Development of a Reliable Method for the Spectrophotometric Determination of Palladium(II) with o-Methoxyphenyl Thiourea: Separation of Palladium from Associated Metal Ions

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ABSTRACT

A simple and sensitive method is described for the solvent extraction and spectrophotometric determination of palladium(II) using low concentrations of o-methoxyphenyl thiourea (OMePT). Trace concentrations of palladium(II) were quantitatively extracted when equilibrated with OMePT in chloroform at 1.0 mol L^{-1} hydrochloric acid media for 10 s. The absorbance of a yellow coloured palladium(II)-OMePT complex was measured at 325 nm. The palladium(II)-OMePT complex was stable for more than 72 h. The composition of extracting species was 1:1, determined by mole ratio, Job's continuous variation method and it was confirmed by a log–log plot. Beer's law was obeyed up to 15.0 μg mL^{-1}. The molar absorptivity and Sandell's sensitivity were 3.38×10^3 L mol^{-1} cm^{-1} and 0.031 μg cm^{-2}, respectively. The method was free from a large number of interferences from cations and anions. The method was applied for separation of palladium(II) from multi-component mixtures and synthetic mixtures corresponding to alloy.

1. Introduction

Palladium is a rare and lustrous silvery white metal. It has a wide range of applications in the chemical industry. Palladium is biologically important for determination of N-acetyl-L-cysteine[1] and nucleic acids.[2] It catalyzes the oxidative degradation of paracetamol.[3] Palladium (II) is used in the jewellery and cosmetics industry in the form of alloys.[4,5] The use of palladium is growing continuously and its health hazards are also observed.[6] The literature review gives a clear representation of the widespread applications of palladium. Hence it is necessary to determine palladium in various samples. Amongst available methods, spectrophotometric methods are widely used as these are easy, with high accuracy and precision. Extraction of palladium is reported using 5-chloro-8-hydroxy-7-iodoquinoline as a chromophore,[7] the method has a narrow Beer's range (0.0–2.6 μg mL^{-1}). A reagent, 1-(2-quinolylazo)-2,4,5-trihydroxybenzene (QATB), forms coloured complexes with palladium in acidic and basic media.[8] With this method iodide, thiosulfate and manganese interfere seriously. The extractive spectrophotometric determination method has been reported using five thiosemicarbazone reagents,[9] although limited parameters were studied, specifically the effect of solvent and that of pH. Spectrophotometric determination of palladium was carried out using p-[N,N-bis(2-chloroethyl)amino] benzaldehyde thiosemicarbazone,[10] while Pt(IV), Cu(II) and I$^-$ interferes with the method.

In our laboratory, we have developed extraction and spectrophotometric determination methods for platinum(IV)[11] and ruthenium(III)[12] using o-methylphenyl thiourea (OMPT). Here we report the analytical applications of OMePT for spectrophotometric determination of palladium(II). The proposed method uses OMePT as a new chromogenic ligand, and when compared with other methods, it is found to be more sensitive and selective (Table 1).[13–26]

2. Experimental

2.1. Instrumentation

A double-beam UV-visible spectrophotometer (Elico, model SL-191) with matching 10 mm quartz cells was used for absorbance measurements. An electronic balance (Contech, model CA-123) was used for weighing purposes. Calibrated glassware were used and are cleaned by soaking in dilute nitric acid followed by washing with soap and rinsed two times with water.

A Systronics 8130 atomic absorption spectrometer equipped with a hydride generator was used for comparative purposes.

2.2. Reagents

All the reagents used were of analytical reagent grade unless otherwise stated. A standard stock solution of palladium (II) was prepared by dissolving 1.0 g palladium (II) chloride (PdCl$_2$) (Loba Chem) in 1.0 mol L^{-1} hydrochloric acid and diluted to 250 mL in a calibrated flask with distilled water and was standardized by a gravimetric method.[27] A working standard solution of palladium (II) 75 μg mL^{-1} was prepared by diluting

Table 1 Comparison of reagents and methods.

