



SYNTHESIS OF AN ANALYTICAL REAGENT, ITS SPECTROSCOPIC CHARACTERIZATION, AND STUDIES OF ITS COMPLEXATION BEHAVIOUR WITH Pd (II) METAL ION & ITS APPLICATION

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Abstract

2,4-Dihydroxy-5-Iodo- α -phenyl acetophenone oxime [DHI- α -PAO] has been used for the gravimetric and spectrophotometric determination of Pd (II) at pH 2.0. Job's method of continuous variation and Yoe and Jones mole ratio method shows metal:ligand ratio in the complex to be 1:2. The molar absorptivity of complex at 420 nm is found to be $4.23 \times 10^2 \text{ lit. mol}^{-1} \text{ cm}^{-1}$ and Sandell's sensitivity is found to be $0.2516 \mu\text{g} / \text{cm}^2$. The stability constant determined spectrophotometrically and Gibb's free energy change for complex formation reaction also been calculated and found to be 4.30×10^9 and $-13.226 \text{ k.cal/mol}$ respectively. The Beer law is obeyed up to 74.49 ppm of Pd(II) ion at 420 nm. From TGA studies, the energy of activation for the decomposition step has been calculated using Broido method. It was found to be 14.76 & 8.43 k.cal/mol for step-I & II respectively. The reagent has been successfully applied to the determination of Pd (II) in palladised carbon.

Keywords-Spectrophotometric determination, Acetophenone oxime, DHI- α -PAO, Gibb's free energy change, Energy of activation

I. INTRODUCTION

Organic reagents forms chelate with metal ions. Formations of coordination compounds by organic reagents with metal ions have been extensively used in analytical chemistry. If an organic molecule is to form a chelate it should contain an acidic group such as $-\text{COOH}$, $-\text{SO}_3\text{H}$, $-\text{OH}$, $-\text{SH}$, $=\text{N-OH}$ etc. From these groups, hydrogen ion is replaced by metal, forming a chelate compound. Chelation also depends upon the relative positions of the groups present in an organic compound. The group must be so located with respect to other group, that the ring which they form will contain four to eight atoms.

Many organic reagents like o-hydroxy oximes⁽¹⁻¹¹⁾, oximes⁽¹²⁻¹⁶⁾, thiosemicarbazones⁽¹⁷⁻²³⁾, chalcone oxime⁽²⁴⁾, anilides⁽²⁵⁾ of aromatic aldehydes and ketones are generally used for this purpose. When they form a chelate with different transition metal ion, they form a ring having four to eight atoms. So these types of chelate are having more stability. The chelates are characterised by their low solubility in water and many of them have high molecular weights and are intense coloured. The formation of chelate ring system depends largely upon the characteristic of transition metal ion. The nature of the organic molecules also influences on the properties of the reagent. Here we have synthesized a reagent 2, 4-Dihydroxy-5-Iodo- α -phenyl acetophenone oxime [DHI- α -PAO] for gravimetric and spectroscopic determination of Pd (II).

II. MATERIALS AND METHODS

Experimental

Spectrophotometric measurements were done on Perkin-Elmer Lambda-35 UV-Visible spectrophotometer and all the pH measurement were done on electronic pH-meter (EQ-614).

Reagent and Solutions

Synthesis of 2, 4-Dihydroxy-5-Iodo- α -phenyl acetophenone oxime [DHI- α -PAO]

2, 4-Dihydroxy- α -phenylacetophenone was prepared from resorcinol, phenyl acetic acid and anhydrous zinc chloride according to the method of H.Nogemi⁽²⁶⁾. The Iodination of 2,4-Dihydroxy- α -phenylacetophenone was done by dissolving it in minimum quantity of glacial acetic acid with KIO_3 and KI gives 2, 4-Dihydroxy-5-Iodo- α -phenyl acetophenone. The reagent was prepared by the reaction with alcoholic solution of 2,4-Dihydroxy-5-iodo- α -phenylacetophenone, aqueous solutions of hydroxylamine-hydrochloride and sodium acetate. A little more alcohol was added to get clear solution. The solution was refluxed in water bath at 75-80°C for 4 hours. The mixture was poured on crushed ice with stirring. White solid separated. It was crystallised from ethanol. It was crystallized from absolute alcohol. M.P. = 205.2°C.

