Solvent Extraction and Spectrophotometric Determination of Palladium with 3-(2-Hydroxy-5-methylphenyl)-5-(*p*-methoxyphenyl)isoxazoline

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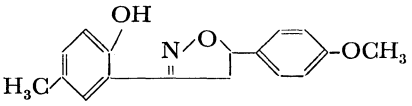
3-(2-Hydroxy-5-methylphenyl)-5-(*p*-methoxyphenyl)isoxazoline (HMPAO) is used for the simultaneous extraction and direct photometric determination of palladium. About 46 μg of palladium was quantitatively extracted at pH 1.0—2.0 with 10 ml of 1.0×10^{-3} M HMPAO in isobutyl alcohol as a yellowish complex. It was measured spectrophotometrically at 332 nm. The system conformed to Beer's law over the concentration range 1.0—20.0 μg of palladium per ml. The colour of the complex was stable for more than 48 h. Palladium was extracted quantitatively and was determined in the presence of large excess of ions which are associated with it. The extractable species was 1:2 (Pd: HMPAO) in nature. The equilibrium constants were determined according to the methods of Yatsimirskii and Leden with suitable modification.

3-(2-Hydroxy-5-methylphenyl)-5-(*p*-methoxyphenyl)-isoxazoline (HMPAO) is the isomer of 2'-hydroxy-4-methoxy-5'-methylchalcone oxime (HMMCO). The latter has been widely used and studied for the extraction of palladium[1-3] and copper.[3,4] HMPAO has the structural formula



The above reagent forms a light yellow complex with palladium around pH 2.0 which can be measured spectrophotometrically at 332 nm.

The present paper deals with extraction studies of palladium with HMPAO in isobutyl alcohol. The proposed method for determination of palladium is simple, selective and sensitive.

Experimental

Apparatus and Reagent. A model DU 2 Beckman spectrophotometer with 10.0 mm quartz cells, and a model LI-10, ELICO pH meter with glass electrode and saturated calomel electrode and a Ganson Shaker were used.

HMPAO was synthesised from 2'-hydroxy-4-methoxy-5'-methylchalcone as per the method of Borkhade[5] and was crystallised from ethanol. About 0.002 M reagent in isobutyl alcohol was used. Fresh solutions were used.

A stock solution of palladium was prepared by dissolving chloride-free palladium hydroxide obtained from 1 g palladium chloride (Johnson-Matthey) in perchloric acid and was standardized gravimetrically with dimethylglyoxime.[6] The dilute solutions were prepared by appropriate dilution.

General Procedure. An aliquot of solution containing about 46 μg of palladium was taken. After addition of water, the pH of the solution was adjusted to 2.0 with 0.1 M perchloric acid or sodium hydroxide and was made to 10 ml volume. It was then transferred into a 250 ml separatory funnel. The solution was equilibrated with 10 ml of 1.3×10^{-3} M HMPAO in isobutyl alcohol for about 10 min. The light yellow organic phase was measured spectrophotometrically at 332 nm against a reagent blank similarly processed. The amount of palladium was then calculated from the calibration curve.

For interference studies a solution containing the desired ion was added before the pH adjustment.

Table 1. Spectral properties of HMPAO in isobutyl alcohol

λ_{max} / nm	Molar extinction coefficient $\times10^{-4}$	Beer's law range $\times10^{5}$ M
230	2.85	0.4—5.5
258	0.96	0.2—17.0
312	0.50	1.0—23.0

Results and Discussion

Absorption Spectra of HMPAO. The reagent HMPAO exhibits peaks of absorption at 230, 258, and 312 nm in isobutyl alcohol. Spectral data are given in Table 1.

Distribution of Reagent. A 10 ml solution of HMPAO of known concentration, $[HMPAO]_{tot}$, in the isobutyl alcohol was equilibrated with equal volume of aqueous solutions at pH 1.0—12.5 and ionic strength 0.2 M ($NaClO_4$). The concentration of HMPAO in the organic phase, $[HMPAO]_{org}$ was determined by noting the absorbance of the solution at 258 nm against the similarly processed solvent as a blank and reading from the calibration curve. The distribution ratio of HMPAO is thus:

$$D_R = [HMPAO]_{org}/[HMPAO]_{tot} - [HMPAO]_{org}.$$

The results of HMPAO for isobutyl alcohol and water system are shown in Fig. 1. The distribution decreases above pH 11.0 which may be due to dissociation of the phenolic –OH.

