Solvent Extraction and Spectrophotometric Determination of Palladium(II) Using P-Methylphenyl Thiourea as a Complexing Agent

Shashikant R. Kuchekar, Somnath D. Bhumkar, Haribhau R. Aher, Bhaskar H. Zaware, Ponnadurai Ramasami

Abstract—A precise, sensitive, rapid and selective method for the solvent extraction, spectrophotometric determination of palladium(II) using para-methylphenyl thiourea (PMPT) as an extractant is developed. Palladium(II) forms yellow colored complex with PMPT which shows an absorption maximum at 300 nm. The colored complex obeys Beer's law up to 7.0 µg ml^{-1} of palladium. The molar absorptivity and Sandell's sensitivity were found to be 8.486 x 10^3 l mol^{-1}cm^{-1} and 0.0125 µg cm^{-2} respectively. The optimum conditions for the extraction and determination of palladium have been established by monitoring the various experimental parameters. The precision of the method has been evaluated and the relative standard deviation has been found to be less than 0.53%. The proposed method is free from interference from large number of foreign ions. The method has been successfully applied for the determination of palladium from alloy, synthetic mixtures corresponding to alloy samples.

Keywords—Para-methylphenyl thiourea, palladium, spectrophotometry.

I. INTRODUCTION

IN present days an increasing demand of precious metals for technological application is due to their exceptional physical and chemical properties. Solvent extraction is the potential analytical technique used for the separation of precious metals due to its simplicity and wide applications. The technique has been extensively utilized in the mining industry; it is one of the most important processes for the recovery of the precious metals from waste water or scraps [1]. Palladium is a lustrous silver-white platinum group metal. It is strongly resistant to corrosion and to the action of acids except nitric acid at ordinary temperature. It forms many compounds and several complex salts. Abundance of palladium in earth's crust is 0.015 ppm [2]. Among the platinum group metals, palladium has lowest density and melting point. It is an important industrial catalyst. It exists in minerals like stibopalladinate, brageite and in several nickel sulphide ores. It has great

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affinity to absorb hydrogen up to 900 times to its own volume at room temperature.

Over the last 10 years several research groups published the review articles on the application of palladium complexes as potential anti-cancer and anti-tumer agents [3].

The metal may enter the environment and interact with complexing materials, such as humic substances. Palladium has no biological role; its compounds are highly toxic and potentially carcinogenic [4]. In recent years various reagents have been studied for liquid-liquid extraction of palladium(II) including hexadecylpyrimidinium bromide [5], 1-octyltheobromine [6], pyridoxal-4-phenyl-3-thiosemicarbazone [7], 5-chloro-8-hydroxy-7-iodoquinoline [8].

A common extractive spectrophotometric determination method has been reported with five thiosemicarbazone derivatives [9]. With these reagents very few parameters viz. effect of pH and effect of solvents were studied. 3, 4, 5-trimethoxybenzaldehyde thoi semicarbazone-palladium complex was studied after multiple extractions using 3 ml chloroform [10]. Synergic extraction of palladium was carried out using p-[4(3, 5-dimethylisoxazolyl) azophenylazo] calyx (4) arene [11], it requires 1 h centrifugation and 10 min standing time.

Derivative spectrophotometry is also effective method for the simultaneous determination of two metal ions. First order derivative spectrophotometric determination of palladium(II) has been reported using diacetylmonoxime-(*p*-anisyl)-thiosemicarbazone [12] and 2-(2-thiazolylazo)-5-dimethylaminobenzoic acid [13]. 2-hydroxy-3-methoxy benzaldehyde thiosemicarbazone (HMBATSC) has been used for direct and second derivative spectrophotometric determination of palladium [14]. Third order derivative spectrophotometric determination of vanadium and palladium using 2-hydroxy-1-naphthaldehyde-p-hydroxy benzoichydrazone [15] and 3-hydroxy-2-methyl-1-phenyl-4-pyridone were reported [16]. Solid phase extraction process was used for the determination of palladium using variety of reagents viz. 2-(2-quinolylazo)-5-dimethylaminoaniline [17], 4-(2-pyridylazo)-5 diethylaminobenzoic acid [18], and 1-phenyl-3-methyl-4-benzoyl-5-pyrazone [19].

In present work we report the analytical method for spectrophotometric determination of palladium(II) using PMPT. The comparison of present method with existing methods was reported [20]-[43] in Table I.

