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Selective liquid-liquid extraction and separation of palladium(II) from salicylate media with *n*-octylaniline in xylene: analysis of catalyst, alloys

Ashwini Gaikwad¹, Vishal Suryavanshi¹, Mansing Anuse¹

¹Analytical Chemistry Laboratory, Department of Chemistry, Shivaji University, Kolhapur 415311

*E-mail: maanuse@gmail.com

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Abstract: Solvent extraction method for separation of palladium(II) was developed from salicylate medium. The optimized extraction condition of palladium(II) was successfully utilized for the separation of palladium(II) from its various binary and ternary mixtures of associated metal ions. The effect of temperature on palladium(II) extraction was investigated. The stoichiometry of the extracted species of palladium(II) - salicylate was determined from log-log plot and it is observed as 1:3:1. The applicability of the proposed method was checked by analyzing various catalyst and alloy samples.

Keywords: Liquid-liquid extraction, Palladium(II), Sodium salicylate, *n*-Octylaniline, Alloys and catalyst

1. Introduction

Solvent extraction has attracted much attention as an effective and energy saving category of separation technique for precious metals. The extraction technique is one of the most important process for the recovery of precious metals from waste water and scraps as well as in the mining industry. At present, there is a growing demand of precious metals for technological applications due to their outstanding physical and chemical properties [1]. The abundance of palladium in the earth's crust is 0.01-0.02 $\mu\text{g mL}^{-1}$ and it exists in various natural minerals,

soils and rocks [2]. This element is of immense importance to the electronic industries [3]. Palladium and its alloys have a wide range of applications both in the chemical industry and in instrument making. It also has widespread use in dental and medicinal devices and jewellery manufacture [4]. The carcinogenicity of palladium(II) compounds in rats and mice and their toxicity to mammals, fish and higher plants are cause for environmental concern [5]. Therefore, these compounds are usually considered as environmental pollutants [6]. Palladium(II) forms a number of complexes that are soluble in organic solvents because

of the labile character of its chloro complex, PdCl_4^{2-} towards several hydrophobic ligands [7]. This leads to the formation of several highly extractable complexes at room temperature. Palladium prefers to coordinate most strongly with polarizable atoms which have focused the development of extracting agents on those with donor atoms such as sulfur, phosphorus and nitrogen. Nitrogen containing reagents particular, amines and their derivatives are efficient extractants for some platinum group metals (PGMs) and are widely used in technology and analysis. Modern techniques for the extraction of PGMs provide rational approaches to choosing extractants from the standpoint of their availability, selectivity and development of processes for one-step extraction of the target metal and its separation from the associate metals.

In recent year's various reagents have been studied for liquid-liquid extraction and separation of palladium(II) like hexadecylpyrimidinium bromide [8], 1-octylthiobromine [9], LIX84I [10]. These methods were applicable for extraction separation of either individual metal ion or group of platinum metals. The extraction properties of bis-acylated diethylenetriamine [11] was studied for the extraction of palladium(II) from HCl solution. Method required higher reagent concentration to ensure the complete extraction. The synergistic extraction behavior of palladium(II) with 1-phenyl-3-methyl-4-(2-methoxy-benzoyl)-pyrazolone-5-one, trialkylamine [12] and tri-*n*-octylamine [13] has been studied. The methods are based on antagonistic synergistic extraction of palladium(II) and were used for the separation of palladium(II) from radioactive fission products. Tri-octylamine [14-16] was reported for separation of palladium(II) from PGMs. *N-n*-octylaniline [17] and alamine 336 [18] were also used for the quantitative extraction of palladium(II). Extraction study of palladium(II) by 2-dodecylaminopyridine from oxalate

media was investigated [19]. The extraction of palladium(II) from hydrochloric acid solution with *N*-benzyl aniline in chloroform was also investigated [20].

The extraction of chloropalladium complexes by Cyanex 301 [21] in toluene over a wide range of aqueous acidities was investigated. Liquid-liquid extraction of palladium(II) with Cyanex 921 [22] from aqueous hydrochloric acid media and Cyanex 923 [23] in chloride media in toluene was studied. Extraction of palladium(II) was carried out from spent autocatalysts [22, 23]. Phosphonium ionic liquid: trihexyl (tetradecyl) phosphonium chloride (Cyphos[®]IL 101) [24] has been used as a reagent in the presence of toluene to extract palladium(II) from hydrochloric acid solutions of various concentrations. Extraction of palladium(II) from hydrochloric acid solutions with pyridinecarboxamides and ACORGA[®]CLX50 [25], LIX 63 [26] was carried out.

Previously we have reported the solvent extraction methods for various PGMs with the help of high molecular weight amines [27-37]. In this work, *n*-octylaniline-salicylate system was studied to investigate the extraction of aqueous palladium(II) solution as a function of concentration of extractant, different weak organic acids, pH, diluents, various strippants, equilibrium time, loading capacity of extractant etc. The proposed method was used for rapid and selective separation of palladium(II) from associated elements. It was also tested for the separation and determination of palladium(II) from real samples such as alloys and catalysts. The previously reported liquid-liquid extractive separation method for palladium(II) is given in Table 1.

