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**CHAPTER - III**

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OF PALLADIUM(II) WITH  
4'-CHLORO-2'-TOLYL-TPT**

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## INTRODUCTION :

The platinum group metals Ru, Rh, Pd, Os, Ir, Pt are widely used as catalyst in petroleum and chemical process. They find wide applications in automotive exhaust gas control converters and are immense importance to the electrical industry.

Amongst them palladium is mainly used in organic synthesis as a catalyst. Addition of trace amount of palladium increases the resistance of stainless steel. High chromium steel renders the titanium resistant to the action of boiling solutions of mineral acids<sup>1,2</sup>. Alloy of Pd(II) with noble or rare metals are used as electrical contacts, resistances, thermoelectrodes and solders etc. Palladium-base alloys usually contain silver and often varying amount of Pt, Au, Ru. Dental alloys may also contain nonprecious metals such as Tin, Indium, Gallium, Zinc or Copper. Because of its great intrinsic value the recycling of the metal from hundreds of different forms of scraps is an essential factors in the overall management of its economy. In the present work emphasis is placed on the need to tailor the analytical method according -

- (i) to the form in which the metal occurs,
- (ii) its enrichment and
- (iii) desired sensitivity and precision.

Beamish<sup>3</sup> reviewed the reagents used for colorimetric determination of Pd(II). A critical survey of determination of the platinum group elements is recently published by Kallmann<sup>4</sup>. Dimethylglyoxime solution in chloroform has been used for more than 75 years as a precipitant for palladium<sup>5</sup>.

Isonitroso derivatives of acetylacetone<sup>6</sup>, dibenzoylmethane<sup>7</sup>, benzoylacetone<sup>8</sup>, ethylacetoacetate<sup>9,10</sup>, ethylbenzoylacetate<sup>11</sup>, acetophenon<sup>12</sup> have been reported as the chromogenic reagent for palladium. These methods however, suffer from drawback for example extraction of palladium with isonitrosoacetylacetone requires high reagent concentration and quantitative extraction occur only in the presence of mercuric nitrate. Common ion such as chloride, thiosulphate, tartarate, citrate interfere in the determination of palladium with isonitrosoacetophenon as well as isonitrosoethylacetoacetate.

A great many other dioximes have been suggested over the years. Amongst those furildioxime<sup>13</sup> is the one whose complex with palladium can be extracted with chloroform and measured directly without back extraction. Other oximes which are recently reported as a extractive photometric reagent for Pd(II) include pyridine-2-aldoxime<sup>14</sup>, 2,2'-dipyridyl ketoxime<sup>15</sup>, 2-2'-pyridyl monoxime<sup>16</sup>, di-2-quinolyketoxime<sup>17</sup>, 4-heptonone

oxime<sup>18,19</sup>, 3'-bromo-2'-hydroxy-4-methoxy-5'-methylchalcone oxime<sup>20</sup>, 3'-bromo-2'-hydroxy-5'-methyl acetophenone oxime<sup>21</sup>, halogen substituted benzoyl acetone oxime<sup>22</sup>, pyridyl-2-thienyl ( $\alpha$ ) ketoxime<sup>23</sup>, biacetylmonoxime glycinimine<sup>24</sup>, 3'-5'-dichloro-2'-hydroxyacetophenone oxime<sup>25</sup>. However some of these methods have certain limitations e.g. in extraction of Pd(II) with 3'-5'-dichloro-2'-hydroxyacetophenone oxime into MIBK at pH 2-4,5, waiting period of 10 min before extraction is required and this method needs multiple extraction. In some methods scrubbing of organic phase is needed to remove excess reagent before measurement of absorbance. spectrophotometric determination of Pd(II) using various hydrazones have been found to be highly sensitive. Amongst those which are recently reported include picolinaldehyde-4-nitrophenyl hydrazone<sup>26</sup>, 2-2'-bipyridyl-2-quinolyldiazine<sup>27</sup>, 3'-bromo-2'-hydroxy-5'-methylacetophenone hydrazone<sup>28</sup> biacetyl-monoxime-2-pyridylhydrazone<sup>29</sup>, di-(2-pyridyl) ketone benzoylhydrazone<sup>30</sup> and di-(2-pyridyl) ketone 2-quinolyldiazine<sup>31</sup>. However, these methods are subjected to interference of metal ion commonly associated with palladium. For extractive photometric determination of Pd(II) with picolinaldehyde-4-nitrophenylhydrazone, the absorbance of chloroform extraction at 500 nm needs to be measured after 40 min waiting. Thioligands have recently attracted the attention of chemists as they possess a versatile chelating ability towards platinum metals. However, few ligands have been reported in literature for determination of Pd(II). These include 1,1-dimethyl-3-(4-