TABLE I
COMPARISON OF PRESENT METHOD AND REPORTED METHODS

Reagent	Acidity/pH	Solvent	λ max nm	Beers range/ µg ml^{-1}	Molar absorptivity/ l mol^{-1} cm^{-1}	Remark	Reference
2-mercaptoethanol	pH= 4	water	315	1.39-8.36	2.2634×10^4	No extraction	[20]
2-[(E)-N-(2—{[2-[(E)-[(2-hydroxyphenyl) methylildene] amino] phenyl (methyl) amino} phenyl) carboximidoyl] phenol (HHMCP)	pH= 9.0	chloroform	560	0-100	4.7×10^1	1.5 min shaking time, very few diverse ions studied	[21]
2-hydroxy-5 methylacetophenone isonicotinoyl hydrazone (HMAINH)	0.010-0.015 mol l^{-1} sulphuric acid	chloroform	385	2.0 - 9.0	5.320×10^3	Effect of diverse ions was not studied	[22]
4-(4′- pyrazolon azo) resorcinol (APAR)	pH =5.5	Ethanol	595	0.2-1.4	1.11×10^4	Narrow Beers range	[23]
4-[N'-(4-imino-2-oxo-thiazolidin-5-ylidene)-Hydrazine]-benzenesulfonic acid (ITHBA)	pH = 2.0–12.0	water	438	0.2–2.2	7.5×10^3	No extraction	[24]
2,4-dihydroxybenzoylhydrazone	pH =5.5	water	375	1.06-8.51	8.5×10^3	Pd^{2+} & Au^{3+} determined simultaneously	[25]
1-(2-pyridylazonapthol)	2.0 mol l^{-1} HNO$_3$	n-butanol	659, 681	0.0-2.9 ng mL^{-1}	NR	10 min equilibration time	[26]
Dahlia Violet	0.02 mol l^{-1} H$_2$SO$_4$	water	585	0.001-0.028	NR	Heating at 100°C for 60 min & sudden cooling	[27]
1,3-bis(hydroxymethyl)benzimidazole-2-thione	0.3-3.5 mol l^{-1} HClO$_4$	Methyl isobutyl ketone	370	6.00	1.543×10^4	Thiocynate, thiourea, thiosulphate interferes	[28]
2-Hydroxy-3-methoxy benzaldehyde t hiosemicarbazone	pH =3	water	445	0.21-12.78	NR	Simultaneous determination of Pd^{2+}& Ru^{3+}	[29]
2-(2-Quinolylazo)-5-diethylaminobenzoic acid	5 mL of 5 mol l^{-1} HCl	water	625	0.01-0.6	1.51×10^5	6 hour stability.	[30]
thioglycollic acid	pH =11	water	385	8.00	2.0692×10^4	Stable for 24 hours	[31]
2-(5- bromo-2- oxoindolin-3-ylidene) hydrazine carbothioamide	pH=0.0-4.0 and 0.1-3.0 mol l^{-1} HCl	n-amyl alcohol	520	1.0 - 30	7.450×10^3	Stability not mentioned	[32]
NaHMICdt·2H$_2$O	pH=0.5-2.0	toluene	435	0.2-0.8	7.54×10^3	applications to real samples results are not reported	[33]
Pyridoxal thiosemicarbazone	pH=2.0	water	420	0.9-10.0	1.63×10^4	low stability	[34]
4-amino-3-mercapto-6-methyl-1, 2, 4-tirazine (4-H)-5-one	pH = 11	water	384	10.4	2.1121×10^4	Zr^{4+}, Mg^{2+} seriously interfere.	[35]
4-(5-bromo-2-pyridyl)-azo-1,3-diaminobenzene	1.0 mol l^{-1} sulfuric acid		566	0-1.0	6.44×10^4	6 min heating Pb^{2+}, Ag^+ and Cr^{6+} interferes	[36]
5-hydroxyimino-4-imino-1,3-thiazolidin-2-one	pH = 5.0	water	350	NR	5.9×10^3	10 min heating required	[37]
Cinnamaldehyde thosemicabazone (CMTSC).	pH= 4.0.	Triton-X (100) (5%) (micellar medium)	400	0.212-1.064	5.0×10^4	Fe^{3+}, Cu^{2+} and Mo^{6+} interferes	[38]
L-Cystine	pH= 4.0.	water	369	2.12 -16.9	2.69×10^4	--	[39]
cefixime	pH =2.6	water	352	0.7502–16.5004	1.224×10^4	few interfering ions were studied	[40]
Benzyloxybenzaldehyde thiosemicarbazone (BBTSC)	pH =5	cyclohexanol	365	5-60	4×10^3	Cu^{2+}, Ni^{2+} interferes seriously	[41]
Azure I	pH=4.0	Water	200	5.0–200.0	NR	Au^{3+}, Pt^{4+}, Hg^{2+} interferes	[42]
N-Ethyl-3-cabazolecarboxaldehyde thiosemi-carbazone (ECCT)	pH=4.0	n-butanol	410	0.0–6.6	1.6×10^4	Pb^{2+}, Hg^{2+},Cd^{2+}, Ni^{2+}, Cu^{2+}, Zn^{2+}, U^{6+}, Se^{4+} and Ce^{4+}; Interferes seriously, even when present at trace level	[43]
PMPT	0.05 mol l^{-1} HBr	Chloroform	300	0-7.0	8.486×10^3	Requires Low acid and reagent concentration.	PM

PM-Present Method

II. MATERIALS AND METHODS

A. Instrumentation

Spectrophotometric study of Pd(II)-PMPT complex were carried out with Systronics double-beam UV-visible spectrophotometer (model AU-2701) using matching 1 cm quartz cells. Contech make electronic balance (model CA-123) was used for weighing.