Reagents	Acidity/mol L^{-1} or pH	Beer's range /µg mL^{-1}	Molar absorptivity /L mol^{-1} cm^{-1}	Remark	Ref.
1-nitroso2-hyd roxynapthalene-3,6-disulphonate	pH 2.0	0.015–0.3	8.77 × 10^5	Narrow Beer's range, heating time 5 min	13
2-[(2-carboxy-4-iodophenyl)azo]4,5diphenylimidazole	pH 9.0	0.1–0.9	4.33 × 10^4	10 min standing time	14
4-(2-Pyridyl azo)-resorcinol	pH 9.0–11.0	0.1–2.0	8.0 × 10^5	90 °C, 4.0 min heating	15
Picramineepsilon	H$_2$SO$_4$ 5.0	0.02–0.4	2.01 × 10^4	Heating 10 min, Narrow Beer's range	16
2-Hydroxy-5-methylacetopheneoneisonicotinoyllhydrazone	H$_2$SO$_4$ 0.01–0.015	2.0–9.0	5.32 × 10^3	Limited interference study	17
Hexylbenzimidazolylsulfide	HCl 0.01–0.1	0.01–0.6	2.08 × 10^5	Narrow Beer's range	18
N-ethyl-3-carbazole carbaxaldehyde thiosemicarbazone	pH 4.0	0.0–6.6	1.64 × 10^4	3.0 min shaking, multiple extraction	19
3-Hydroxy-2-methyl-1-phenyl-4-pyridone	pH 1.5–3.0	0.28–8.0	1.89 × 10^4	Shaking time 35 min	20
3,4,5-trimethoxybenzaldehyde thiosemicarbazone	Conc. HCl 0.8 mL	0.0–12.0	8.35 × 10^4	Multiple extraction, 2.0 min shaking	21
Benzildithiosemicarbazone	pH 2.5	0.25–3.5	3.01 × 10^4	Analysis of synthetic mixtures and hydrogenation catalyst	22
3-Methoxysalicylaldehyde-4-hydroxybenzoylhydrazone	pH 4.5	0.287–4.256	1.03 × 10^3	Presence of surfactant, analysis of catalyst	23
2-(quinolylazo)-5-diethylaminobenzoic acid	HCl 0.05–0.5	0.01–1.2	1.43 × 10^5	Narrow Beer's range, standing time 10 min	24
Azure I	pH 4.0 acetate buffer	5.0–200.0	NM	No applications studied, Au(III), Pt(IV), Hg(II) interferes	25
Dahlia Violet	H$_2$SO$_4$ 0.02	0.001–0.028	NM	100 °C, 60 min heating and sudden ice cooling	26
o-Methoxyphenyl thiourea	HCl 1.0	0–15	3.38 × 10^3	Selective and sensitive, low reagent concentration	PM

NM: not mentioned; PM: present method.

the standard stock solution with distilled water. OMePT was prepared using the method reported by Frank and Smith.[28] The working reagent solution (1.0×10^{-4} mol L^{-1}) of OMePT was prepared in chloroform. Other standard solutions of different metal ions were prepared by dissolving their respective salts in water and diluted suitably. Double-distilled water was used throughout the work.

2.3. Recommended Procedure

Hydrochloric acid was added to an aliquot of solution containing 75 μg of Pd(II) in a 25 mL calibrated flask, to maintain the acidity of 1.0 mol L^{-1} on dilution up to mark with distilled water. The aqueous solution was equilibrated with 10 mL, 1.0×10^{-4} mol L^{-1} OMePT in chloroform for 10 s, in a 125 mL separatory funnel. The two phases were allowed to separate, where the organic phase containing the yellow coloured palladium (II)-OMePT complex was collected and dried over anhydrous sodium sulphate. The total volume of organic phase was made up to 10 mL with chloroform and the absorbance of palladium(II)-OMePT complex was measured at 325 nm against the reagent blank.