2. Experimental

2.1 Apparatus

Table: 1 Comparison of the present method with earlier reported solvent extraction methods for extraction of palladium(II)

Sr. No.	Extractant	Solvent	Acidity/pH	Stripping reagent	Determination method	Eq. Time	Ref.
1	N- <i>n</i> -octylaniline	Xylene	1.0 M HCl	1:1 NH ₃ Solution	Spectrophotometer	1.0 min.	4
2	1-Octylthio-bromine	Toluene	HCl	thiourea	Spectrophotometer	24 H	9
3	Tri-octylamine	Kerosene	HCl	--	ICP - AES	--	14
4	Tri- <i>n</i> -octylamine	Toluene	HCL	8 M HCl	AAS		15
5	Tri-octylamine	Toluene	HCL	--	Spectrophotometer	2 H	16
6	N- <i>n</i> -octylaniline	Xylene	0.025 M Sodium Salicylate, pH= 3.0	7.0 M NH ₃	Spectrophotometer	1.0 min.	17
7	Alamine 336	Toluene	HCL	HCl + Thiourea	ICP OES	30 min	18
8	Cyanex 921	Toluene	HCl	--	Spectrophotometer	10 min	22
9	Cyanex 923	Toluene	HCl	HCL: HClO ₄ (1:1)	Spectrophotometer	5 min	23
10	Cyphos [®] IL 101	Toluene	0.1 M & 3.0 M HCl	0.5 M NH ₄ OH	AAS/ ICP-OES	0.5 & 30.0 min.	24
11	Alamine 300	Kerosene	0.5 M HCl	Sodium Thiosulphate	--	30.0 min.	50
12	Cynex 921	Toluene	6.0 M HCl	HCl:HClO ₄ 2.0 M/ 2.0 M	Mass Balance	5.0 min.	51
13	<i>n</i> -Octylaniline	Xylene	0.085 M Sodium Salicylate, pH = 1.5	Ammonia 5.0 M	Spectrophotometer	5.0 min	PM

P.M= Present Method

An Optizen- α digital UV visible spectrophotometer with 10 mm quartz cell was used for the absorbance measurement and pH measurements were carried out using an Elico digital pH-meter model LI-127. All weighing operations were done by using digital weight balance Mettler Toledo (Model ML 204/AOI, Switzerland).

2.2 Reagents

2.2.1 Standard palladium(II) solution

A stock solution of palladium(II) was prepared by dissolving 1 g of palladium chloride hydrate (Johnson Matthey, UK) [38] in dilute analar HCl (1 M) and diluted to 250 mL with water

and standardized. A working solution of 100 $\mu\text{g/mL}$ was made by diluting the stock solution with water.

2.2.2 *n*-Octylaniline

The reagent *n*-octylaniline was prepared by the method of Pohlandt's [39] and its 0.07 M solution was prepared in xylene. All solutions were prepared from A. R. grade reagents. Aqueous solutions were prepared with water. Double distilled water was used throughout the experimental study.

2.2.3 Preparation of 4'-Chloro PTPT

1-(4'-Chlorophenyl)-4,4,6-trimethyl-(1H,4H)-

pyrimidine-2-thiol (4'-Chloro PTPT) were prepared by the method of Mathes [40-43]. A stock solution (0.02 M) was prepared by dissolving 0.5329 g of 4'-Chloro PTPT in 100 mL chloroform. Reagent solution is colorless and stable.

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

2.3 General procedure for extraction and determination of palladium(II)

To an aliquot solution containing 200 μg palladium(II) in 25 mL volumetric flask 0.034 g of sodium salicylate was added to get the concentration of solution 0.085 M. The pH of the resulting solution was adjusted to 1.5 with dilute HCl and NaOH solution. The aqueous solution was equilibrated with 10 mL of 0.07 M *n*-octylaniline in xylene for 5 min in separating funnel. After the phase disengagement, the organic phase was stripped with three 10 ml portions of 5 M ammonia. The stripped aqueous phase was evaporated to moist dryness in order to remove excess of ammonia. The residue was dissolved in minimum amount of *aqua regia*, and evaporated twice with 2 mL portions of concentrated HCl to remove oxides of nitrogen. The residue was dissolved in 0.1 M HCl and palladium(II) was determined spectrophotometrically by 4'-Chloro PTPT [44]. All the experiments were repeated on an average five times and the accuracy determination of the metal concentration in the loaded organic phase was realized by mass balance and checked by complete stripping of the loaded organic phase followed by analysis of the stripped solution.

3. Results and Discussion

3.1 Extraction of palladium(II) as a function

of pH

The influence of pH on the extraction of palladium(II) was studied in the pH range from 0.3 to 10 with *n*-octylaniline in xylene from 0.085 M sodium salicylate. The result shows that as pH increases the extraction of palladium(II) increases and become quantitative in pH range 1.0 to 2.0. Beyond pH 2 the ion-pair formation was not possible resulting is the decrease in extraction. Hence all the extractions of palladium(II) were carried out at pH 1.5 with 0.07 M *n*-octylaniline in xylene (Fig.1).