phenyl-2-thiazolyl thiourea)<sup>32</sup>, N-N-dimethyl-N'-(4-methyl-5-nitro-2-thiazolyl)thiourea<sup>33</sup>, 1-phenyltetrazoline-5-thione<sup>34</sup>, thiosalicylamide<sup>35</sup>, thiodibenzoylmetane<sup>36</sup>, acetothioacetanilide<sup>37</sup>, thiocaprolactum<sup>38</sup>, Michler's thioketone<sup>39</sup>, 6-aminoquinoxaline-2-3-dithiol<sup>40</sup>, O-mercaptoacetoacetanilide<sup>41</sup>, thiodibenzoylmethane<sup>42</sup>. However, some of these reagents possess disadvantage e.g. amino derivatives of QDT is highly light sensitive hence it needs a special care while performing batch extraction of Pd(II). 4-(2'-Thiazolylazo)-rosacetophenone oxime<sup>43</sup> is reported for determination of palladium by reverse phase HPLC. Spectrophotometric methods of determination for Pd(II) in alloys and catalyst using various oximes include : 2-methyl-4-naphthoquinol-4-oxime<sup>44</sup>, p-methylisonitrosoacetophenone<sup>45</sup>. But during determination, interference of foreign ions like iodine, thiocyanate, thiosulphate and cyanide must be removed by boiling the solution with potassium persulphate and conc. HNO<sub>3</sub>.

During last two decades a new technique of analysis of metals by solid-liquid separation after liquid-liquid extraction at elevated temperature using naphthalene has become increasingly popular as it facilitates the rapid and quantitative separation using this technique the extraction of Pd(II) with xanthates<sup>46,47</sup>, trithiocarbonate<sup>48</sup> pyrrolidine-1-carbodithionate<sup>49</sup>, 1-phenyl-4',4,6-trimethyl-(1H,4H)-pyrimidine-2-thiol<sup>50</sup> and 3-hydroxy-2-methyl-1-4-naphthoquinone<sup>51</sup> have been reported.

During the last few years methods using thioligands have appeared in large number in the literature for the determination of Pd(II). These include dithiocarbamidohydrazine<sup>52</sup>, 3-5-di-chlorosalicylaldehyde-4-phenyl-3-thiosemicarbazone<sup>53</sup>, isonitrothiocamphor<sup>54</sup>, 2-mercaptanaphthothiazole<sup>55</sup>, thiocyanatetrabutyl ammonium ion<sup>56</sup> etc. However, these ligands suffer from either low sensitivity or interference of platinum group metals and base metals and low stability of complex.

Spectrophotometric determination of Pd(II) using mixed ligands has been recently developed and has attracted the attention. These include thiolactams and eriocrome cyanide<sup>57</sup>, 4(2-pyridylazo) resorcinol (PAR) and xylometazonium cation (XMH)<sup>58</sup>, 4-nitrosoresorcinol and pyridine/substituted pyridine<sup>59</sup>, 4-methoxybenzene dithiocarboxylic acid<sup>60</sup>, pyridine/ $\alpha$ -picoline/ $\beta$ -picoline/ $\gamma$ -picoline/2,4,6-collidine and iodine<sup>61</sup>, iodine and cetyltrimethylammonium bromide<sup>62</sup> etc.

The following are the reagents reported during the last six years for spectrophotometric determination of Pd(II). 6-(2'-hydroxyphenyl)-2,4-dithio-1-phenyl 1,3,5-triazine<sup>63</sup>, -O-hydroxy acetophone and thiosemicarbazone<sup>64</sup>, 5-6-dimethyl-1,3-indanedione-2-oxime<sup>65</sup>, 2-(2-benzothiazolylazo)-5-dimethylamino 4-tolylarsonic acid<sup>66</sup>, sodium pentamethylene dithiocarmate<sup>67</sup>, isonitrosomalonidylanilide<sup>68</sup>, 1-phenyl-1-hydrazonyl-2-amino-1,2-ethanedione<sup>69</sup> etc.

Reagents like diphenylthiovioluric acid<sup>70</sup> and N-m-chloro-phenyl-p-methoxy-benzohydroxamic acid<sup>71</sup> are reported for the extractive spectrophotometric determination of palladium from synthetic mixtures and catalyst. But common ions like chloride, thiosulphate, fluoride, citrate etc. interfere in the determination of Pd(II).

Pyridimethiol are also known as cycl<sup>c</sup>ithiourea proved to be analytically useful reagents. Singh et al reviewed the analytical aspects of the chemistry of the substituted pyrimidinethiol<sup>72</sup>. Mercaptopyrimidines react with Pd(II) to form extractable complexes in either weakly acidic or strongly acidic medium in presence of 12 to 20 fold molar excess reagent. However, attempts have not been made by Singh et al to separate Pd(II) quantitatively from micro or macro amounts of base and platinum metals.