B. Reagents

AR grade reagents were used throughout the study. The stock Pd(II) solution (3.6 mg mL^{-1}) was prepared by dissolving 1.0 g of palladium(II) chloride in 20 mL 1.0 mol L^{-1} of hydrochloric acid and diluting in 250 mL volumetric flask with distilled water [44] and was standardized by a gravimetric method [45]. A working standard solution of palladium(II) (50 µg ml^{-1}) was prepared by suitable dilution of

the stock solution with distilled water.

PMPT was synthesized according to method in [46]. The stock solution of reagent (0.01 mol l^{-1}) was prepared by dissolving 0.0415 g of PMPT in 25.0 ml chloroform. The working reagent solution (5.0 × 10^{-5} mol l^{-1}) of PMPT was prepared in chloroform by suitable dilution of stock solution. Solutions of different metal ions for foreign ion study were prepared by dissolving their salts in distilled water and diluted suitably.

C. Recommended Method

To an aliquot of solution containing 50 μg of Pd(II) in a 25 ml calibrated flask enough AR grade concentrated hydrobromic acid was added, to maintain the acidity of 0.05 mol l^{-1} on dilution up to the mark with distilled water. The aqueous solution was equilibrated with 10 ml, 5.0 × 10^{-5} mol l^{-1} PMPT in chloroform for 10 seconds, in a 125 ml separatory funnel. The two phases were allowed to separate. The organic phase containing the yellow colored palladium(II)-PMPT complex was collected in 10 mL standard flask, dried over anhydrous sodium sulphate and made up to the mark with chloroform [44]. The absorbance of palladium(II)-PMPT complex was measured at 300 nm against the reagent blank.

III. RESULTS AND DISCUSSION

A. Absorption Spectra

The absorption spectra of the extracted palladium(II)-PMPT complex shows maximum absorption at 300 nm, while the absorption due to reagent blank at that wavelength was negligible (Fig. 1). Hence all the absorbance measurements were done at 300 nm against the reagent blank.
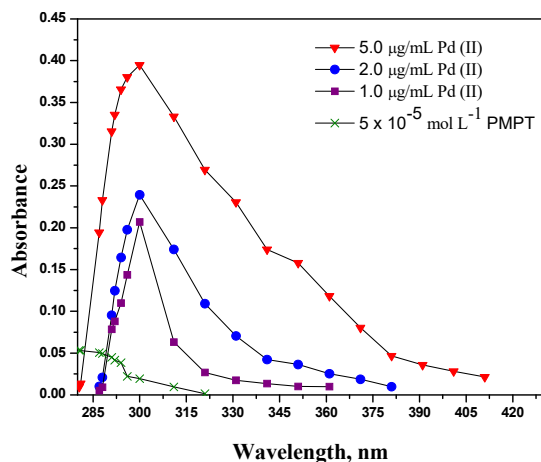

Fig. 1 Absorption spectra of Pd(II)-PMPT complex

B. Effect of Acid Concentration

Extraction of palladium(II) was studied using hydrobromic acid, in concentration range of 0.01 to 3.0 mol l^{-1} using 5.0 × 10^{-5} mol l^{-1} reagent in chloroform. Complete complexation of palladium(II)-PMPT with maximum absorbance was observed in the range of 0.01 to 0.05 mol l^{-1} hydrobromic acid media (Fig. 2). Therefore 0.05 mol l^{-1} hydrobromic acid
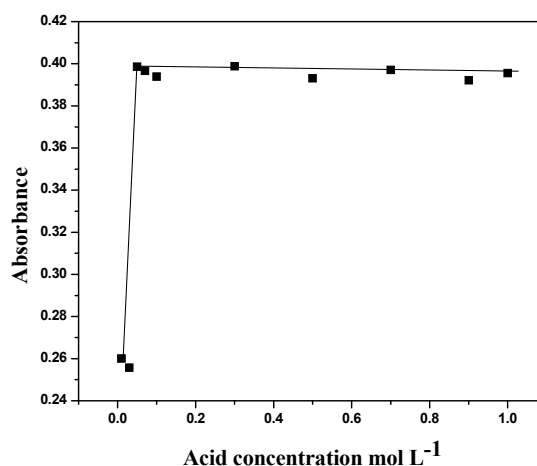
concentration was fixed for further work.