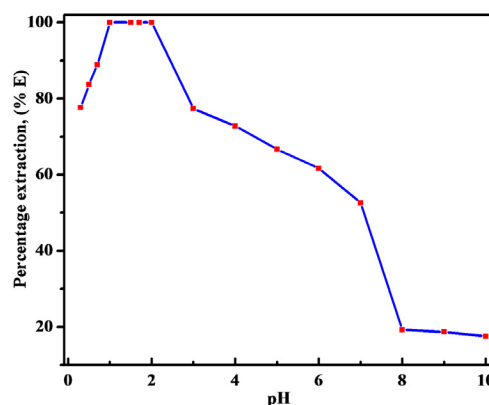


Fig. 1: Extraction of palladium(II) as a function of pH

Conditions: Palladium(II) = 200 μg , sodium salicylate = 0.085 M, *n*-octylaniline = 0.07 M in xylene, shaking time = 5 min

3.2 Extraction as a function of *n*-octylaniline concentration

In the effect of reagent concentration, extractions were carried out with various molar concentrations of *n*-octylaniline in xylene. The extraction of palladium(II) starts at 0.01 M and increases along with the concentration of *n*-octylaniline and was found to be quantitative in the range of 0.06 - 0.08 M *n*-octylaniline in xylene. The extraction decreases above 0.08 M *n*-octylaniline concentration due to dissociation of ion-pair complex. However, 10 mL of 0.070

M *n*-octylaniline in xylene was used for general extraction procedure (Fig 2).

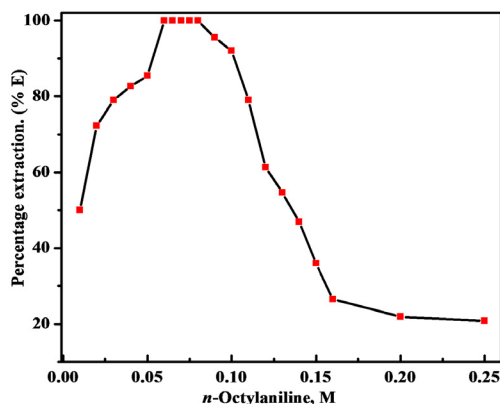


Fig. 2: Extraction of palladium(II) as a function of *n*-octylaniline concentration

Conditions: Palladium(II) = 200 μ g, pH = 1.5, sodium salicylate = 0.085 M, shaking time = 5 min

3.3 Extraction of palladium(II) as a function of weak organic acid concentration

The extraction of palladium(II) was carried out at pH 1.5 with 10 ml of 0.07 M *n*-octylaniline in xylene in presence of varying concentration of salicylate, succinate and malonate as weak carboxylic acid media (25 mL). The extraction of palladium(II) was found to be quantitative in the sodium salicylate. The extraction starts at 0.01 M sodium salicylate and increases with increase in concentration of sodium salicylate. The extraction of palladium(II) becomes quantitative in the range of 0.08 to 0.1 M. However, the extraction of palladium(II) was incomplete in sodium succinate (66.4 %) and sodium malonate (61.7 %) media. Thus, 0.085 M of sodium salicylate was used for the further extraction study (Fig 3).

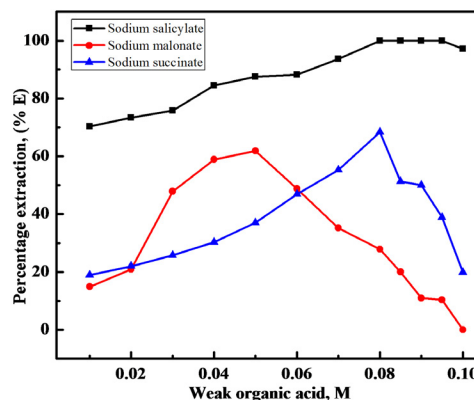


Fig. 3: Extraction of palladium(II) as a function of weak organic acid concentration

Conditions: Palladium(II) = 200 μ g, pH = 1.5, *n*-octylaniline = 0.07 M in xylene, shaking time = 5 min

3.4 Effect of diluents on extraction of palladium(II)

The studies were performed to find out the most suitable solvent for *n*-octylaniline to ensure quantitative extraction for palladium(II). The solution of *n*-octylaniline (0.07 M) was prepared in various diluents like benzene, toluene, xylene, *n*-butyl alcohol, amyl alcohol and used for the extraction of palladium(II). The result shows that benzene, toluene, xylene, *n*-butyl alcohol, amyl alcohol provides quantitative extraction of palladium(II), while chloroform (25.1 %), carbon tetrachloride (61.0 %), methyl isobutyl ketone (91.9 %), 1, 2-dichloroethane (51.9 %), kerosene (46.4 %) and amyl acetate (28.3 %) shows incomplete extraction. Xylene showed minimum toxicity and it provides better phase separation, as compared to other diluents so it was recommended for general extraction procedure (Table 2).