Pd (II)-metal solution: A stock solution of Palladium (II) (0.01M) was prepared by dissolving an accurately weighed amount of palladium chloride (0.4433gm for 250ml) in concentrated hydrochloric acid and diluting with deionized water. Solutions of other ions were prepared by dissolving their salts (A.R) in deionized water.

Characterization of Reagent

The oxime reagent under present investigation is characterized by following different analytical techniques.

Elemental analysis: Elemental analysis of the reagent was carried out on Perkin-Elmer 2400 elemental analyzer. The percentage elements, found are in agreement with its molecular formula. The results are given in the following Table-I.

Table-I

Reagent	% Found (Calculated)		
	Carbon	Hydrogen	Nitrogen
DHI- α -PAO	45.52 % (45.55%)	3.30 % (3.28%)	3.76 % (3.79%)

TG Studies: Thermogravimetric analysis of the complexes was done on Universal V₃-OG TA Instrument.

UV-Visible spectral studies: The absorbance measurements were done on a single beam spectrophotometer (Spectronic-20) and "Shimadzu UV-1601 UV-Visible Spectrophotometer" and "Perkin-Elmer Lambda-25 UV-Visible Spectrophotometer". Wavelengths of maximum absorptions were found to be 212, 274 and 304 nm that fall in UV region.

FT-IR Spectral studies: The IR spectra of the ligand and the complexes were recorded on Spectrum DX FTIR Spectrophotometer in KBr pallet. Absorption bands observed are shown in Table-II.

Table-II

Reagent	ν^{O-H} stretching	ν^{N-OH} stretching	ν^{C-H} stretching	$\nu^{C=N}$ stretching	ν^{C-O} stretching	ν^{N-O} stretching
DHI- α -PAO	3338cm ⁻¹	3080cm ⁻¹	2875-2972cm ⁻¹	1580cm ⁻¹	1286cm ⁻¹	980cm ⁻¹
Pd(II)-DHI- α -PAO	3330 cm ⁻¹	3050 cm ⁻¹	2840-2940 cm ⁻¹	1532 cm ⁻¹	1245-1255cm ⁻¹	970-910 cm ⁻¹

¹H and ¹³C NMR spectral studies of 2, 4-Dihydroxy-5-Iodo- α -phenyl acetophenone oxime [DHI- α -PAO]

	gm			
1.5	0.1677	21.17	-0.11	-0.52
1.5	0.1676	21.16	-0.12	-0.56
2.0	0.1682	21.23	-0.05	-0.23
2.0	0.1681	21.22	-0.06	-0.28
2.5	0.1679	21.19	-0.09	-0.42
2.5	0.1680	21.21	-0.07	-0.33
3.0	0.1676	21.16	-0.12	-0.56
3.0	0.1674	21.13	-0.15	-0.71
3.5	0.1673	21.12	-0.16	-0.75
3.5	0.1675	21.14	-0.14	-0.66
4.0	0.1670	21.08	-0.20	-0.94
4.0	0.1672	21.11	-0.17	-0.80
4.5	0.1665	21.02	-0.26	-1.23
4.5	0.1668	21.06	-0.22	-1.04
5.0	0.1664	21.01	-0.27	-1.28
5.0	0.1667	21.04	-0.24	-1.14
5.5	0.1650	20.83	-0.45	-2.16
5.5	0.1651	20.84	-0.44	-2.11

Salt = PdCl₂

Drying Temperature = 110-115°C

p^H: 2.0

GRAVIMETRIC DETERMINATION OF Pd (II) IN DIFFERENT ALIQUOTS:

TABEL-V

Pd (II) taken in mg	Pd (II) complex in gm	Pd (II) found in mg	Error	
			in mg	%
15.96	0.1260	15.90	-0.06	-0.37
15.96	0.1262	15.93	-0.03	-0.18
21.28	0.1682	21.23	-0.05	-0.23
21.28	0.1681	21.22	-0.06	-0.28
26.60	0.2100	26.51	-0.09	-0.33
26.60	0.2102	26.54	-0.06	-0.22

EFFECT OF DIVERSE IONS:

To study the effect of foreign ions on gravimetric determination of Pd (II), 8-10 mg of various cations were added to a solution containing 21.28 mg of Pd (II) at p^H 2.0 and gravimetric estimations were done. It was observed that Ca (II), Ba (II), Sr (II), Mg (II), Cd (II), Mn (II), Co (II), Zn (II), Na (I) and K (I) do not interfere at this p^H, but Cu (II) and Fe (III) interfered seriously. Many common anions like chloride, bromide, iodide, sulphate, nitrite and nitrate were not found to interfere.

