1993.
52. R. Palaniappan; *Curr. Sci.* 58, 958, 1989.

53. A. Asuero, A.M. Jimenez and M.A. Herrader; *Analyst* 111, 747, 1986.
54. M.T. Montana Gonzalez and J.L. Gomez Arizo; *Microchem. J.* 25, 360, 1980; *Chem. Abstr.* 93, 142289 v, 1980.
55. H. Sikorska - Tomicka; *Chem. Anal.* 24, 635, 1979; *Chem. Abstr.* 92, 87402 d, 1980.
56. B.K. Deshmukh and M.G. Awari; *Chem. Anal.* 32, 369, 1987; *Chem. Abstr.* 109, 16264 u, 1988.
57. T. Sakai, N. Ohno, M. Noriko, T. Mori and H. Sasaki; *Bunseki Kagaku* 37, 488, 1988, *Chem. Abstr.* 109, 176300 f, 1988.
58. H. Puzanowska - Tarasiewicz, A. Kojlo and M. Tarasiewicz; *Chem. Anal.* 25, 1053, 1980; *Chem. Abstr.* 95, 161338 t, 1981.
59. A.I. Vogel, "A Text-Book of Quantitative Inorganic Analysis", 4th Ed., Longmans, London p. 474, 1978.
60. K. Satyanarayana and R.K. Mishra; *Anal. Chem.* 46, 1609, 1974.
61. A.I. Vogel, "A Text-Book of Quantitative Inorganic Analysis", 4th Ed., Longmans, London p. 45, 1978.
62. P.W. West; *J. Chem. Educ.* 18, 528, 1941.
63. G.D. Christian, "Analytical Chemistry", 4th Ed., John Wiley and Sons, New York 1986.
64. E.B. Sandell, "Colorimetric Determination of Traces of Metals", 3rd Ed., INC., New York p. 97., 1959.