Proton-Ligand Stability Constant of HMPAO. If K_1^H is the proton-ligand association constant and P_R the partition constant of HMPAO, then the distribution ratio D_R can be given by[7]

$$1/D_R = 1/P_R + 1/P_R \cdot K_1^H[H^+]. \quad (1)$$

At low pH, $D_R=P_R$, Thus Fig. 1 gives the value of $\log P_R$. The $\log P_R$ for HMPAO between isobutyl alcohol and water becomes 1.82.

The negative slope region of Fig. 1 satisfies the relation

$$\log\frac{(P_R-D_R)}{D_R} = pH - \log K_1^H. \quad (2)$$

This gives the value of $\log K_1^H$ (12.08) for HMPAO (Fig. 2).

Absorption Spectrum of Pd–HMPAO Complex. The

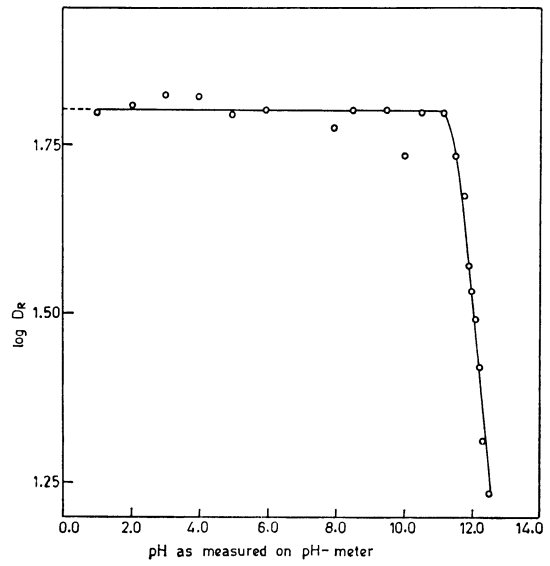


Fig. 1. Distribution of HMPAO between isobutyl alcohol and water as a function of pH-meter reading.

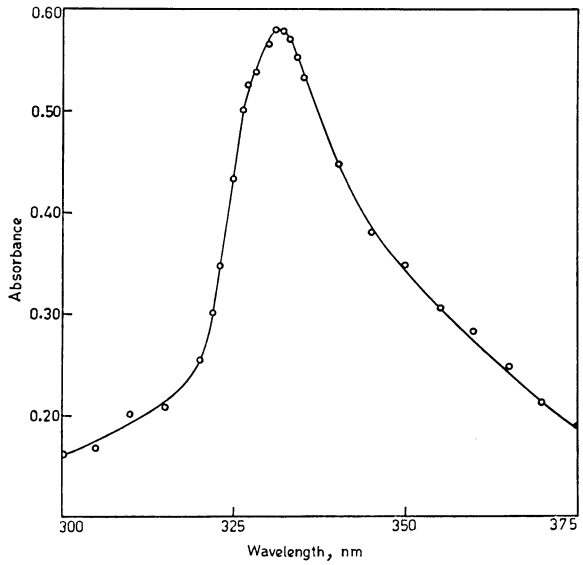


Fig. 3. Absorption spectrum of Pd(II)-HMPAO complex in isobutyl alcohol.

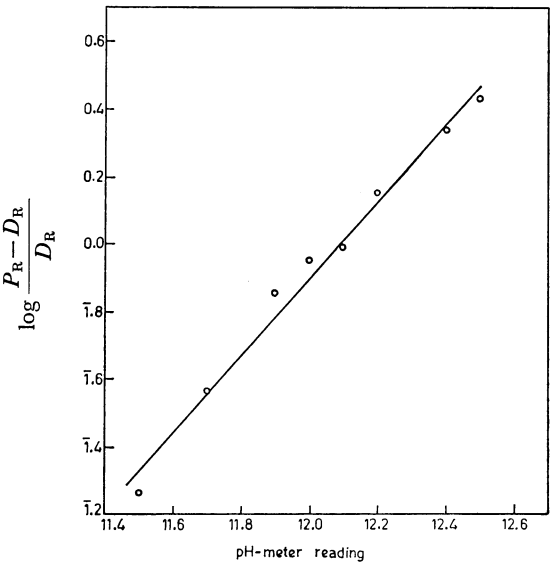


Fig. 2. Plot of $\log \frac{P_R - D_R}{D_R}$ *vs.* pH.