Table 2: Extraction of palladium(II) with various diluents

Solvent	Dielectric constant, (ϵ)	Percentage extraction, (% E)
Xylene*	2.30	100
Toluene	2.38	100
Benzene	2.27	100
Chloroform	4.80	25.1
Amyl Acetate	4.80	28.3
Methyl <i>iso</i> butyl ketone (MIBK)	13.10	91.9
1,2 Dichloro ethane	10.50	51.9
Amyl alcohol	13.9	100
<i>n</i> -Butyl alcohol	17.80	100
Kerosene	-	46.4
Carbon tetrachloride	2.24	61.0

*Recommended for general extraction procedure
Conditions: Palladium(II) = 200 μ g, pH = 1.5, aq: org ratio = 2.5: 1, sodium salicylate = 0.085 M, extractant = 0.07 M *n*-octylaniline, strippant = 5 M ammonia (3 $\times$ 10 mL)

3.5 Effect of stripping agents

Stripping is the reverse of extraction, so it should be promoted by those factors that affect extraction negatively, such as alkalies and salt media. Acids were unsuccessful because the anion complex adhered in the organic medium under these conditions. Ammonia solution (5 M) was preferred because it was easier to remove from the aqueous phase by evaporation prior to determining palladium(II) spectrophotometrically with 4'-ChloroPTPT as compared to ammonia buffer solution. Hence ammonia and ammonia buffer are the most effective stripping agents for palladium(II). The stripping percentage was calculated relative to the initial amount of palladium(II) in organic

layer. It was found that stripping was incomplete in HCl, H₂SO₄, HNO₃, NaOH, KOH, water and acetate buffer. Therefore, 5 M ammonia (10 $\times$ 3 mL) was used as a strippant for palladium(II) (Table 3).

Table 3: Choice of electrolyte solution for the stripping of palladium(II) from the organic extract

Strippant	M	Percentage extraction, (% E)
Ammonia*	1-10	100.0
HCl	1-5	48.1
H ₂ SO ₄	1-5	5.5
HNO ₃	1-5	No stripping
CH ₃ COOH	1-5	20.1
Water	-	4.7
NaOH	0.1-0.2	13.7
KOH	0.1-0.2	18.7
Acetate buffer	pH-4.7	39.3
Ammonia buffer	pH-10	100.0

*Recommended for general extraction procedure,

Conditions: Palladium(II) = 200 μ g, pH = 1.5, sodium salicylate = 0.085 M, extractant = 0.07 M *n*-octylaniline in xylene aq: org ratio = 2.5: 1, xylene

3.6 Extraction of palladium(II) as a function of equilibrium time

The equilibration period was varied from 1 to 30 min. The extraction of palladium(II) was quantitative over a period of 3 min shaking of the solution, but with prolonged shaking over 20 min there was decrease in the percentage extraction of palladium(II) due to the dissociation of ion-

pair complex. Thus, equilibration time for 200 µg palladium(II) extraction was kept about 5 min throughout the study (Fig. 4).

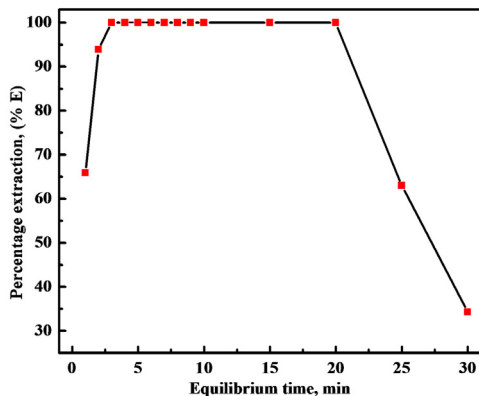


Fig. 4: Extraction of palladium(II) as a function of equilibrium time

Conditions: Palladium(II) = 200 µg, sodium salicylate = 0.085 M, pH = 1.5, *n*-octylaniline = 0.07 M in xylene

3.7 Extraction behavior of palladium(II) as a function of metal loading capacity

Varying concentrations of palladium(II) (100 to 5000 µg/mL) were extracted with 10 mL portions of 0.07 M *n*-octylaniline in xylene from 0.085 M sodium salicylate media. It was observed that 10 mL of 0.07 M *n*-octylaniline extract palladium(II) quantitatively up to 1500 µg/mL.

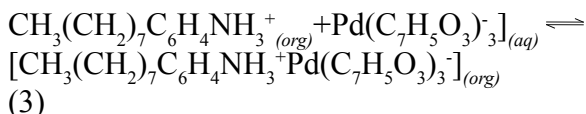
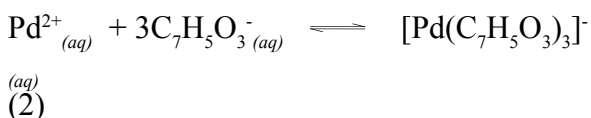
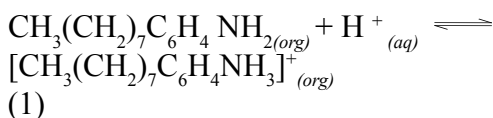
3.8 Extraction behavior of palladium(II) as a function of aqueous to organic volume ratio

Palladium(II) was extracted from 10 mL to 50 mL aqueous solutions containing 0.085 M sodium salicylate with 10 mL of 0.07 M *n*-octylaniline in xylene. The extraction of palladium(II) was quantitative when the ratio was in the range 1:1 to 5:1 beyond that the extraction decreases because of the unavailability of the reagent to form ion-pair complex. Therefore, for further

study 1:2.5 ratio was adopted.