The recommended method was successfully applied for separation and determination of palladium (II) from associated metal ions. After extraction of Pd(II) from a synthetic sample, added metal ions W(VI) and Mo(VI) were determined spectrophotometrically in aqueous solution using the thiocynate method at 403 and 470 nm wavelength, respectively.[29] Mn(II) was determined spectrophotometrically by the permanganate method at 528 nm while Mg(II) was determined at 545 nm with Titan yellow.[29] To enhance the extraction of palladium (II) in the presence of Co(II), this metal ion was masked with EDTA and the recommended method was followed for quantitative extraction of palladium(II) into 10 mL chloroform, where the aqueous phase contained the masked Co(II). It was de-masked by treatment with 3.0 mL nitric acid and evaporated to moist dryness followed by 3.0 mL concentrated hydrochloric acid treatment. The residue was cooled, dissolved in water and Co(II) was determined spectrophotometrically at 620 nm.[29]

Palladium(II) was extracted and determined in synthetic mixtures corresponding to alloys. Various synthetic mixtures were prepared as per the composition of alloys to maintain the proportion of metals in the respective alloy, *viz*. jewellery alloy, low-melting dental alloy, Okay alloy and Pd-Cu alloy.

3. Results and Discussion

3.1. Absorption Spectra

Figure 1 shows the absorption spectra of the palladium(II)-OMePT complex in chloroform with a maximum at 325 nm, whereas the absorption spectrum due to reagent blank is negligible. Therefore, all the absorbance measurements were made at 325 nm against the reagent blank for further spectrophotometric determination of palladium(II).

3.2. Effect of Acid Type and Concentration

For finding the optimum acid conditions, the extraction of palladium(II) was studied using different mineral acid media *viz*. hydrochloric acid, sulphuric acid, nitric acid and perchloric acid using 1.0×10^{-4} mol L^{-1} reagent in chloroform, in a range of 0.1 to 10.0 mol L^{-1} acid concentrations. Complete complexation of palladium(II)-OMePT complex with maximum absorbance was observed in the range 1.0 to 8.0 mol L^{-1} hydrochloric acid media (Fig. 2). Therefore 1.0 mol L^{-1} hydrochloric acid concentration was used for this work.
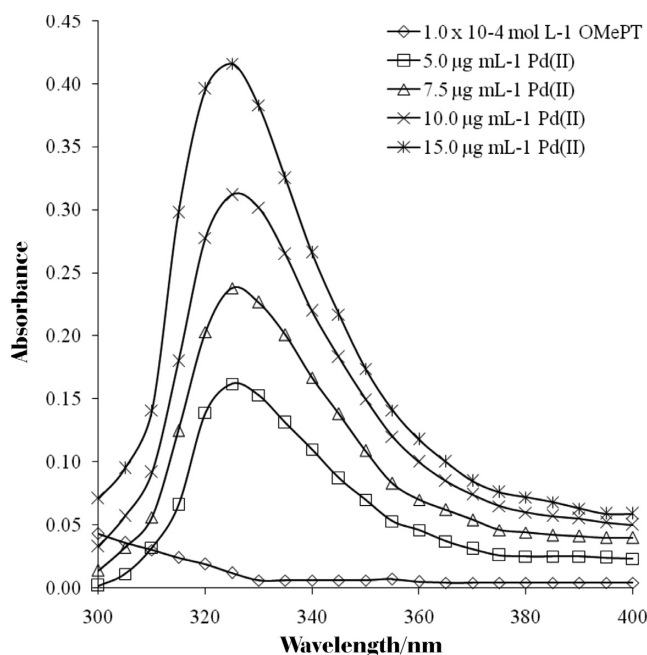