Fig. 2 Effect of HBr concentration

C. Effect of Extraction Solvent

Toluene, xylene, benzene, n-butanol, n-butyl acetate, isoamyl alcohol and chloroform were studied as extracting solvents for quantitative extraction of the palladium(II)-PMPT complex. Amongst the solvents studied, quantitative extraction was obtained in chloroform (Fig. 3.)

D. Effect of Reagent (PMPT) Concentration

The effect of reagent concentration was investigated by varying PMPT concentration from 1 × 10^{-5} to 1.0 ×10^{-3} mol l^{-1} in chloroform. It was observed that the absorbance of Pd(II)-PMPT complex increases with increase in reagent concentration from 1.0 × 10^{-5} mol l^{-1} to 5.0 ×10^{-5} mol l^{-1}. After this range absorbance becomes constant (Fig. 4). The excess of reagent does not have any adverse effect.
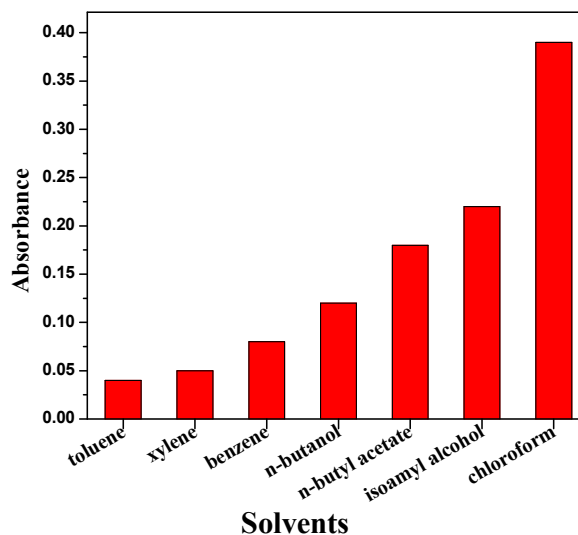

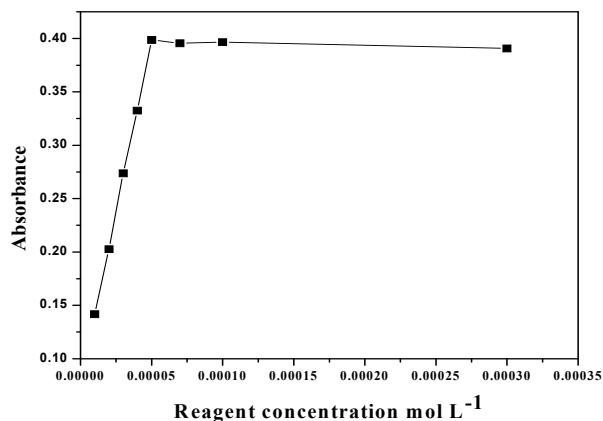Fig. 3 Effect of extraction solvents on Pd(II)-PMPT complex

Fig. 4 Effect of PMPT concentration on Pd(II)-PMPT complex

E. Effect of Equilibration Time and Stability of the Complex

The study of variation in absorbance with equilibration time was carried out over 5 seconds to 10 minutes. It has been observed that 10 seconds equilibration was sufficient for extraction and prolonged equilibration do not affect extraction of the palladium(II)-PMPT complex. Thus 10 seconds of equilibration time was fixed for further studies. The stability of palladium(II)–PMPT complex was studied at room temperature by monitoring the absorbance at regular time intervals of 1.0 h, showing that complex was stable for more than 48 hours.

F. Beer's Law, Molar Absorptivity, Sandell's Sensitivity and Correlation Coefficient

The system obeyed Beer's law up to 7.0 µg ml^{-1} of palladium(II) at 300 nm (Fig. 5). The molar absorptivity and Sandell's sensitivity were 8.486 x 10^3 l mol^{-1} cm^{-1} and 0.0125 µg cm^{-2}, respectively. The optimum range as defined by Ringbom's plot is 2.0 to 7.0 µg cm^{-3} (Fig. 6). Slope of Ringbom's plot is 0.6248. The correlation coefficient value of Pd(II)-PMPT complex with an independent variable as concentration in µg ml^{-1} and a dependent variable as absorbance was found to be 0.831, indicating a clear linearity between these variables. The slope and intercept for the best fitted lines were 0.0064 and 0.043 respectively. Therefore the content of iridium(III) in real samples can be determined using the straight line equation y = 0.0064 x + 0.043.The obtained analytical parameters were summarized in Table II.