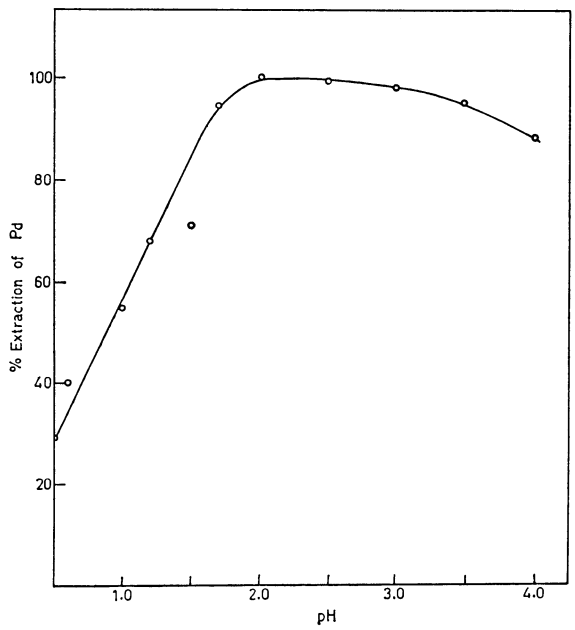


Fig. 4. Effect of pH on extraction of Pd(II).

absorption spectrum of Pd–HMPAO complex (Pd= 46 μg) extracted at pH 2.0 against the reagent similarly processed as a blank is shown in Fig. 3. The light yellow Pd–HMPAO chelate solution shows maximum absorption at 332 nm. The molar absorptivity is 1.3×10^4 at 332 nm and the sensitivity (as per Sandell's definition) is 0.0055 μg/cm^2.

Extraction as a Function of pH. The solvent extraction behaviour of Pd–HMPAO system was studied in the pH range 0.5—6.0 (Fig. 4). It was observed that the extraction is quantitative at pH 2.0. Beyond pH value 2.5 the percentage extraction decreases. Varying amounts of palladium ranging from 1.0 to 20.0 μg per ml were taken. They were extracted at pH 2.0 with 1.3×10^3 M HMPAO in isobutyl alcohol. The light yellow palladium HMPAO system followed Beer's law at 332 nm in the concentration range 1.0—20.0 μg/ml of palladium (Fig. 5). The effective working range from Ringbom curve is 1.0—6.0 μg/ml.

Stability of Colour of the Complex. The absorbance of the coloured complex was measured at interval of 0.5, 8, 16, 24, 48, 96, and 120 h. The value of the absorbance was found to be constant *viz.*, 0.575 until 48 h. The absorbance after 72 h was about 0.500.

Period of Equilibration. With all other factors constant the period of shaking was varied from 2—120 min. The extraction was quantitative when the period of equilibration exceed 10 min.

Effect of Reagent Concentration. The concentration of the reagent was varied from 2.5×10^{-4} to 2.0×10^{-3}M. Extraction was quantitative for the reagent concentration of greater than 1.3×10^{-3} M. It was incomplete

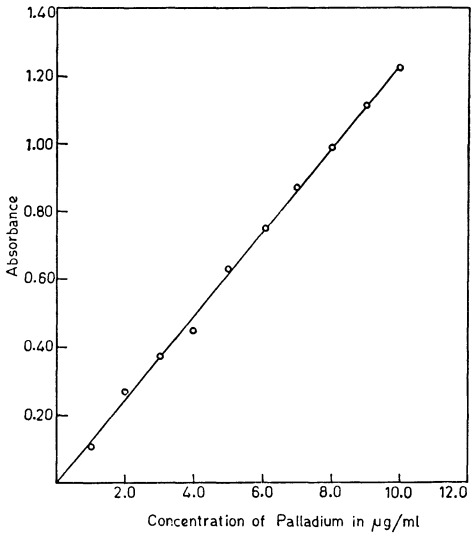


Fig. 5. Beer's law for Pd(II)-HMPAO in isobutyl alcohol.

for lower concentrations of the reagent.

Effect of Palladium Ion Concentration. The effect of Pd concentration on the extraction was examined at different pH values. It was found that the possibility of polymerization can be ruled out in the working range of metal ion concentration 1.0—20.0 μg/ml.

Effect of Ionic Strength. The distribution of palladium was studied at various concentrations of sodium perchlorate (0.2—2.0 M) at pH 2.0. The extent of extraction remains the same up to 0.8 M $NaClO_4$. Above 1.0 M, however, the extent decreases.

Effect of Solvents. Various solvents such as isobutyl methyl ketone, 1-butanol, ethyl acetate, isoamyl alcohol and cyclohexanol were also tried. However, isobutyl alcohol is preferred as it gives a clear separation of the two phases and a less reagent blank absorbance.

Effect of Diverse Ions. The interference of several ions on the extraction behaviour of palladium was studied. The tolerance limit was calculated as the amount necessary to cause ±2% error in the recovery of palladium. The results (Table 2) indicate that moderate amounts of many ions are tolerable. The ions showing strong interference include Cr(III), Sn(II), Ga(III), In(III), Tl(I), and Pt(IV).

Precision and Accuracy. The absorbance obtained for fifteen determinations of 46 μg Pd was 0.575 ±0.005 at 332 nm. Average relative and standard deviations were found to be 1.0 and 1.1%, respectively.