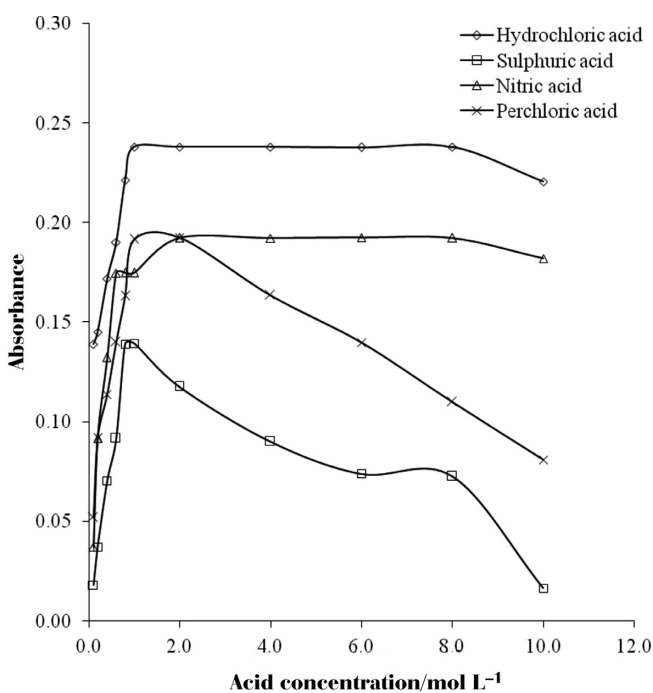**Figure 1** Absorbance spectra of Pd(II)-OMePT *vs*. OMePT reagent blank.

Figure 2 Effect of acid type and concentration on Pd(II)-OMePT complex formation.

3.3. Choice of Solvent

Various extraction solvents *viz*. toluene, xylene, benzene, n-hexane, n-butanol, n-butyl acetate, and chloroform were studied for quantitative extraction of the palladium(II)-OMePT complex (Fig. 3). Amongst the extraction solvents studied, quantitative extraction with maximum absorbance values were obtained in chloroform.

3.4. Effect of Reagent Concentration

The effect of the concentration of OMePT was also investigated, a reagent concentration of 1.0×10^{-4} mol L^{-1} was chosen because it ensured a sufficient reagent in excess. The excess of reagent does not have any adverse effect. Different molar
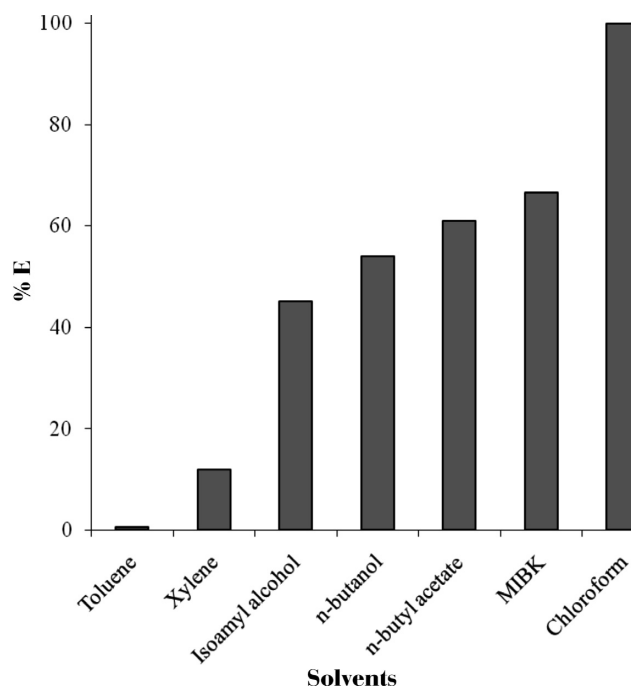
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S. Kuchekar, R. Naval and S.-H. Han,
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229

Figure 3 Effect of extraction solvent on Pd(II)-OMePT complex.

Figure 5 Applicability of Beer's law to Pd(II)-OMePT complex.

concentrations of OMePT from 1.0×10^{-5} mol L^{-1} to 1.0×10^{-3} mol L^{-1} in chloroform were studied for quantitative extraction of palladium(II)-OMePT complex (Fig. 4).