In present work the reagent 4'-chloro-2'-tolyl TPT is used for extractive photometric determination of traces of Pd(II). This method is simple, selective and reproducible.

## EXPERIMENTAL

### Standard Pd(II) Solution :

Standard solution of palladium (0.6 mg/ml) was prepared by dissolving 1 gm of pure palladium chloride (Fluka AG) in 20 ml conc. hydrochloric acid and diluting to 1000 ml with distilled

water. The solution was standardised gravimetrically with DMG<sup>73</sup> working solutions of lower concentration were made from it by diluting the stock solution with distilled water as required.

Reagent Solution :

A stock solution (0.01 M) was prepared by dissolving 0.281 g pyrimidinethiol in 100 ml chloroform. Reagent solution is colourless and stable.

Standard solutions of diverse ions were prepared by dissolving AR grade reagents in distilled water or dil HCl. All the organic solvents were used after double distillation. All chemicals used were of AR grade.

Apparatus :

All absorbance measurements were carried out with Elico spectrophotometer model CL-27 with 1 cm quartz cells.

Recommended Procedure :

Adjust the acidity of palladium(II) solution (0.1-8.0 M) taken in a separating funnel. Use 10 ml of 0.01 M pyrimidine-thiol in chloroform. Shake for 15 min. Collect the organic phase. Make upto volume. Measure the absorbance at 420 nm of the yellow complex against the solvent blank. Compute the metal content from a calibration graph.



## RESULTS AND DISCUSSION

Spectral Characteristics :

The absorption spectra of the complex of Pd(II) with pyrimidinethiol in chloroform are shown in Fig.1. The solution of pyrimidinethiol in chloroform is colourless and hence does not absorb significantly in the visible region. Pyrimidinethiol in chloroform extracts palladium(II) quantitatively from hydrochloric acid medium with 15 min shaking, Palladium(II) pyrimidinethiol complex exhibits sharp absorption maximum at 420 nm. The molar extinction coefficient as determined from Beer's law plot is  $4268 \text{ l mole}^{-1}, \text{cm}^{-1}$ . The Sandell sensitivity of the reaction was  $25 \text{ ng cm}^{-2}$  at 420 nm. ( Table-1.)

Effect of Acidity :

The optimum acidity range for the quantitative extraction of palladium(II) was determined by varying HCl concentration over the range 0-8 M HCl using 100  $\mu\text{g}$  of palladium(II) and 110 fold molar excess of the reagent. The complex was extracted as per the recommended procedure. The extraction of palladium(II) with chloroform solution of pyrimidinethiol from aqueous medium containing  $\text{H}_2\text{SO}_4$ ,  $\text{HClO}_4$  and  $\text{HNO}_3$  was in the range 0.1 to 10, 0.1 to 8, 0.1 to 3 N respectively.

However, the extinction coefficient of the complex was maximum in HCl medium. Hence extraction from HCl medium was recommended for all the subsequent extraction. Fig.2.