G. Stiochiometry of Complex

The probable composition of the extracted complex was studied by the slope ratio, Job's method of continuous variation and the mol ratio methods. The plot of log D $_{Pd(II)}$ against log C$_{PMPT}$ at 0.02 and 0.03 mol l^{-1} hydrobromic acid concentration was linear with slope 1.406 and 1.407 resp. (Fig. 7). Hence the probable composition of the Pd(II): PMPT complex 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).
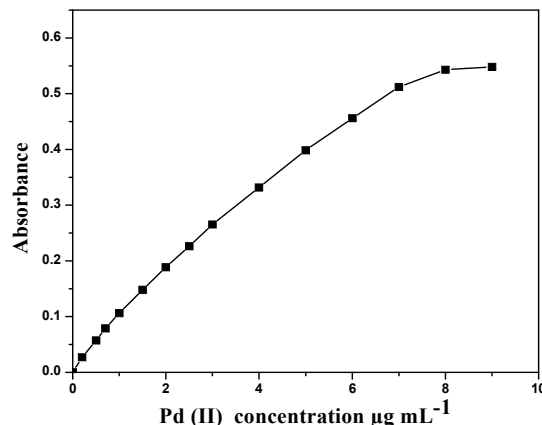

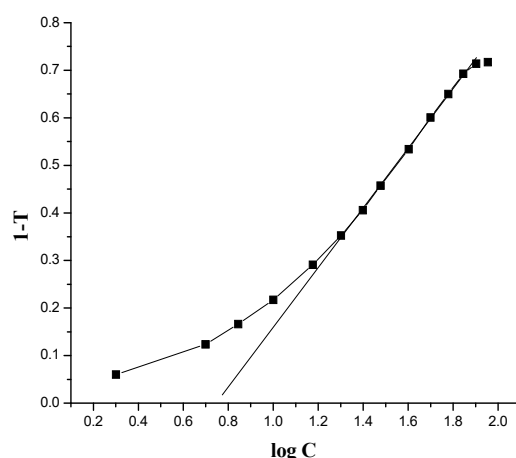Fig. 5 Beers Law range for Pd (II) –PMPT complex

Fig. 6 Ringbom's plot of Pd (II)-PMPT complex

TABLE II
SPECTRAL AND PHYSICOCHEMICAL CHARACTERISTICS OF PALLADIUM(II)-PMPT COMPLEX STUDY

Parameter	Specification
Hydrobromic acid concentration	0.05 mol l^{-1}
Extraction solvent	Chloroform
Reagent concentration	5 x 10^{-5} mol l^{-1}
Equilibration time	10 seconds
λmax	300.0 nm
Molar Absorptivity	8.486 x 10^3 l mol^{-1} cm^{-1}
Sandell's sensitivity	0.0125 µg cm^{-2}
Beers Law range	up to 7.0 µg ml^{-1}
Ringbom's optimum range	2.0 to 7.0 µg ml^{-1}
Correlation coefficient	0.813
Relative Standard Deviation	0.53 %
Stiochiometry of the complex	1:1 (Pd(II):PMPT)
Stability of complex	>48 Hrs.
Limit of detection (LOD)	0.06295 µg ml^{-1}

H. Interference Study

The effect of various foreign ions on quantitative extraction of palladium(II) was studied. Variable amounts of foreign ions were added to a fixed amount of palladium(II) (±2% error in the absorbance value was considered to be tolerable). The interference of Ru(III) was removed by masking with EDTA.

(Table III).

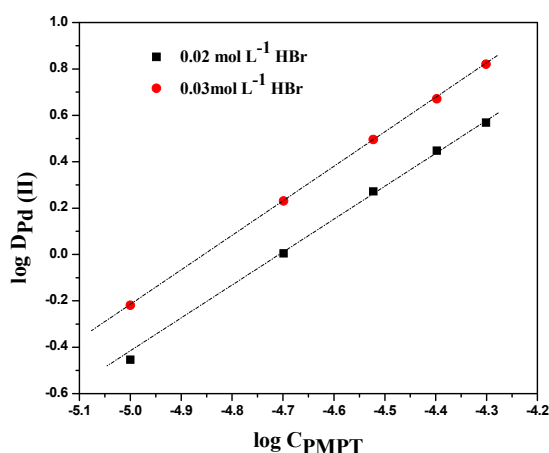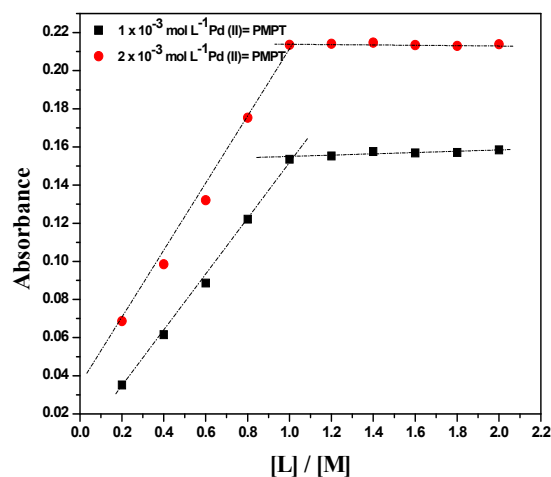Fig. 7 Plot of log $D_{Pd\,(II)}$ Vs log C_{PMPT}