3.5. Effect of Equilibration Time and Stability of the Complex

The study of change in absorbance with variation in equilibration time was carried out over 5 s to 30 min. It has been observed that extraction was completed in 5 s and there was no any adverse effect of prolonged equilibration on extraction of the palladium(II)-OMePT complex up to 30 min. Hence 10 s equilibration time was fixed for further studies. The absorbance of the palladium(II)-OMePT complex remained stable and constant for at least 72 h.
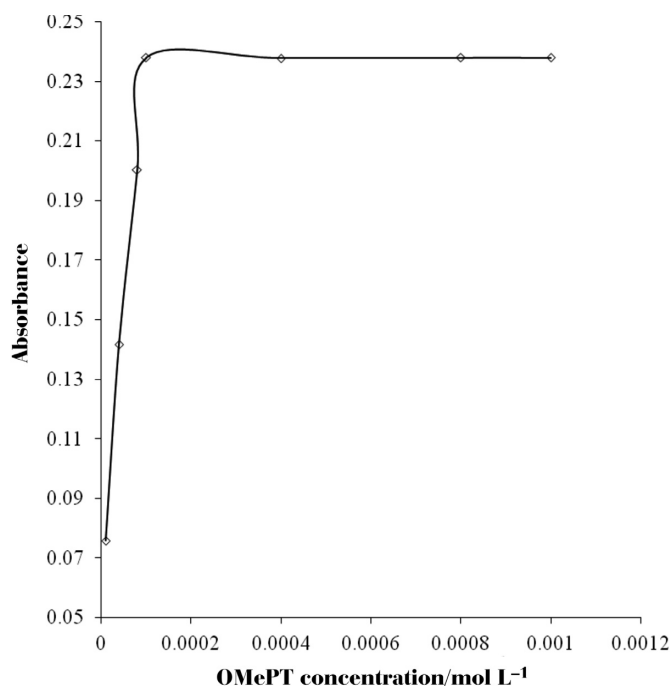
4. Analytical Figures of Merit

The system obeyed Beer's law up to 15.0 μg mL^{-1} of palladium(II) at 325 nm (Fig. 5). The molar absorptivity and Sandell's sensitivity were 3.38×10^3 L mol^{-1} cm^{-1} and 0.031 μg cm^{-2}, respectively. The optimum range as defined by Ringbom's plot[30] (Fig. 6) is 3.98 to 15.00 μg cm^{-3}; slope of Ringbom's plot is 0.7110. Hence, the ratio between the relative error in concentration and photometric error is 3.2391. A literature survey revealed that the proposed method is advantageous in that it has a wide range of validity of Beer's law (Table 1). The correlation coefficient value of Pd(II)-OMePT complex with an independent variable as concentration in μg mL^{-1} and a dependent variable as absorbance was found to be 0.96, indicated a clear linearity
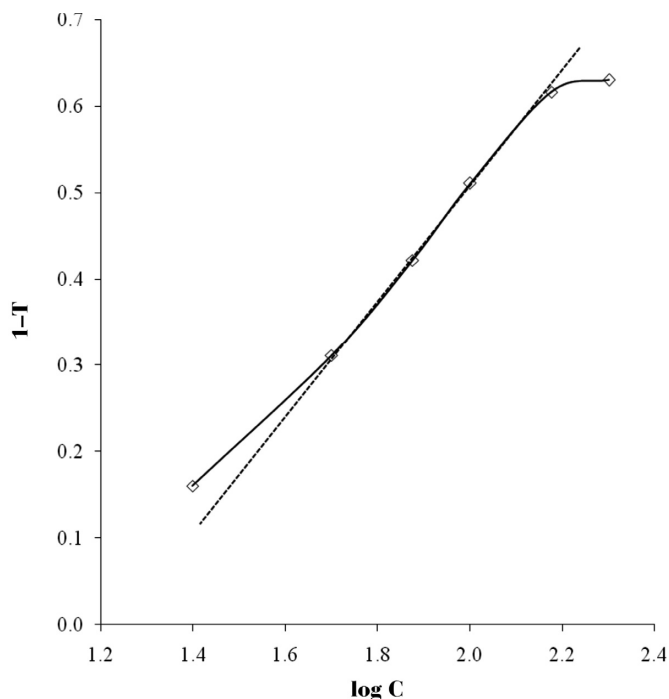

Figure 4 Effect of reagent concentration on Pd(II)-OMePT complex.