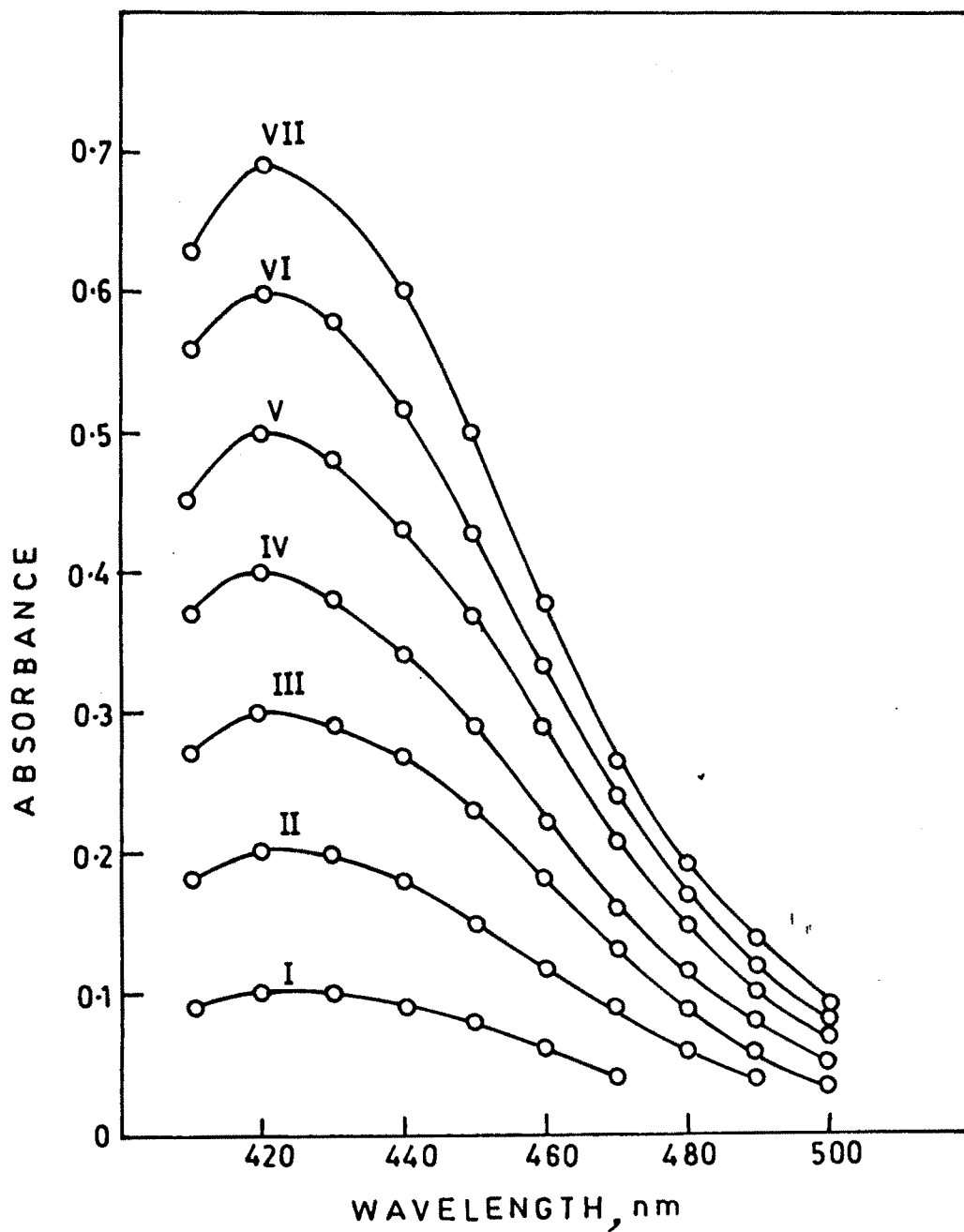


Fig. 1 — ABSORBANCE CURVES FOR Pd(II)-PYRIMIDINETHIOL COMPLEX .

Pd (II) : I , 2.5 PPM ; II , 5.0 PPM ; III , 7.5 PPM ;  
 IV , 10.0 ppm ; V , 12.5 PPM ; VI , 15.0 PPM ;  
 VII , 17.5 PPM .

**TABLE-1 :** Characteristics of Pd(II)  
Complex of pyrimidinethiol  
Pd = 10.00 ppm

Sr.No.	Characteristics	Pd(II)-pyrimidinethiol complex
1.	Solvent	Chloroform
2.	$\lambda$ max, nm	420
3.	$\epsilon$ max, L mole <sup>-1</sup> cm <sup>-1</sup>	4256
4.	Acidic medium for max. colour development	1 to 6 M HCl
5.	Stability in hr	> 24
6.	Beer's range	1-17.5
7.	Sandell's sensitivity ng/cm <sup>2</sup>	25
8.	Molar ratio of pyrimidinethiol needed for complete complexation	110

#### Effect of time of shaking and stability of the complex :

In order to establish the optimum time for quantitative extraction of palladium(II) complex, the time of shaking was varied from 1,2,4,5,8,10,15,20,30 min. The curve (fig.3) of the absorbance versus shaking time indicate that, shaking for 10 min is sufficient for quantitative recovery of 10 ppm of palladium(II). In the present work the mixture was shaken for 15 min in order to ensure complete extraction. The yellow complex of palladium(II) was measured at 420 nm at regular interval of time. Absorbance of complex remained stable for more than 24 hr.

#### Effect of Reagent Concentration :

In order to find the amount of reagent necessary for full colour development of palladium(II) (10 ppm) varying volumes of 0.005 M reagent from 0.1 to 20 ml were used. The palladium(II) from 2 M HCl was extracted with the reagent in chloroform as per the recommended procedure. It was observed that the extraction of Pd(II) was complete and reproducible with 8 ml of reagent. This corresponds to 40 fold excess reagent relative to Pd(II). 110 fold molar excess of reagent was recommended in order to ensure complete extraction. Fig.4.