The method is rapid, simple and selective and permits separation and determination of palladium at tracer levels. The entire operation takes only 30 min.

Composition of the Extractable Species. The 1:2 (Pd: HMPAO) composition of the extractable species was determined by Job's[8] method as applied by Irving and Pierce[9] and slope ratio[10] method as modified by Bhatki *et al.*,[11] which was further supported by the distribution data analysis.

Table 2. Effect of diverse ions

[Pd] = 46 μg, pH = 2.0 [HMPAO] = 0.0013 M

Foreign ion	Added as[a]	Tolerance limit μg
Ag^{+}	$AgNO_3$	500
Al^{3+}	$Al_2(SO_4)_3$	2500
Au^{3+}	$HAuCl_4$	6000
Cd^{2+}	$CdSO_4$	5500
Co^{2+}	$CoSO_4$	12000
Cr^{3+}	$Cr(NO_3)_3$	500
Cu^{2+}	$CuSO_4$	12000
Fe^{2+}	$FeSO_4$	17000
Fe^{3+}	$Fe(NO_3)_3$	3500
Ga^{3+}	$Ga(NO_3)_3$	2600
Hg^{2+}	$HgCl_2$	20000
In^{3+}	$In(NO_3)_3$	600
Mn^{2+}	$MnCl_2$	1000
Ni^{2+}	$NiSO_4$	10000
Os^{8+}	OsO_4	500
Pt^{4+}	H_2PtCl_6	1000
Rh^{3+}	$RhCl_3$	600
Ru^{3+}	$RuCl_3$	300
Sn^{2+}	$SnCl_2$	25000
Th^{4+}	$Th(NO_3)_4$	12000
Ti^{4+}	$TiCl_4$	1000
Tl^{+}	$TlClO_4$	1500
VO^{2+}	$VOSO_4$	6000
Zn^{2+}	$ZnSO_4$	13000
ZrO^{2+}	$ZrOCl_2$	None
F^{-}	KF	22000
Cl^{-}	KCl	36000
Br^{-}	KBr	40000
SCN^{-}	KSCN	6000
$S_2O_3^{2-}$	$Na_2S_2O_3$	23000
SO_4^{2-}	Na_2SO_4	19000
NO_2^{-}	$NaNO_2$	30000
NO_3^{-}	$NaNO_3$	25000
$Mo_7O_{24}^{6-}$	$(NH_4)_6Mo_7O_{24}$	3000
WO_4^{2-}	Na_2WO_4	2500
PO_4^{3-}	Na_3PO_4	6000
$C_2O_4^{2-}$	$H_2C_2O_2$	6200
CH_3COO^{-}	CH_3COOH	1300
$Malonate^{2-}$	$(COOH)_2CH_2$	1800
$Tart^{2-}$	Tartaric acid	2200
$Citr^{3-}$	Citric acid	2400
$Ascorb^{-}$	Ascorbic acid	10000
$EDTA^{4-}$	EDTA (disodium salt)	800

a) Water of crystallisation omitted for the sake of brevity.

Metal-Ligand Formation Constants. The equilibrium constants of Pd–HMPAO chelate were determined from the spectrophotometric data by Yatsimirskii's[12,13] and Leden's[14] methods and are incorporated in Table 3.

It can be seen that the values of $\log k_1$, $\log k_2$, $\log \beta_{ext}$, and $\log \beta_{abs}$ obtained by different methods are in good agreement.

Table 3. Primary parameters and equilibrium constants for Pd(II)-HMPAO-isobutyl alcohol system
$\mu=0.2$ M (H^+, Na^+, ClO_4^-): Temperature=30±1 °C.

Yatsimirskii's method		Lenden's method	
Primary parameter	Stability constant	Primary parameter	Stability constant
$a_1\times10^{-8}=6.9$	$\log k_1=4.85\pm0.02$	$\psi_1\times10^{-5}=0.78$	$\log k_1=4.89\pm0.03$
$a_2\times10^{-11}=-1.58$	$\log k_2=4.71\pm0.05$	[HR]→0	
$b_1\times10^{-4}=1.35$	$\log \beta_2=9.56\pm0.08$	$\psi_2\times10^{-9}=1.20$	$\log k_2=4.20\pm0.05$
$b_2\times10^{2}=-7.5$	$\log \beta_{ext}=33.36\pm0.1$	[HR]→0	$\log \beta_2=9.09\pm0.08$
	$\log \beta_{abs}=31.84\pm0.1$		$\log \beta_{ext}=32.89\pm0.1$
			$\log \beta_{abs}=31.37\pm0.1$

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