Figure 6 Ringbom's plot for Pd(II)-OMePT complex.

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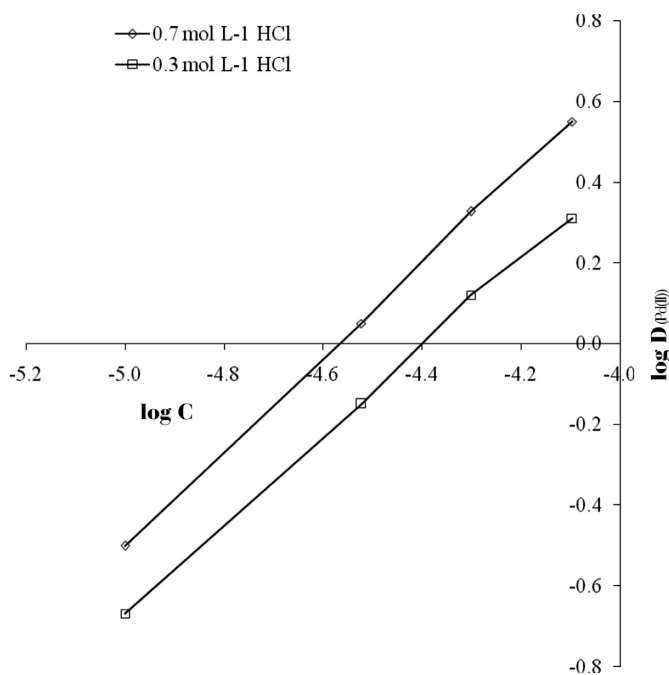
230

Figure 7 Plot of log $D_{Pd(II)}$ *vs.* log $C_{(OMePT)}$.

between these variables. The slope value and intercept for the best fitted line were obtained are 0.0209 and 0.0634. Therefore the content of palladium(II) in real samples can be determined using the straight line equation $y = 0.0209x + 0.0634$.

The molar ratio of palladium(II) to OMePT in the complex was determined by the slope ratio, Job's method of continuous variation and the mole ratio methods. The plot of $\log D_{Pd(II)}$ against $\log C_{OMePT}$ at 0.7 mol L^{-1} and 0.3 mol L^{-1} hydrochloric acid concentrations shows linearity with slopes 1.17 and 1.09, respectively, as shown in Fig. 7. The probable composition of the complex Pd(II) : OMePT was therefore 1:1. This composition was also verified by the mole ratio method (Fig. 8) and was confirmed by Job's continuous variation method (Fig. 9).
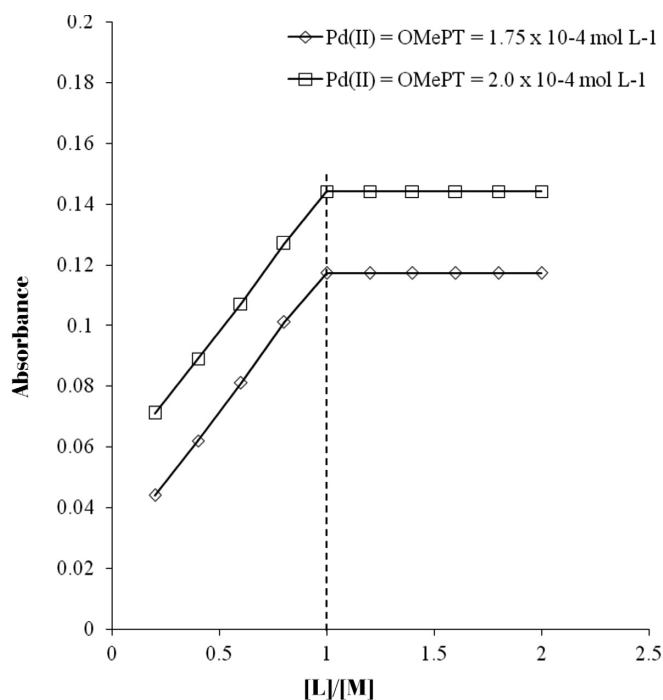