#### Effect of Solvent :

Of the various solvents examined as an extractants for Palladium(II) - pyrimidinethiol complex, it was observed that,

FIG. 2  
EFFECT OF  
ACIDITY HCl  
Pd(II) = 10 ppm

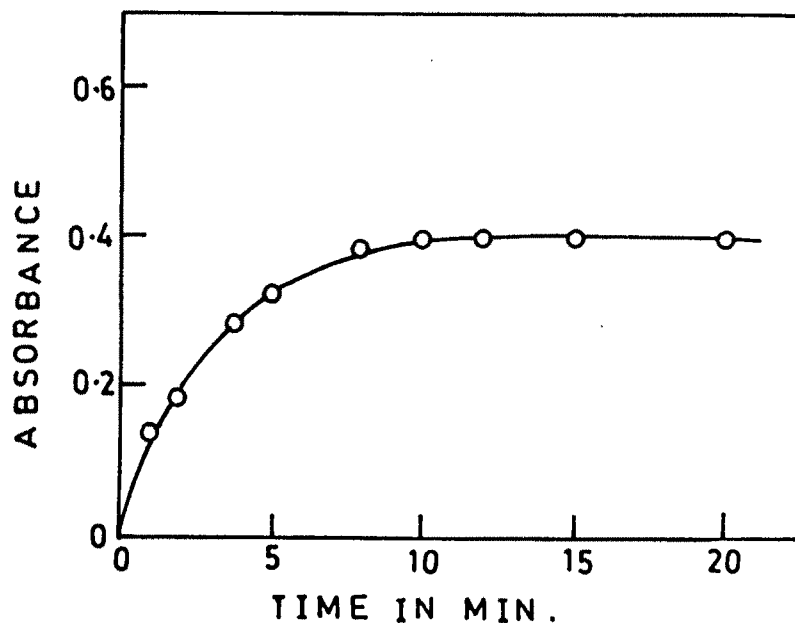
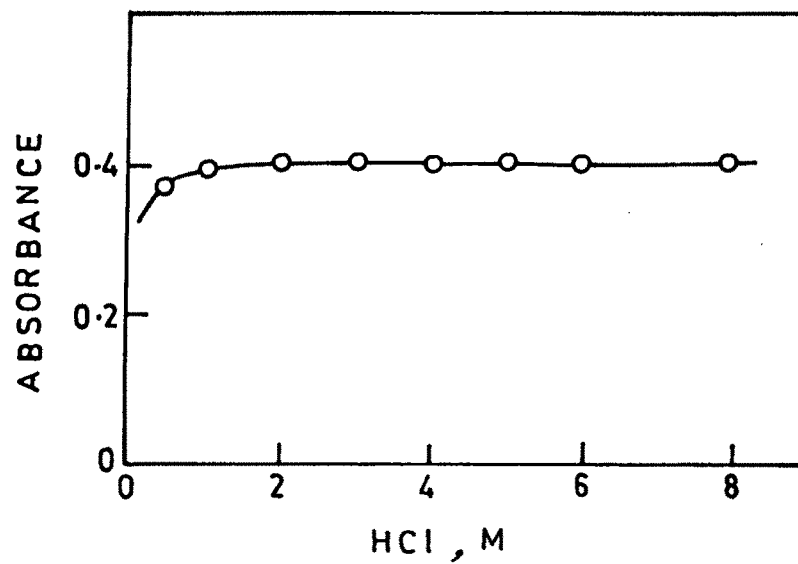


FIG. 3  
EFFECT OF SHAKING  
TIME, MIN.  
Pd(II) = 10 ppm

the complex was extractable into solvents such as chloroform, benzene, 4-methyl-2-pentanol, isobutyl methyl ketone (MIBK), toluene, carbontetra chloride, n-butanol. However, chloroform was chosen as it offers a clear cut separation of phases and because of high distribution of the complex in it. (Table-2).

#### Validity of Beer's Law :

The solutions containing different amounts of Palladium(II) in the range 1-20 ppm were used for the study of the validity of Beer's law. The palladium(II) in the aqueous phase at 2 M HCl was extracted with 10 ml of (0.01 M) reagent in chloroform following the recommended procedure. The complex was measured at 420 nm against chloroform blank. The absorbance was plotted versus the ppm of palladium taken fig-5. The curve indicates that there is rectilinear relationship between the absorbance and concentration of palladium(II) in the range 1 to 17.5. However, the optimal concentration range was found to be 5 to 16.5 ppm corresponding to absorbances in the range between 0.2 to 0.8.

#### Composition of the Complex :

The combining ratio of the reagent to metal ion in the extracted species was determined by Job's method of continuous variation modified for a two phase system and mole ratio method<sup>74-77</sup>. An equimolar solution of the metal and the reagent ( $1.0 \times 10^{-3}$  M) were used for Job and Mole ratio methods. The solution of palladium(II) ion and that of reagent in chloroform

**TABLE-2** : Extraction of Pd(II) pyrimidinethiol complex  
from aqueous phase into the organic solvents.

Pd(II) = 10 ppm

Pyrimidinethiol = 0.01 M

Wavelength = 420 nm

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Sr.No.	Solvent	% Extraction	Distribution Ratio, D
1.	Benzene	61.25	3.95
2.	MIBK	85.0	14.16
3.	4-methyl-2-pentanol	72.5	6.59
4.	Carbontetrachloride	No Extraction	-
5.	Chloroform	100.00	$\infty$
6.	n-butanol	52.5	2.76
7.	Toluene	58.2	3.48