3.9 Nature of extracted species

The probable composition of extracted species was ascertained by plotting the graphs of $\log D_{[\text{Pd(II)}]}$ against $\log C_{[\text{n-octylaniline}]}$ at fixed sodium salicylate concentration (0.085 M). The graphs were found to be linear and having the slopes of 0.89 and 0.82, values at pH 4.0 and 7.0, respectively (Fig. 5). Also plots of $\log D_{[\text{Pd(II)}]}$ against $\log C_{[\text{Salicylate}]}$ at fixed *n*-octylaniline concentration (0.07 M) were linear and the slope values were found to be 2.8 and 2.7 at pH 4.0 and 7.0, respectively (Fig. 6). The probable composition of the extracted species was calculated as 1:3:1 (metal: acid: extractant). The possible mechanism of ion- pair complex is as follow: -



The possible mechanism of the ion-pair complex extracted appears to be protonated *n*-octylaniline which form cationic species as $\text{CH}_3(\text{CH}_2)_7\text{C}_6\text{H}_4\text{NH}_3^+$ while salicylate combines with palladium(II) to form anionic species as $[\text{Pd}(\text{C}_7\text{H}_5\text{O}_3)_3]^-$ and both of them associate to form ion-pair of the type $[\text{CH}_3(\text{CH}_2)_7\text{C}_6\text{H}_4\text{NH}_3^+\text{Pd}(\text{C}_7\text{H}_5\text{O}_3)_3]_{(org)}$, which being neutral constituted extractable species.

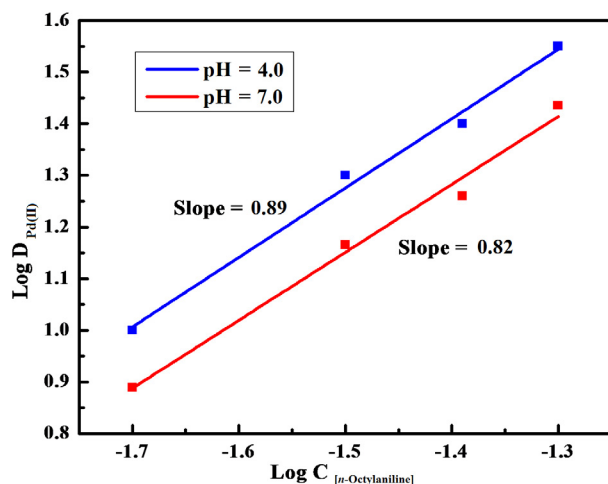


Fig 5: Log D_[Pd(II)] against Log C_[n-Octylaniline] at fixed sodium salicylate

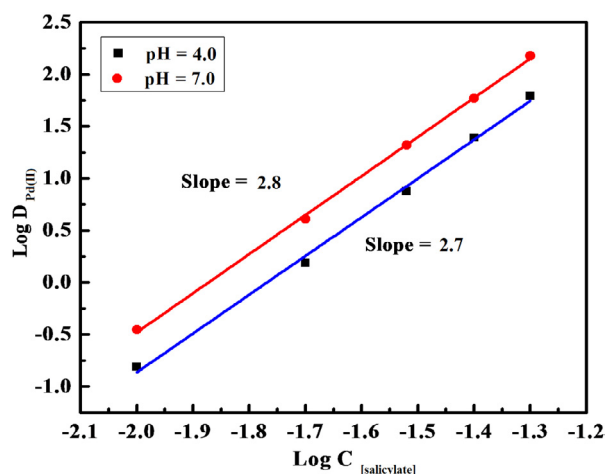


Fig 6: Log D_[Pd(II)] against Log C_[Salicylate] at fixed *n*-octylaniline concentration

3.10 Effect of temperature on extraction of palladium(II)

The effect of temperature on the extraction of palladium(II) in the range 302-314 K was studied in a solution of ionic strength 0.085 M sodium salicylate at pH 5.0 with 0.07 M *n*-octylaniline in xylene. It was found that, the distribution coefficient increases with rise in temperature.

The change of the extraction equilibrium constant K_{ex} with temperature is expressed by van't Hoff equation.

$$\Delta \log K_{ex} / \Delta (1/T) = \Delta H / (-2.303 R) \quad (4)$$

Where, T is absolute temperature and R is the gas constant.

The plot of K_{ex} versus $1000/T$ is linear with a slope value of -3.407 and the enthalpy change of the extraction carried out at constant pH 5.0 was evaluated as $\Delta H = 65.23 \text{ KJ mol}^{-1}$ which means it is an endothermic process. The free energy ΔG and entropy ΔS were calculated from equation (5) and (6) and are reported in Table 4.

$$\Delta G = -2.303 RT \log K \quad (5)$$

$$\Delta S = (\Delta H - \Delta G) / T \quad (6)$$

The negative values of free energies imply that reaction is spontaneous. The positive enthalpy value indicates that the extraction of palladium(II) with *n*-octylaniline in xylene is favorable with rise in temperature (Fig. 7).

