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Liquid-liquid extraction of Palladium (II) with Cyanex 302 i.e.  
bis (2,4,4-trimethylpentyl) monothiophosphinic acid

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A method is proposed for the extraction of Pd (II) from 1.0M HCl medium using Cyanex 302 in toluene. Palladium (II) is determined in the organic phase by direct spectrophotometry at 336nm. Various parameters such as acid concentration, reagent concentration, time and effect of foreign ions were studied. The probable extracted species is determined by the logD - logC plot. The method is simple, rapid and permits separation of Pd(II) from closely associated metals like Pt(IV), Rh(III) Ru(III), Fe(III) and Ni(II). It has been applied for analysis of Pd (II) in commercial samples. The proposed method is reproducible with a relative standard deviation of  $\pm 1.0\%$ .

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Palladium is one of the important platinum group metals (PGM) for variety of reasons, ranging from its use as catalyst in various hydrogenation processes and catalytic converters for pollution control. It also finds applications in petrochemicals, electrical contracts, jewellery, decoratives, medical devices and dental alloys.

The extraction chemistry of PGMs has often been found to be complicated due to the slow rate of formation of their extractable complexes and also perhaps due to the various oxidation states of these metals in aqueous solution<sup>1</sup>.

Beamish<sup>2</sup> has critically evaluated the methods for the determination of Pd(II). Several new methods using compounds like oximes, xanthates, thio-compounds,  $\beta$ -diketones, etc. have been known to form coloured complexes with Pd(II) and are occasionally used for the extraction of Pd(II)<sup>3-9</sup>. Takahiko *et al.*<sup>10</sup> have reported the extraction of Pd(II) with Cyanex 301 and Cyanex 302 however these suffer from longer equilibration period and use of salting-out agent. Recently, a method has been developed for the extraction of Pd(II) in presence of tin(II)chloride with PC-88A<sup>11</sup>.

However, these methods are known to lack in sensitivity<sup>5-9</sup>, interferences from PGMs<sup>3</sup> and associated metals<sup>4</sup>. In the present communication an extractive method for Pd(II) with Cyanex 302 (bis (2,4,4-trimethylpentyl) monothiophosphinic acid) has been reported.

### Experimental Procedure

*Apparatus and reagents*—A GBC 911A UV-visible spectrophotometer and a Elico pH meter with combined glass electrode were used for absorbance and pH measurements.

The stock solution of palladium(II) was prepared by dissolving appropriate amount of palladium chloride in minimum quantity of HCl and standardised by literature method<sup>12</sup>. The desired concentration of this solution was prepared by further diluting with double distilled water.

The extractant Cyanex 302 i.e. bis (2,4,4-trimethylpentyl) monothiophosphinic acid was gifted by Cytec Canada Inc. and was used without further purification. All other chemicals used were of analytical grade.

*General procedure*—Extraction of palladium(II) (10  $\mu\text{g}$ ) at a fixed concentration of 1.0M HCl with  $5 \times 10^{-3}$  M Cyanex 302 in toluene was studied. The two phases were equilibrated by shaking for a period of 3.0 min. The two phases were separated and palladium(II) which formed a yellow coloured complex exhibited a maximum absorption at 336 nm against reagent blank in the organic phase.

### Results and Discussion

The extraction of palladium(II) with varying concentration of Cyanex 302 from  $2 \times 10^{-4}$  -  $1 \times 10^{-1}$  M dissolved in toluene and 0.1 - 8.0 M HCl acid concentration were carried out. The optimum concentration of Cyanex 302 and HCl required for the

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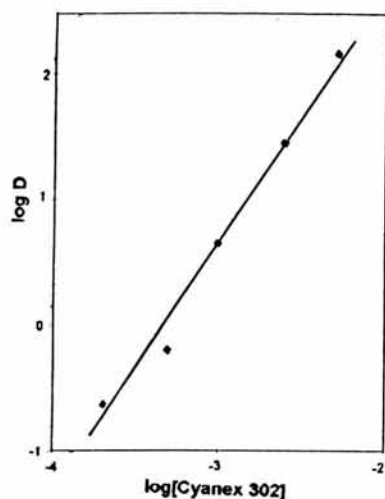


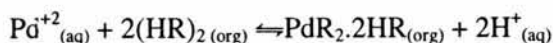
Fig. 1—A graph of log *D* versus log[Cyanex 302] in presence of 1.0M HCl.

quantitative extraction of palladium were  $5 \times 10^{-3}$  M and 1.0 M respectively.

The two phases were equilibrated by shaking for a period ranging from 1.0 - 20.0 min. The extraction was complete within 3.0 min. Longer extraction time did not affect the equilibrium.

Different diluents with  $5 \times 10^{-3}$  M Cyanex 302 were tried for extraction of Pd(II). The extraction was found to be quantitative with toluene, chloroform and Benzene. However with other diluents like xylene (96.5%), hexane (88.9%), cyclohexane(82.5%) and carbon tetrachloride(85.3 %) the extraction was incomplete. Hence all extraction studies were carried out using toluene as diluent as it gave better phase separation and less toxicity.

*Nature of the extracted species*—The nature of the extracted species was evaluated by the plot of log *D* versus log[Cyanex 302] at fixed concentration of 1.0 M HCl. From the results obtained it was found that palladium-extractant complex for Cyanex 302 was 1:2 (Fig. 1). The probable reaction mechanism may be given as follows,



*Absorption spectra for palladium*—Palladium(II) which was extracted in the organic phase exhibited a maximum absorption at 336 nm against reagent blank. The complex was found to be stable for 48 h. Beer's law was obeyed upto 22  $\mu\text{g}/\text{mL}$  of palladium. The molar absorptivity and Sandell's sensitivity were found to be  $4.79 \times 10^3 \text{ Lmol}^{-1}\text{cm}^{-1}$  and  $0.0699 \text{ mg cm}^{-2}$  respectively.