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FIG. 4  
EFFECT OF  
REAGENT  
CONCENTRATION.  
Pd(II)=10 PPM

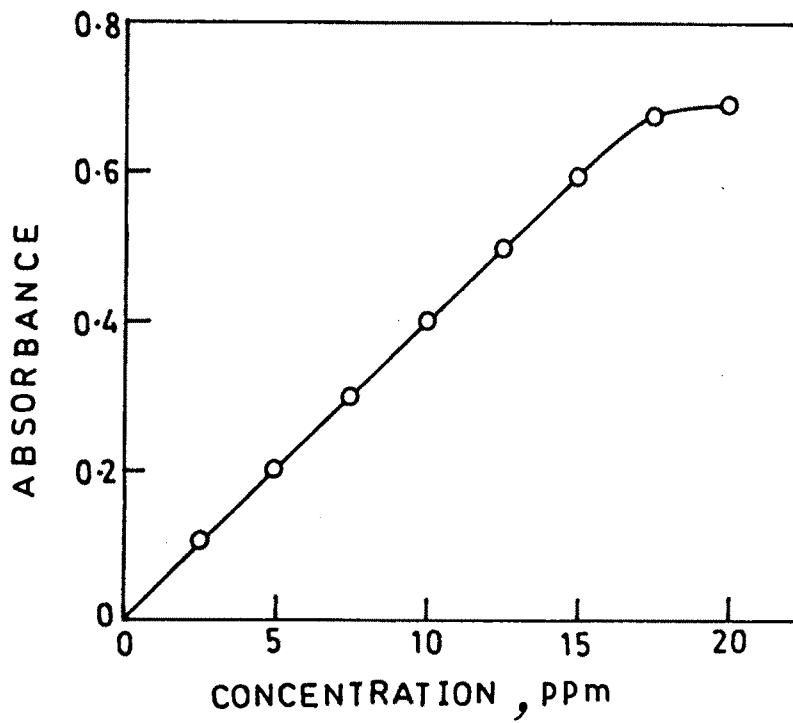
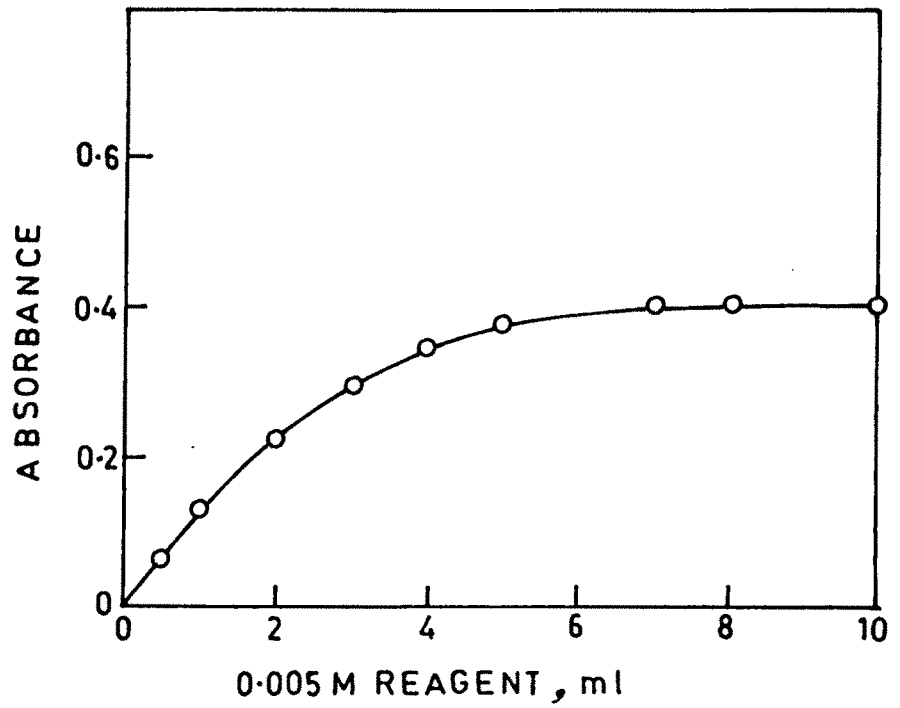


FIG. 5  
VALIDITY OF  
BEER'S LAW.



were mixed in different ratios in a 125 ml separatory funnel, keeping the total volume 10 ml. Requisite amount of HCl and water were added so that the aqueous layer had a volume of 25 ml which was 2 M in HCl. The measured volume of chloroform to keep the volume of organic layer to 10 ml were added to each case. The mixture was shaken for 15 min. The layers were allowed to separate. Then organic layer, after drying over anhydrous sodium sulphate was measured at 420 nm. The Job's curve in fig.-6 indicate that palladium(II) forms 1:4 complex with pyrimidinethiol.