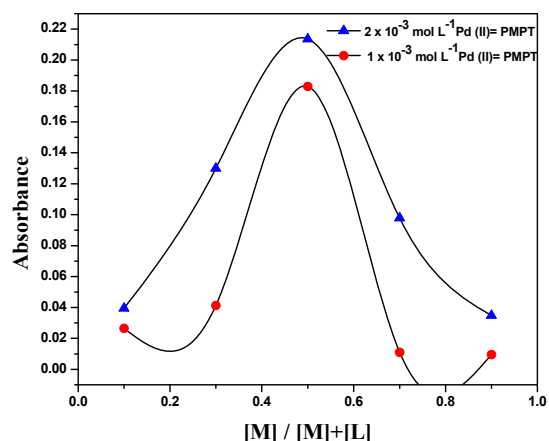Fig. 8 Mole ratio plot for Pd (II) – PMPT complex

Fig. 9 Jobs continuous variation method

Interference study reveals that the developed method was free from interferences from large number of cations and anions.

TABLE III
EFFECT OF FOREIGN IONS ON EXTRACTION OF PALLADIUM(II)-PMPT COMPLEX

Foreign ion	Added as	Tolerance limit, mg
Ni(II)	$NiCl_2.6H_2O$	0.75
Mn(II)	$MnCl_2.6H_2O$	10.0
Cu(II)	$CuSO_4.5\,H_2O$	0.10
Zn(II)	$ZnSO_4.7H_2O$	0.75
Bi(III)	$BiCl_3$	1.50
Co(II)	$CoCl_2.6\,H_2O$	0.75
Cr (III)	$CrCl_3$	0.10
Ti (III)	$Ti_2(SO_4)_3$	1.00
Sn(II)	$SnCl_2.2\,H_2O$	0.25
Hg(II)	$HgCl_2$	0.10
Pb(II)	$PbCl_2$	0.10
Al(III)	$AlCl_3.6\,H_2O$	0.01
Li(I)	LiCl	10.0
Tl(III)	Tl_2O_3	1.00
Fe(III)	$(NH_4)Fe(SO_4)_2.12\,H_2O$	1.00
Se (IV)	SeO_2	10.00
La(III)	$LaCl_3.7\,H_2O$	5.00
Mg(II)	$MgCl_2.6\,H_2O$	0.10
Ca(II)	$CaCl_2.2\,H_2O$	5.00
Cd(II)	$CdCl_2.2\,H_2O$	10.0
Ru(III)[a]	$RuCl_3.3\,H_2O$	0.10
Ba(II)	$BaCl_2.6\,H_2O$	5.00
Rh(III)	$RhCl_3$	0.50
Os(IV)	$OsO4$	0.20
Au(III)	$HAuClO_4.H_2O$	7.50
Sb(III)	Sb_2O_3	1.00
W(VI)	$Na_2WO_4.2\,H_2O$	0.50
Pt(IV)	$H2PtCl_6$	0.10
In(III)	$InCl_3.4H_2O$	0.50
Fluoride	NaF	100
Succinate	$CH_3(COONa)_2.6H_2O$	100
Tartrate	$(CHOH:COOH)_2$	100
EDTA	Na_2EDTA	100
Citrate	$C_6H_8O_7.H_2O$	80.0
Malonate	$CH_2(COONa)_2$	80.0
Oxalate	$Na_2C_2O_4.2H_2O$	80.0
Bromide	KBr	10.0

a: masked with 100 mg EDTA

I. Precision and Detection Limit

To check the reproducibility and accuracy of the method, absorbance of five identical sample solutions were measured. The average of these five measurements and relative standard deviation was determined. The relative standard deviation was less than 0.53%. These results indicate that the developed method was accurate and precise. The limit of detection (LOD) for palladium(II) for recommended method was 0.06295 μg ml^{-1}. It is determined as amount corresponding to thrice the standard deviation blank value.

IV. APPLICATIONS

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

Palladium(II) was extracted and determined in binary synthetic mixtures. After extraction of Pd(II), added metal

ions Co(II) and W(VI) were determined spectrophotometrically in aqueous solution using the thiocynate method at 625 nm and 420 nm wavelength, respectively. Mn(II) was determined spectrophotometrically by the periodate method at 525 nm and Mg(II) was determined at 545 nm by Erichrome Black T method. Estimation of added Ni(II) was carried out with DMG [47] (Table IV).