Table 1a—Effect of diverse ions

Ratio of ions	Pd(II) - 10 mg	
	Cations	Anions
1:50		$\text{Cl}^-$ , $\text{NO}_2^-$ , $\text{Br}^-$
1:20	$\text{Ca}^{2+}$ , $\text{Sr}^{2+}$ , $\text{Ba}^{2+}$ , $\text{Cu}^{2+}$ , $\text{Tl}^+$	$\text{NO}_3^-$ , $\text{SO}_4^{2-}$ , $\text{SO}_3^{2-}$
1:10	$\text{Li}^+$ , $\text{Na}^+$ , $\text{K}^+$ , $\text{Cs}^+$ , $\text{Mg}^{2+}$ , $\text{Mn}^{2+}$ , $\text{Pb}^{2+}$	$\text{I}^-$ , $\text{SCN}^-$ , EDTA
1:7	$\text{Rb}^+$ , $\text{Ni}^{2+}$ , $\text{Ru}^{3+}$	—
1:5	$\text{V}^{5+}$ , $\text{Cr}^{3+}$ , $\text{Al}^{3+}$ , $\text{Fe}^{3+}$ , $\text{Co}^{2+}$ , $\text{In}^{3+}$ , $\text{Be}^{2+}$ , $\text{Rh}^{3+}$ , $\text{Pt}^{4+}$	Oxalate, citrate
1:3	$\text{Zn}^{2+}$ , $\text{Cd}^{2+}$ , $\text{As}^{3+}$	—
1:2	$\text{Sb}^{3+}$ , $\text{Bi}^{3+}$	—
1:0	$\text{Hg}^{2+}$ , $\text{Au}^{3+}$	—

Table 1b—Separation of palladium(II) from multicomponent

Metal Ions	Conc (mg)	Aqueous Phase	Mixtures	
			[Cyanex 302] (M)	% Recovery
Pd(II)	10	1.0 M HCl	$5 \times 10^{-3}$	100
A	100		unextracted	99.2
Pd(II)	10	1.0 M HCl	$5 \times 10^{-3}$	100
B	100		unextracted	98.3
Pd(II)	20	1.0 M HCl	$5 \times 10^{-3}$	99.0
Au(III)*	100			99.2
Pd(II)	20	1.0 M HCl	$5 \times 10^{-3}$	99.0
Au(III)	100			100
Pt(IV)	100		unextracted	99.2
Pd(II)	20	1.0 M HCl	$5 \times 10^{-3}$	99.0
Au(III)	100			100
Rh(III)	100		unextracted	99.1
Pd(II)	50	1.0 M HCl	$5 \times 10^{-2}$	99.2
Au(III)	100			100
Ru(III)	100		unextracted	98.3

A - Pt(IV) / Rh(III) / Ru(III)

B - Fe(III) / Co(II) / Ni(II)

\*-Au(III) co-extracted stripped with 0.1M  $\text{Na}_2\text{S}_2\text{O}_3$

Table 2—Analysis of palladium in real samples

Palladium Sample	Present,	Found, <sup>†</sup>	Recovery,	R.S.D.
	%	%	%	%
Pd on $\text{CaCO}_3$	5.0	4.97	99.47	0.69
Pd on charcoal	5.0	4.96	99.2	0.84

<sup>†</sup>Average of triplicate determinations

*Effect of foreign ions*—The effect of various interfering ions was studied for the extraction of Pd(II) with  $5 \times 10^{-3}$  M Cyanex 302 in toluene. The tolerance limit of the interfering ions was determined with an error of 2 % (Table 1a).

*Separation of palladium from multicomponent mixtures*—Palladium was separated from mixtures of other noble metals and transition metals taking advantage of their difference in the extraction conditions of these metals with Cyanex 302 (Table 1b).

*Analysis of palladium in real samples*—The proposed method was extended for determination of palladium in Pd-charcoal and Pd-CaCO<sub>3</sub> catalysts. 0.1 g of palladium-charcoal (S.D.Fine Chemicals Ltd., India) sample was taken in a silica combustion tube and incinerated for 8 h to ash the carbon completely. The sample was treated with 5 mL of formic acid (1+4 mL) and dried on hot plate. The resulting compound was dissolved in 6M HCl and 2 M HNO<sub>3</sub> and then diluted to 100 mL with distilled water.

0.1 g of palladium-calcium carbonate catalyst (S.D. Fine Chemicals Ltd., India) was taken in a beaker, treated with aqua regia and evaporated to dryness. The residue was leached with water, hydrochloric acid was added and then diluted to 100 mL with double distilled water. Aliquots of these samples were analysed by the proposed method. The results obtained were in close agreement with theoretical values (Table 2).

### Conclusion

The proposed method using Cyanex 302 facilitates quantitative extraction and separation of Pd(II) from associated metals. The method is simple, rapid, selective and sensitive as the complete extraction could be achieved with low reagent concentration and short equilibrium period and free from the drawbacks as reported by earlier proposed methods using  $\alpha$ -

furildioxime, 2-carboxy-2'-hydroxy-5-methylazobenzene, *n*-butyl xanthate, 2-mercaptobenzamide, miphénylthiovioluric acid, 2'-hydroxy-4-methoxy-5'-chloroalcone oxime and diphenylthiosemicarbazone.

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