SPECTROPHOTOMETRIC STUDY OF Pd (II)-[DHI-α-PAO]:

Pd (II)-[DHI-α-PAO] chelate has been found to be soluble in chloroform, carbon tetrachloride, ethyl acetate, 1,4-dioxan, dimethyl formamide and dimethyl sulphoxide. This enabled to verify the Beer law and its application for spectrophotometric determination.

ABSORPTION SPECTRA:

To take the absorption spectra of the chelate, 20 ppm solution of chelate was prepared in CHCl₃ + DMSO (80:20, v/v) mixture and absorption spectra of this solution was recorded in the wavelength range of 300 to 800 nm. It was observed that the absorbance of the coloured solution of chelate increases continuously towards the shorter wavelength. All the absorbance measurements were carried out at 420 nm. The graph is shown in Fig.

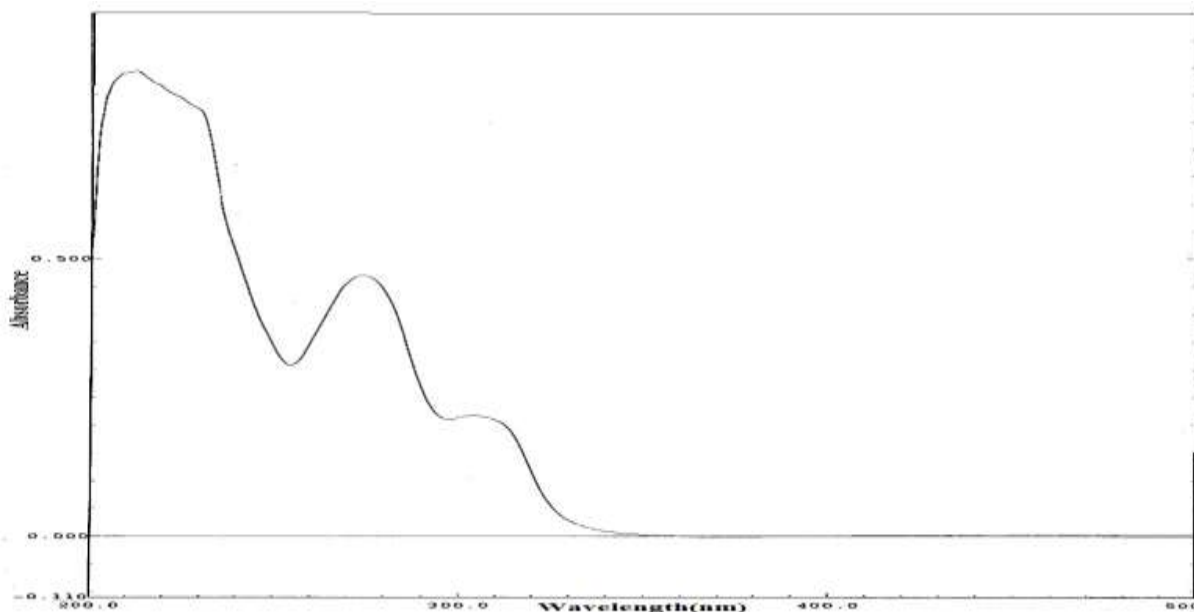
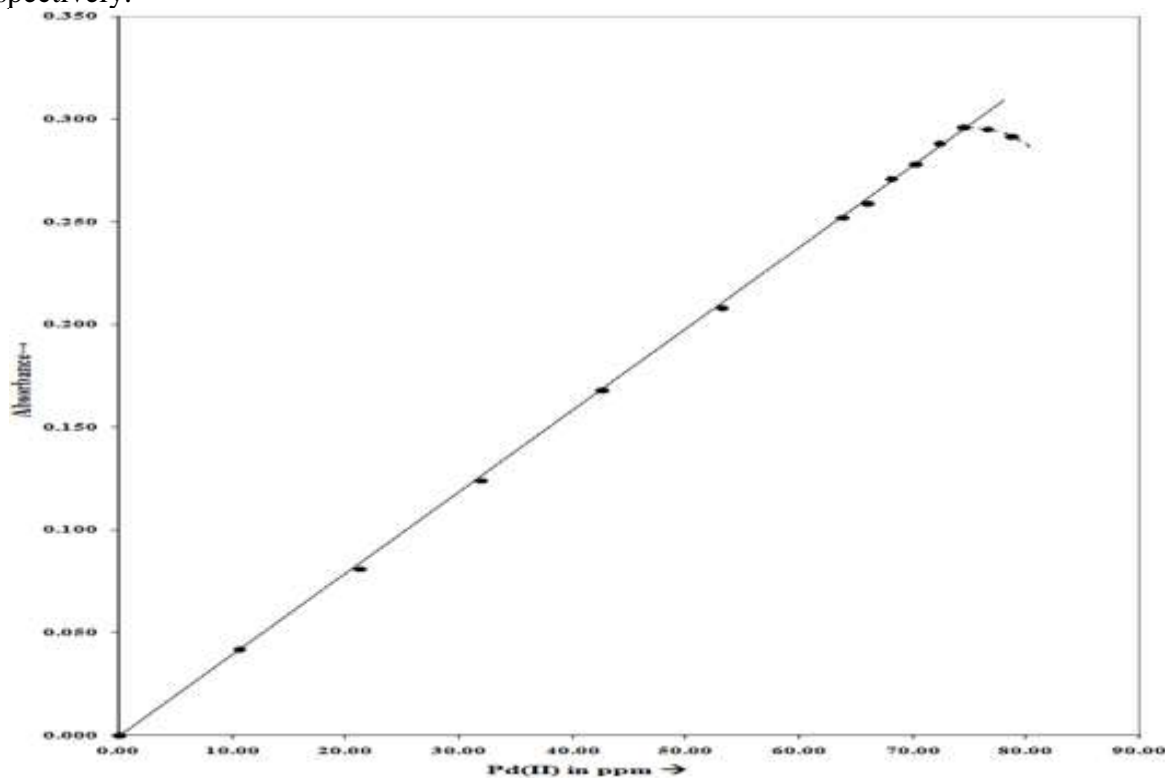