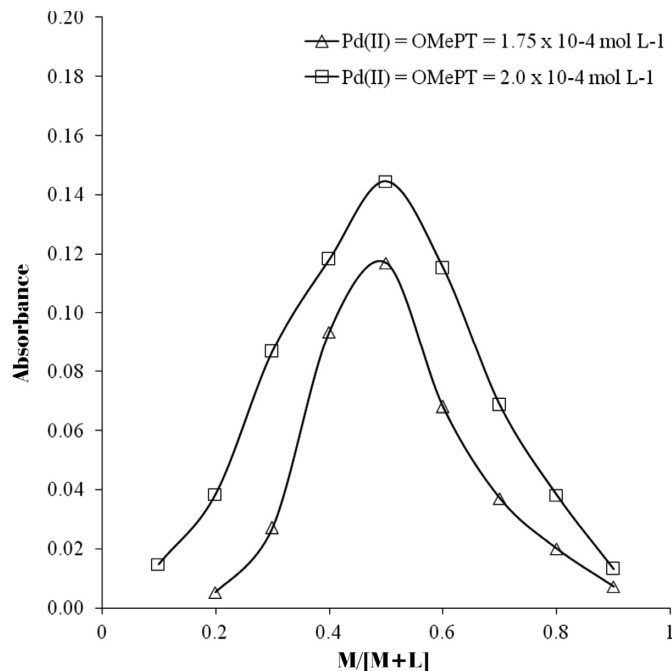**Figure 8** Mole ratio method for Pd(II)-OMPT complex.

Figure 9 Job's continuous variation method for Pd(II)-OMePT complex.

4.1. Interference Study

Various amounts of foreign ions were added to a fixed amount of palladium(II) in order to find the tolerance limits of these ions in extraction spectrophotometric determination of Pd(II) (Table 2). An error of ±2% in the absorbance values was considered to be tolerable. The only interfering ion was silver(I) because of its precipitation as silver chloride.

4.2. Precision and Detection Limit

To test the precision of the method, five successive measurements on the sample solution were carried out. The small RSD indicated a high precision. The detection limit for palladium(II) was 0.038 μg mL^{-1}, and it is determined as amount corresponding to thrice the standard deviation blank value.

5. Applications

5.1. Separation and Determination of Palladium(II) from Binary Synthetic Mixtures

The proposed method permits separation and determination of palladium(II) from associated metal ions containing Mn(II), Mo(VI), W(VI), Mg(II) and Co(II). Palladium(II) was separated from Mn(II), Mo(VI), W(VI) and Mg(II) as per the recommended procedure (section 2.3). The results are reported in Table 3. The percentage relative standard deviation indicates good accuracy of the method.

5.2. Separation of Palladium (II) from Synthetic Mixtures Corresponding to Alloys

As real samples were not available in the laboratory, palladium was determined in synthetic mixtures corresponding to alloys. From these alloys palladium was selectively determined by the method presented here. The results were in good agreement with those obtained by atomic absorption spectroscopy. The results are reported in Table 4.

6. Conclusion

The proposed method was simple, sensitive, selective, reproducible and rapid with low OMePT concentration. The quantita-

Table 2 Influence of foreign ions.