Table 4: Effect of temperature and thermodynamic functions related to palladium(II) extraction system

Temperature (K)	1000/K	Log K_{ex}	$-\Delta G$ (KJ/mol)	ΔS (J/ K/ mol)	ΔH (KJ/mol)
302	3.31	2.20	-12.75	275.58	
305	3.28	2.22	-13.00	278.11	
308	3.25	2.33	-13.74	291.2	65.23
311	3.22	2.43	-14.48	303.82	
314	3.18	2.54	-15.31	318.33	

Conditions: Palladium(II) = 200 µg, sodium salicylate = 0.085 M, aq: org ratio = 2.5: 1, extractant = 0.07 M *n*-Octylaniline in xylene, strippant = 5 M ammonia (3×10 mL)

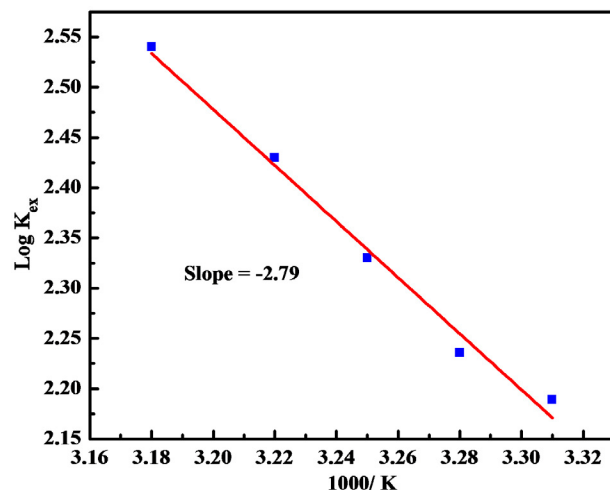


Fig 7: Effect of temperature on palladium(II) extraction

3.11 Effect of various diverse ions on percentage extraction of palladium(II)

The effect of large number of foreign ions on the extraction of 200 µg/mL of palladium(II) with *n*-octylaniline was investigated. The result shows that the proposed method is free from large number of cations and anions. The tolerance limit of individual foreign ions was set so that error in percentage recovery was not more than $\pm 2\%$. The cations and anions creates interference in the extraction of palladium(II) were masked by suitable masking agents before extraction. Some anions like thiourea, tartrate, oxalate, EDTA, thiocyanate, thiosulphate, ascorbate interfere in the extraction procedure of palladium(II) (Table 5).

Table 5: Effect of foreign ions on the extraction palladium(II)

Ratio of ions Palladium: ion	Mass tolerated, mg	Foreign ion
2:500	50	Iodide
2:250	25	Citrate, malonate, Zn(II)
2:150	15	Ni(II), Te(IV), Tl(III), Mo(VI), Se (IV), Ba (II), Ce (IV)
2:100	10	Mg(II), Cd(II), Sb(III), V(V), Pb(II), Sn(II), Bi(III), fluoride
2:50	5	Cu(II), Co(II), Fe(III)
2:20	2	Fe(II), Hg(II), Cr(VI)
2:6	0.6	Ag(I), Pt(IV), Rh(III)
2:5	0.5	Au(III)
2:4	0.4	Ru(III) ^a

^a Masked by 25mg citrate.

Conditions: Palladium(II) = 200 µg, pH = 1.5, sodium salicylate = 0.085 M, aq: org ratio = 2.5: 1, extractant = 0.07 M *n*-octylaniline in xylene, strippant = 5 M ammonia (3×10 mL)

4. APPLICATIONS

4.1 Separation of palladium(II) from associated metal ions

The method permits separation and determination of palladium(II) from binary mixtures containing Pt(IV), Rh(III), Ir(III), Cu(II), Fe(III), Co(II), Ni(II), Se(IV), Au(III) and Te(IV) (Table 6). Palladium(II) was separated from these associated metal ions, under the optimum extraction conditions of palladium(II) where, all the added metal ions were remained quantitatively in aqueous phase from which they are determined spectrophotometrically by standard methods [44-49]. Palladium(II) from organic phase was stripped and estimated spectrophotometrically

by 4'-ChloroPTPT method. Palladium(II) was separated from Ru(III) by masking with 25 mg of citrate when palladium(II) was extracted with 0.07 M *n*-octylaniline in xylene at pH 1.5. While Ru(III) remained in aqueous phase. Palladium(II) from the organic phase was stripped with ammonia and determined by spectrophotometrically. The masked Ru(III) was demasked with concentrated HClO₄ and determined spectrophotometrically by standard method (Table 6).