Fig. (Absorption spectra of DHI- α -PAO)

VERIFICATION OF BEER'S LAW:

0.005 M Pd (II) soln. In varying proportion was mixed with 5.0 ml 0.01M ligand solution and pH was maintained 2.0 using acetic acid-hydrochloric acid buffer. The insoluble complex precipitated was extracted with three 5.0 ml portion of chloroform. 5 ml DMSO was added to this chloroform extract and final volume of this solution was adjusted to 25 ml. The absorbance of these solutions was measured at 420 nm against the ligand blank. Absorbances were plotted against concentration of Pd (II). It was found that Beer's law was obeyed up to 74.49 ppm of Pd (II). Molar absorptivity and Sandell's sensitivity⁽²⁷⁾ were found to be $4.23 \times 10^2 \text{ lit. mol}^{-1} \cdot \text{cm}^{-1}$ and $0.2516 \mu\text{g}/\text{cm}^2$ respectively.



(Beer's law plot)

Fig.

Job's method⁽²⁸⁾ and Mole ratio method⁽²⁹⁾ was used to determine the stoichiometry of the complex. It was found to be 1:2[M: L]. Stability constant was calculated using the following formula:

$$K_s = (1-\alpha) / 4 \alpha^3 C^2 \quad \text{where, } \alpha = (E_m - E_s) / E_m$$

E_m = Maximum absorbance obtained at the inter sect of the two lines.

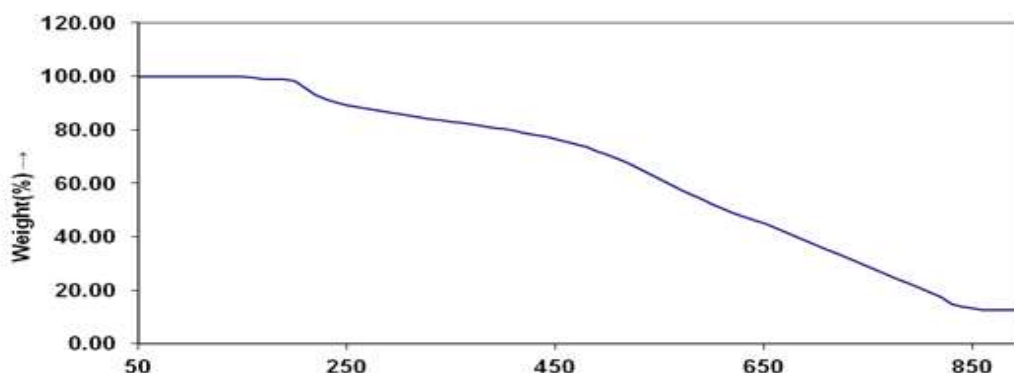
E_s = Absorbance at the stoichiometric molar ratio of the metal to reagent in the complex.