The composition was verified by Mole ratio method. A series of solutions was prepared containing a fixed volume of palladium(II) and adjusted to 2 M in HCl. The metal was extracted with varying volumes of reagent by recommended procedure. The absorbance of the solution was measured at 420 nm against chloroform blank. The result plotted in fig.7 confirmed the composition as determined by Job's method.

#### Effect of Diverse ions :

The effect of large number of diverse ions on the determination of 0.100 mg of Pd(II) with the reagent was investigated, following the recommended procedure initially foreign ion was added to the Pd(II) solution in large excess : 100 fold for cations and 500 fold for anions. When the interference was intensive, the tests were repeated with successively smaller amount of ion. The tolerance limit was set at that amount of

FIG. 6  
 JOB'S PLOT Pd(II)-  
 PYRIMIDINETHIOL  
 COMPLEX .

$[M]=[L]=1.0 \times 10^{-3} M$

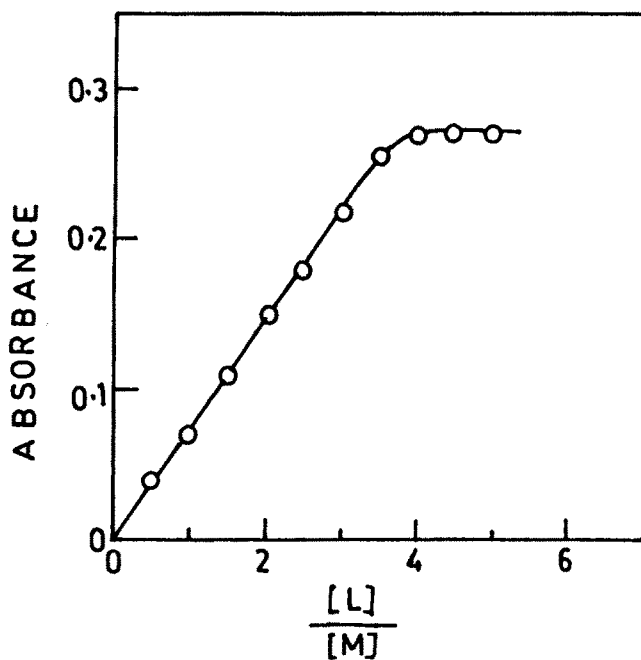
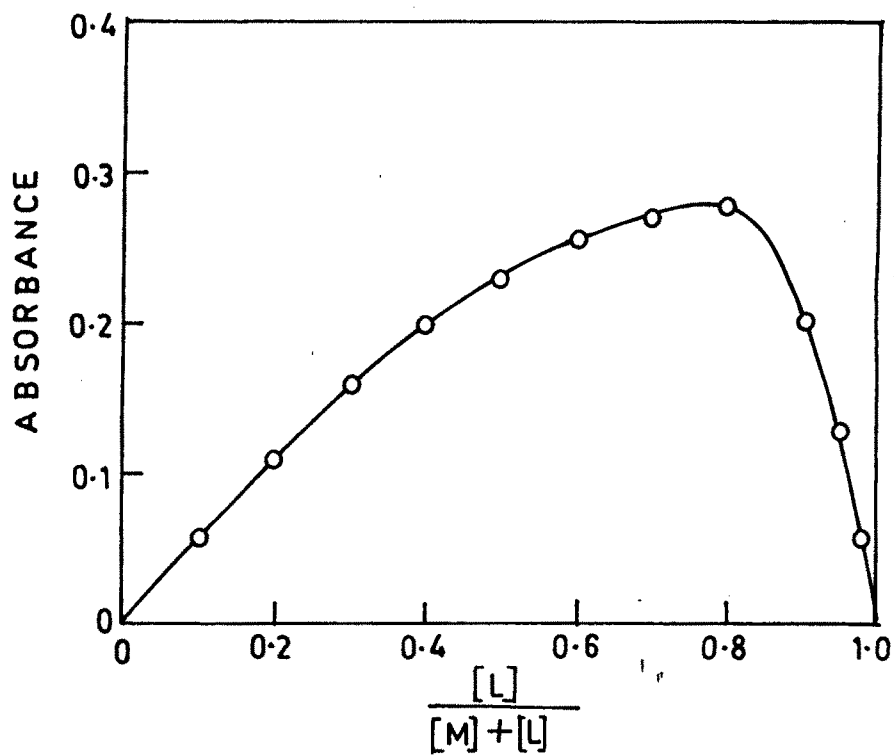


FIG. 7  
 MOLE RATIO PLOT Pd (II)-  
 PYRIMIDINETHIOL COMPLEX .  
 $[M] = [L] = 1.0 \times 10^{-3} M$

foreign ion which gave an error less than 2% in the absorbance of complex at 420 nm. The tolerance limit of ions tested were shown in Table-3.