Table 6: Separation of palladium(II) from associated metal ions

Metal ions	Palladium(II) taken, µg	R* %	Chromogenic ligand	Ref.
Pd(II)	200	99.6	4'-Chloro	[44]
Ru(III) ^a	400	99.5	PTPT	
Pd(II)	200	99.7	SnCl ₂ - HBr	[45]
Ir(III)	100	99.6		
Pd(II)	200	99.7	SnCl ₂	[45]
Pt(IV)	300	99.6		
Pd(II)	200	99.8	KI + SnCl ₂	[45]
Rh(III)	200	99.5		
Pd(II)	200	99.7	Thiocyanate	[45]
Fe(III)	1000	99.6		
Pd(II)	200	99.8	SnCl ₂	[45]
Au(III)	150	99.6		
Pd(II)	200	99.8	4'-Chloro	[46]
Cu(II)	2000	99.6	PTPT	
Pd(II)	200	99.7	Thiocyanate	[47]
Co(II)	1000	99.6		
Pd(II)	200	99.8	DMG	[47]
Ni(II)	5000	99.6		
Pd(II)	200	99.8	4'-Bromo	[48]
Se(IV)	300	99.7	PTPT	
Pd(II)	200	99.7	4'-Bromo	[49]
Te(IV)	200	98.4	PTPT	

^a Masked by 25 mg citrate, * Average recovery Pd(II).

Conditions: Palladium(II) = 200 µg, pH = 1.5, sodium salicylate = 0.085 M, aq: org ratio = 2.5: 1, extractant = 0.07 M *n*-octylaniline in xylene,

strippant = 5 M ammonia (3×10 mL)

4.2 Sequential separation of palladium(II), rhodium(III) and ruthenium(III) from their mixture

Palladium(II) and rhodium(III) are used as auto exhaust catalyst as well as palladium(II) and ruthenium(III) are used as hydrogenation catalyst in organic chemistry. Hence, their separation and determination from mixture has great importance (Table 7).

Palladium(II) was separated from ternary mixtures of rhodium(III) and ruthenium(III) at pH 1.5, from 0.085 M sodium salicylate media by 0.07 M of *n*-octylaniline in amyl alcohol. Rhodium(III) and ruthenium(III) remain quantitative in aqueous phase while, palladium(II) was extracted into organic phase. Separation is based on the use of amyl alcohol as a solvent for palladium(II). Palladium(II) form organic phase was stripped with 5 M ammonia (3×10 mL). The ammonia was evaporated and palladium(II) was determined by 4'-Chloro PTPT [44].

The aqueous phase was evaporated to moist dryness and adjusted to 0.03 M sodium malonate, and then pH was adjusted 9.0. Rhodium(III) was extracted with 0.1 M of *n*-octylaniline in xylene. It is back stripped with 1 M HCl (2×10 mL). It was determined spectrophotometrically by KI + SnCl₂ method [45].

The aqueous phase containing ruthenium(III) was again evaporated to moist dryness. It was adjusting to 0.05 M sodium malonate, the pH was maintained 3.5 and extracted into 0.1 M of *n*-octylaniline in xylene. The organic phase was stripped with 2% NaCl + 1 M HCl (4:1) solution. Back stripped ruthenium(III) in aqueous phase was estimated by 4'-Chloro PTPT [44] (Flow sheet 1).

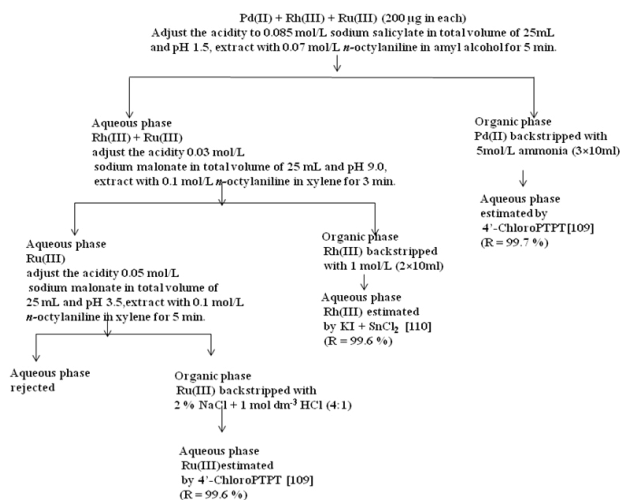
Table 7: Sequential separation of palladium(II), rhodium(III) and ruthenium(III) form their mixture

Metal ion	Amount taken, μg	Aqueous phase (25 mL)	Stripping agent	Determination method	Percentage recovery *
Pd(II) ^a	200	pH=1.5, 0.085 M salicylate, 0.07 M <i>n</i> -octylaniline in amyl alcohol	5 M (3×10 mL)	4'-ChloroPTPT [44]	99.7
Rh(III) ^a	200	pH=9.0, 0.03 M malonate, 0.1M <i>n</i> -octylaniline in xylene	1 M HCl (2×10 mL)	SnCl ₄ + KI [45]	99.6
Ru(III)	200	0.05 M malonate, pH=3.5, 0.1M <i>n</i> -octylaniline in xylene	2 % NaCl + 1 M (4:1)	4'-ChloroPTPT [44]	99.6

* Average of six determinations

Flow Sheet

Sequential separation of palladium(II), rhodium(III) and ruthenium(III) form their mixture



4.3 Determination of palladium(II) from synthetic mixture and synthetic mixture corresponding to alloys

The proposed method was applied to the

extraction and determination of palladium(II) from salicylate media at pH 1.5 in various ternary mixtures. Palladium(II) is extracted with 0.07 M *n*-octylaniline in xylene while Pt(IV), Ir(III), Te(IV), Se(IV) remained unextracted in the aqueous phase. However, Ru(III) masked by 25 mg citrate. The extracted palladium(II) was stripped with 5 M ammonia (3×10 mL) and determined by 4'-Chloro PTPT method spectrophotometrically (Table 8).