C = concentration of the complex.

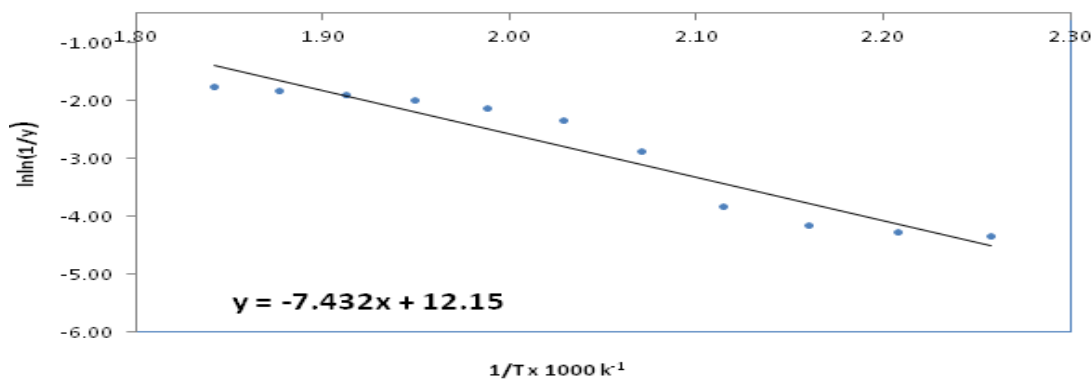
The Average stability constant from two methods is 4.30×10^9 and Gibb's free energy change for complex formation reaction was calculated using the formula $\Delta G^\circ = -RT \ln K_s$ is found to be $-13.226 \text{ k.cal.mol}^{-1}$ at 27°C .

Thermo gravimetric analysis:

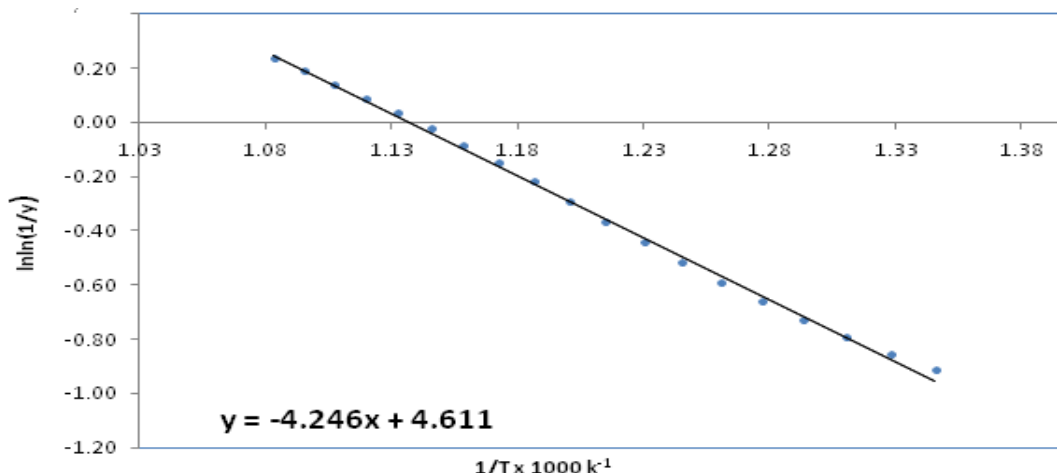
Thermo gravimetric analysis of palladium chelate was done on Universal V₃-OG TA Instrument. A definite quantity of chelate was taken in an alumina crucible and was put on a hanger of microbalance and crucible was kept in a furnace. The temperature of the furnace was raised from 50°C to 900°C in a programmed manner at the heating rate of $10^\circ\text{C}/\text{min}$. From thermo gravimetric analysis of the Pd (II) chelate, it was found that there is no mass loss up to 140°C , indicating that the chelate can be dried safely without decomposition at 140°C . Loss in mass above 140°C to 860°C is due to decomposition of chelate and loss of ligand molecules. Mass of final residue corresponds to Pd metal is in accordance with the formula $(\text{C}_{14}\text{H}_{11}\text{O}_3\text{NI})_2 \text{ Pd}$. The observed loss and mass expected as per formula of chelate in which M: L ratio is 1:2 in the complex. Broido method⁽³⁰⁾ was applied to TG thermo grams of Pd (II) chelate obtained with heating rate $10^\circ\text{C}/\text{min}$. Activation Energy E_a was calculated using this method for thermal decomposition of chelates. The value of 'Ea' was found to be 14.76 and 8.43 kcal/mole for first and second decomposition step respectively.