Foreign ions	Added as	Tolerance limit/mg	Foreign ions	Added as	Tolerance limit/mg
Mn(II)	$MnCl_2.6H_2O$	12.0	Ba(II)	$BaCl_2 6H_2O$	50.0
Cd(II)	$CdCl_2.2H_2O$	8.00	Ca(II)	$CaCl_2 2H_2O$	50.0
Fe(III)	$(NH_4)Fe(SO_4)_2.12H_2O$	10.0	Tl(III)	Tl_2O_3	0.40
Hg(II)	$HgCl_2$	4.50	In(III)	$InCl_3.4H_2O$	0.12
Bi(III)	$BiCl_3$	22.0	Rh(III)	$RhCl_3$	1.00
Ni(II)[b]	$NiCl_2.6H_2O$	9.80	Pt(IV)	H_2PtCl_6	1.00
Cu(II)[b]	$CuSO_4.5H_2O$	5.00	Os(IV)	OsO_4	0.03
Al(III)	$AlCl_3.6H_2O$	21.0	Ru(III)	$RuCl_3.3H_2O$	1.00
La(III)	$LaCl_3.7H_2O$	1.00	As (III)[b]	As_2O_3	1.2
Li(I)	LiCl	20.0	W(VI)	$Na_2WO_4.2H_2O$	4.5
Mg(II)	$MgCl_2.6H_2O$	25.0	Fluoride	NaF	100
Sn(II)	$SnCl_2.2H_2O$	0.08	Phosphate	Na_3PO_4	100
Ga(III)	$GaCl_3$	0.10	Sulphate	K_2SO_4	100
Au(III)	$HAuClO_4.H_2O$	0.10	Succinate	$CH_3(COONa)_2.6H_2O$	100
Mo(VI)	$(NH_4)_6MO_7O_{24}.2H_2O$	6.00	Citrate	$C_6H_8O_7.H_2O$	100
V(V)	V_2O_5	10.0	Malonate	$CH_2(COONa)_2$	100
Ce(IV)	$Ce(SO_4)_2.4H_2O$	0.60	Tartrate	$(CHOH:COOH)_2$	100
Pb(II)	$PbCl_2$	8.00	Acetate	$CH_3COONa.3H_2O$	100
U(VI)	$UO_2(CH_3COO)_2.2H_2O$	1.00	Oxalate	$Na_2C_2O_4.2H_2O$	100
Co(II)[b]	$CoCl_2.6H_2O$	12.0	EDTA	Na_2EDTA	100
Ag(I)	$AgNO_3$	0.25			

[b] Masked with 100 mg EDTA.

Table 3 Separation and determination of Pd(II) from binary synthetic mixtures.

Mixture	Amount taken/μg	Recovery[a] /%	%RSD	Chromogenic ligand	Ref.
Pd(II)	75	99.55	0.36	OMePT	–
Co(II)[b]	200	99.47	0.65	Thiocynate	29
Pd(II)	75	99.31	0.52	OMePT	–
Mn(II)	300	99.37	0.56	Permanganate	29
Pd(II)	75	99.54	0.36	OMePT	–
Mo(VI)	40	99.58	0.33	Thiocynate-$SnCl_2$	29
Pd(II)	75	99.48	0.49	OMePT	–
W(VI)	30	99.40	0.82	Thiocynate	29
Pd(II)	75	99.30	0.51	OMePT	–
Mg(II)	30	99.15	0.84	Titan yellow	29

[a] Average of 6 readings.
[b] Masked with EDTA.

tive extraction was carried out in a single step. In comparison, other reported methods (Table 1) suffer from interferences from cations and anions and were less sensitive. The proposed method was free from interferences from a large number of cations and anions. Reported methods need a laborious and lengthy procedure to be adopted; while with the proposed method there was instantaneous complex formation with 1.0 mol L^{-1} hydrochloric acid (Table 1). Minimum acidic conditions also improve the merit of this method. The palladium(II)-OMePT complex was stable for more than 72 h. The proposed method was successfully applied for the determination of palladium(II) from synthetic mixtures corresponding to a range of alloys.

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Table 4 Separation of palladium (II) from synthetic mixtures corresponding to alloys.

Alloy	Composition/%	Amount of palladium (II)			R.S.D.
		Taken/μg	Found/μg		
			AAS	PM[a]	
Jewellery alloy	Pd 95.0; Rh 4.0; Ru 1.0.	75.0	74.93	74.91	0.08
Low-melting dental alloy	Pd 34; Au 10; Co 22; Ni 34	75.0	74.89	74.93	0.11
Okay alloy	Pd 18.2; Pt 18.2; Ni 54.2; V 9.1	75.0	74.98	74.97	0.03
Pd-Cu alloy	Pd 60; Cu 40	75.0	74.93	74.92	0.13

[a] Average of three determinations.

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