Similarly, the proposed method was applied for analysis of synthetic mixture corresponding to alloys such as oakay alloy, jewellery alloy, copper alloy, antimony alloy. The real samples of these alloys were not available at working place, which forced as to use synthetic mixture with corresponding composition to alloys, the palladium(II) was extracted under its optimum extraction conditions and determined spectrophotometrically, the result of analysis are reported in (Table 9).

Table 8: Determination of palladium(II) in synthetic mixtures

Synthetic mixture	Palladium(II) taken, μg	Palladium(II) found, μg	R* (%)	R.S.D., (%)
Pd(II)	200			
Ru(III) ^a	100	199.2	99.6	0.4
Pt(IV)	100			
Pd(II)	200			
Ir(III)	100	199.4	99.7	0.3
Pt(IV)	100			
Pd(II)	200			
Ir(III)	100	199.2	99.6	0.4
Ru(III) ^a	100			
Pd(II)	200			
Pt(IV)	200	199.4	99.6	0.4
Te(IV)	200			
Pd(II)	200			
Pt(IV)	200	199.5	99.8	0.2
Se(IV)	200			

^aMasked by 25mg citrate, * Extraction recovery

Conditions: Palladium(II) = 200 µg, pH = 1.5, sodium salicylate = 0.085 M, aq: org ratio = 2.5: 1, extractant = 0.07 M *n*-octylaniline in xylene, strippant = 5 M ammonia (3×10 mL)

Table 9: Determination of palladium(II) from synthetic mixture corresponding to alloys

Alloys	Palladium(II) taken, µg	Palladium(II) found, µg	R* (%)	R.S.D., %
Oakay alloy:				
Pd-10.5, Pt-20,	105	104.5	99.5	0.5
Ni-60, V-9.5.	90	89.3	99.3	0.4
Pd-18.2, Pt-18,				
Ni-54, V-9.1				
Jewellery alloy				
: Pd-95.5, Ru ^a	105	104.5	99.5	0.5
-4.5				
Pd-Cu alloy	190	189.6	99.7	0.3
Pd-60, Cu-40	120	119.6	99.6	0.4
Pd-75,Sb-25	150	149.7	99.8	0.3

^a Masked by 25mg citrate, * Extraction recovery

Conditions: Palladium(II) = 200 µg, pH = 1.5, sodium salicylate = 0.085 M, aq: org ratio = 2.5: 1, extractant = 0.07 M *n*-octylaniline in xylene, strippant = 5 M ammonia (3×10 mL)

4.4 Determination of palladium(II) in catalysts

A known weight of catalyst was dissolved in a mixture of concentrated HCl and HNO₃, (3:1). After the reaction was over, the solution was heated with two 5 mL portions of concentrated HCl until complete removal of oxides of nitrogen. The residue was dissolved in 10 mL of 1 M HCl and filtered to remove carbon and barium sulphate. The residue was washed with diluted hydrochloric acid. The filtrate and washings were collected and diluted with water in standard volumetric flask. An aliquot of the sample solution was taken and palladium(II)

was extracted and determined by using the recommended procedure (Table 10).

Table 10: Determination of palladium(II) in catalysts

Catalyst	Palladium(II) found (µg)	R (%)	R.S.D., (%)
PdCl ₂ on Carbon	239.2	99.2	0.8
PdCl ₂ on Carbon (5 %)	239.5	99.3	0.7
PdCl ₂ on Carbon (10 %)	239.2	99.2	0.2
PdCl ₂ on CaCO ₃	239.5	99.3	0.7
PdCl ₂ on BaSO ₄	239.7	99.4	0.6

5. Conclusions

1. The developed method is reliable, as can be seen from the complete agreement of the results observed for the analysis of various practical samples with added palladium(II).
2. The satisfactory recovery of palladium(II) from these samples also indicated that the developed method is suitable for the separation and concentration of palladium(II) from solution of complex composition. It permits the separation of palladium(II) from other platinum group metals, gold and base metals.
3. The method is highly selective, rapid, and reproducible and permits the rapid separation and determination of micro amount of palladium(II). The extraction of palladium(II) with *n*-octylaniline in xylene is an endothermic reaction.
4. *n*-Octylaniline synthesized by low cost

with high yield in best purity and recovered for reuse without loss of extraction efficiency. Low reagent concentration (0.07 M) is required for quantitative recovery of palladium(II). It is free from interference of large number of foreign ions which are commonly associated with palladium(II) in its natural occurrence.

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