TABLE IV
SEPARATION OF PALLADIUM (II) FROM BINARY SYNTHETIC MIXTURES

Metal ion	Amount taken (µg)	Recovery [a] (%)	RSD (%)	Chromogenic ligand	Reference
Pd(II)	50	98.61	0.53	PMPT	------
Ni(II)	200	98.69	0.75	DMG	47
Pd(II)	50	99.51	0.20	PMPT	------
Co(II)	100	99.70	0.95	Thiocynate	47
Pd(II)	50	99.78	0.84	PMPT	----
Mn(II)	100	98.70	1.00	Potassium metaperiodate	47
Pd(II)	50	99.74	0.13	PMPT	------
W(VI)	100	99.56	0.16	Thiocynate	47
Pd(II)	50	99.59	0.32	PMPT	------
Mg(II)	50	99.60	0.11	Erichrome Black T	47

a: average of five determinations

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

Various synthetic mixtures were prepared according to the certified composition *viz.* stibopalladinate alloy, jewelry alloy, Pd-Au alloy, low-melting dental alloy, Pd-Ag alloy and Pd-Cu alloy. The recommended method was applied for the extraction and determination of palladium(II). The results obtained were closed to the actual amount of palladium(II) (Table V).

TABLE V
SEPARATION AND DETERMINATION OF PALLADIUM(II) FROM SYNTHETIC MIXTURES CORRESPONDING TO ALLOY

Composition of alloy	Amount of Pd (II) (µg)		Recovery %	RSD %
	Taken	Found [a]		
Stibopalladinate alloy (Pd-75 %, Sb-25%)	50	49.60	99.08	1.31
Jewelry alloy (Pd-95%, Rh-4%, Ru[b]-1%)	50	49.81	99.62	0.40
Pd-Au alloy (Pd-505, Au-50%)	50	49.69	99.36	0.45
Low melting dental alloy (Pd-34%, Au-10%, Co-22%, Ni-24%)	50	49.70	99.39	0.45
Pd-Ag alloy (Pd-60%, Ag-40%)	50	49.50	99.17	0.95
Pd-Cu alloy (Pd-60%, Cu-40%)	50	49.86	99.69	0.16

a: average of five determinations ;
b: masked with 100 mg EDTA

V. CONCLUSIONS

The spectrophotometric properties of PMPT were investigated and it is found out that this reagent forms a stable complex with palladium(II). A simple method of extractive spectrophotometric determination of palladium(II) ion with PMPT, which is characterized by high selectivity, good sensitivity, reproducibility, accuracy and rapidness, is elaborated. It is shown that this is a good method for the determination of palladium(II) when compared to some other

spectrophotometric methods reported earlier. The proposed method has been successfully applied to the determination of palladium in binary mixtures and alloys.