(TGA of Pd (II)-[DHI- α -PAO] complex)



[Broido Method: Pd (II)-[DHI- α -PAO] complex (Step-I)]



[Broido Method: Pd (II)-[DHI- α -PAO] complex (Step-II)]

IR Spectra:

An IR spectrum has proven to be the most suitable technique to give enough information to elucidate the nature of bonding of the ligand to the metal ion. The IR spectra of the free ligand and the metal complex were carried out in the range of 4000-400 cm^{-1} . The spectrum of the ligand shows the broad band at 3383 cm^{-1} which can be attributed to two phenolic -OH groups. The involvement of deprotonated phenolic moiety in complex is confirmed by the shift of $\nu(\text{C-O})$ stretching band, observed at 1286 cm^{-1} in the free ligand to a lower frequency observed at 1245-1255 cm^{-1} in the complex. The shift of $\nu(\text{C-O})$ band to a lower frequency suggests the weakening of $\nu(\text{C-O})$ and the formation of stronger M-O bond. The low intensity bands due to $\nu(\text{O-H})$ modes of N-OH group is observed at 3080 cm^{-1} frequency in ligand. The medium band observed at around 1532 cm^{-1} in complex was assigned to a $\nu(\text{C=N})$ mode. The shift of $\nu(\text{C=N})$ vibration in the complex to a lower frequency suggests that the nitrogen atom of the ring contributes to the complexation. The lower $\nu(\text{C=N})$ frequency also indicates stronger M-N bonding. This is also supported by slight downward shift of $\nu(\text{N-O})$ (at 970 cm^{-1} in the ligand to around 910 cm^{-1} in complex). Another band appeared at around 696 cm^{-1} in the complex which is assigned to the interaction of phenolic oxygen to the metal ion, i.e., the stretching vibration $\nu(\text{M-O})$. Thus, in the chelates, metal is covalently bonded with oxygen and co-ordinately bonded with nitrogen.

V. CONCLUSION

Applied work

Determination of palladium in palladised carbon:

The sample of palladised carbon was weighed exactly (2.7526 gm) and dissolved in concentrated nitric acid by heating on a sand bath. It was heated till little amount of acid was left. Similar treatment was given 2-3 times. The solution was heated on a sand bath to remove excess of acid. 4 to 5 ml of concentrated HCl is added and strongly heated to dissolve the residue. The solution was diluted to 250 ml.

An aliquot of above solution (50 ml) was taken in a clean beaker and palladium was determined gravimetrically using DHI- α -PAO as per the procedure described previously. The results are compared with the percentage of palladium determined using dimethyl glyoxime, a standard method to estimate palladium.

VI. RESULTS

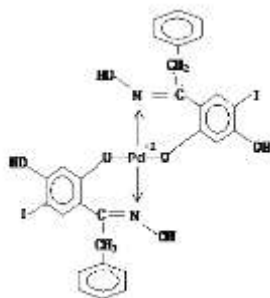
Weight of palladised carbon sample taken: 2.7526 gm

Percentage of Pd (II) in sample determined using dimethyl glyoxime method: 5.01 %

Pd(II)-[DHI- α -PAO] complex obtain from 50 ml	Weight of Pd(II) found in 50 ml diluted solution (mg)	Weight of Pd(II) found in sample(mg)	% of Pd(II) in sample	% RSD of the three	% Error

diluted solution (mg)				results	
215.1	27.16	135.79	4.93	0.55 %	1.59 %
217.2	27.42	137.12	4.98		0.59 %
215.2	27.17	135.86	4.94		1.39%

2, 4-Dihydroxy-5-Iodo- α -phenyl acetophenone oxime [DHI- α -PAO] have been successfully applied for the determination metal content in ores, alloys, catalysts, Industrial samples, synthetic mixtures etc. From above discussion it had been concluded that following is the structure of the complex.



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