The anion are tolerable in fairly in large amount except thiourea, thiosulphate and iodide. It is evident that the method permits the determination of Pd(II) even in presence of base and noble metals.

#### Reproducibility and Accuracy and Sensitive Data :

For study of the reproducibility and accuracy of the method, absorbance measurement with ten different identical solutions containing 10 ppm palladium were performed as outlined in the procedure and concentration determined using the calibration curve. The results are shown in Table-4. It is observed that there is an excellent agreement in the experimental values. The method has high precision and accuracy.

Average of the ten readings are calculated. Deviations from these average readings was found out in each case and then standard deviation was calculated. From the standard deviation the reproducibility of the result with 95% confidence limit was calculated. The Sandell sensitivity of the reaction as calculated from Beer's plot was found out to be  $25.0 \text{ ng/cm}^2$ .

Standard deviation :

**TABLE-3 : Effect of Foreign Ions on the Determination  
of Palladium(II) Pyrimidinethiol**

$\lambda$  max = 420 nm, Pd(II) = 0.100 mg

Foreign ions added	Tolerance limit mg
Acetate, Borate citrate, EDTA, Fluoride oxalate, Phosphate, Tartarate, Salicylate	100.0
Ba(II), Cu(II), Fe(II), K(I), Pb(II), U(VII), Zn(II), Al(III), Mg(II), Co(II), Ni(II), Pt(IV)	20.0
Mn(II), Ca(II), Sn(II), Te(II), Cr(III), Cd(II), Hg(II), W(VI), Se(IV), Ti(IV), thiocynate	10.0
Mo(V)	5
V(V)	2
Au(III), Os(VIII), Ru(III)	1.0
Thiourea, Thiosulphate, Iodide	Interfere

**TABLE-4** : Precision and Accuracy of the Method

Amount of Pd = 10.0 ppm.

Sr.No.	Absorbance observed	ppm of Pd found (x)	$x - \bar{x}$	$(x - \bar{x})^2$
1.	0.395	9.87	-0.14	0.0196
2.	0.400	10.0	-0.01	0.0001
3.	0.405	10.12	0.11	0.0121
4.	0.400	10.0	-0.01	0.0001
5.	0.405	10.12	0.11	0.0121
6.	0.400	10.0	-0.01	0.0001
7.	0.395	9.87	-0.14	0.0196
8.	0.400	10.0	-0.01	0.0001
9.	0.405	10.12	0.11	0.0121
10.	0.400	10.0	-0.01	0.0001
Total		100.1		0.076

$$\text{Average value} = \bar{x} = \frac{100.1}{10}$$

$$\bar{x} = 10.01$$

$$\delta = \sqrt{\frac{(x_1 - \bar{x})^2 + (x_2 - \bar{x})^2 + \dots + (x_n - \bar{x})^2}{n - 1}}$$

$$= \sqrt{\frac{0.076}{10-1}}$$

$$= \sqrt{\frac{0.076}{9}}$$

$$= \sqrt{0.00844}$$

$$\delta = 0.091$$

Reproducibility with 95% confidence limit

$$= \bar{x} \pm 2.26 \times \frac{\delta}{\sqrt{n}}$$

$$= 10.01 \pm 2.26 \times \frac{0.091}{\sqrt{10}}$$

$$= 10.01 \pm 2.26 \times \frac{0.091}{3.16}$$

$$= 10.01 \pm 2.26 \times 0.02879$$

$$= 10.01 \pm 0.0650$$

$$\text{Error (E)} = \text{Observed Reading} - \text{Actual Reading}$$

$$= 10.01 - 10.0$$

$$= 0.01$$

$$\text{Relative Error} = \frac{0.01 \times 100}{10}$$

$$= 0.1 \%$$

Molar extinction coefficient :

$$\epsilon = \frac{A}{C \times L}$$

$$\begin{aligned}
 &= \frac{\text{Absorbance}}{\text{ppm}} \times 1000 \times \text{At.wt.} \\
 &= \text{Slope} \times 1000 \times 106.4 \\
 &= 0.04 \times 1000 \times 106.4 \\
 &= 4256 \text{ L mole}^{-1} \text{ cm}^{-1}
 \end{aligned}$$

#### Sandell Sensitivity

$$S = 10^3 \times A \times C_{\min}$$

where

$$C_{\min} = \frac{D_{\min}}{e \times b}$$

A = Atomic weight

$$= 10^3 \times 106.4 \times \frac{0.001}{4256}$$

$$= 0.025 \mu\text{g cm}^{-2}$$

$$= 25 \text{ ng cm}^{-2}$$

#### Coefficient of variation

$$\text{C.V.} = \frac{\delta \times 100}{\bar{x}}$$

$$= \frac{0.091 \times 100}{10.01}$$

$$= 0.90$$

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