REFERENCES

[1] G. H. Morrison and H. Freiser. Solvent extraction in analytical chemistry, Wiley, New York: pp. 75 (1957)
[2] J.D. Lee, Concise Inorganic chemistry. Blackwell science Ltd. Oxford, UK: pp. 801, (1996).
[3] E. Z. Jahromi, A. Divsalar, A. A. Saboury, and I. Kostova, Journal of Iranian chemical society 13,967–989 (2016).
[4] J. Kielhorn, C. Melber, D. Keller, and I. Mangelsdorf International Journal Hygiene Environmental Health, 205, 417–432 (2002).
[5] N. Alizadh, S. Salimi, and A. Jabbari Anaiytical Sciences, 18,307-311 (2002).
[6] K. Kaikake, and Y. Baba, Solvent Extraction and Ion Exchange, 20, 491-503 (2002).
[7] L.S. Sharma, J.R. Kumar, K.J. Reddy, A.K. Kumar and A.V. Reddy, Analytical sciences, 18,1257-1261 (2002).
[8] S. Nain, N. Agnihotri, and L.R. Kakkar, Journal of Ind. Chem. Society, 85,228-230 (2008).
[9] V.J. Sawant, and S.B. Jagtap International Research Journal, I, 75-77 (2009).
[10] A.M.A. Khader, and K.S. Prasad, Turkish. Journal of Chemistry, 20,222-227 (1996).
[11] A. Kumar, P. Sharma, L .K. Chandel, and B .L. Kalal, J.Incl. Phenom. Macrocycl. chem., 6,335-342 (2008).
[12] A. Varghese, A.M.A. Khader, Indian J. Chem. Technol., 18,177-182 (2011).
[13] A. Bhalotra and B.K. Puri, Microchemica. Acta. , 134, 139-143 (2000).
[14] I. Srivani, P.A. Kumar, P.R. Reddy, and V.K. Reddy, Annali di Chimica., 97, 1237-1245 (2007).
[15] P. G. Chowdary, V. S. Basha, and V.S. Anusuya, Devi, IOSR Journal of Applied Physics, 8 55-59 (2016).
[16] V. Vojkovic, and V. Druskovic, Croatica. Chemica .Acta, 76, 87-92, (2003).
[17] H. Lin, Z.liya, Z. Huang, Q. Hu, G. Zhang and G. Yang, Asian Journal of Chemistry, 19,836-842, (2007).
[18] Y. Dong and Ke. Gai, Bull. Korean Chem. Soc., 26,943-946 (2005).
[19] B. Peng, X. Guo, X. Mao, J. Gao, Cent. Eur .J. Chem., 5,912-921 (2007).
[20] P.Nagaraj, G.N. Bhat, and K.G. Chandrashekhara, Research Journal of Chemical Sciences, 5, 19-26 (2015).
[21] G. B. Sathe, V. V. Vaidya, and R.G. Deshmukh, International Journal of Advanced Research, 3,699-704 (2015).
[22] G.B. Pethe, S.G. Bhadange, M.D. Joshi and A.S. Aswar, Advances in Applied Science Research, 1, 58-64 (2010).
[23] A. Y. Muhi, Baghdad Science Journal, 8, 996-1004 (2011).
[24] L. Lozynska, O. Tymoshuk and T. Chaban, Acta Chim. Slov., 62,159–167 (2015).
[25] M. Challa, and T.S. Reddy, African Journal of Pure and Applied Chem., 5,442-447 (2011).
[26] H. Eskandari, and M. Khoshandam, Microchem. Acta. 175, 291-299 (2011).
[27] B. Du, T., Liu, J. Wang, S.Y. Liu, and Q. Wei, Journal of Anal. Chem., 62, 794-800 (2007) .
[28] S.H. Gaikwad, and M.A. Anuse, Ind. J. Chem. tech., 10,447-453 (2003).
[29] A.P. Kumar , P.R. Reddy, V.K. Reddy, and Y.I. Lee, Anal .Letter, 42,84-93 (2009).
[30] Z. Huang, Q. Wei, X. Yang, Q. Hu, J. Chen, G. Yang, Bull. Korean Chem. Soc., 26, 1623-1626, (2005).
[31] B. Mathew, and D. Innocent, Asian Journal of Chemistry, 22, 7551-7556 (2010).
[32] P. Madan, and V. D. Barhate, Journal of Chemical and Pharmaceutical Research, 7, 1113-1116 (2015).
[33] S. D. Dhanavate, D. J. Garole, V. J. Garole , S. R. Tetgure and A. D.

Sawant, International Letters of Chemistry, Physics and Astronomy, 23,20-28 (2014).

[34] M. Renuka, and H.K. Reddy, Research Journal of Pharma., Biological and Chemical Sciences, 5,118-130 (2014).

[35] B. Mathew, V. Mini, and B. Deepthi, Oriental Journal of Chemistry, 26, 233-238 (2010).

[36] W. Qu and C. Zhou, Advanced Materials Research, 781-784, 51-54 (2013).

[37] L. Lozynska, O. Tymoshuk, and P. Rydchuk, Chem. Met. Alloys, 7,119-122 (2014).

[38] D. Gopalakrishna and Ch. K. Devi, International Journal of Analytical and Bioanalytical Chemistry, 5, 85-87 (2015).

[39] K.G. Chandrashekhara, G.N. Bhat, and P. Nagaraj, International Journal of Chemical Studies, 2, 1-4 (2015).

[40] S. Azmi, B. Iqbal, B. Ruqishi, S. Sayabi, N. Quraini and N. Rahman, Journal of the Association of Arab Universities for Basic and Applied Sciences, 19,29-36 (2016).

[41] S. L. Narayana, K. J. Reddy, S.A. N .Reddy, J.R. Kumar and A. V. Reddy, Journal of the Chinese Chemical Society, 54, 1233-1241 (2007).

[42] M. Zeydvandi and N. J. Pourreza, Anal. Chem., 61,744–747 (2006).

[43] K. J. Reddy, J. R. Kumar, C. Ramachandraiah, S. A. Reddy and A. V. Reddy, Environ Monit Assess. , 136, 337–346 (2008).

[44] Y. S. Shelar, H. R. Aher, S.R. Kuchekar, S. H. Han, Bulgarian Chemical Communications, 45, 172 – 179 (2012).

[45] N.H. Furman, Standard Methods of Chemical Analysis. 6th edn. Malabar Florida (1962).

[46] R.L. Frank, P.V. Smith, Org. Synth., 28, 89-89 (1948).

[47] E.B. Sandell, Colorimetric Determination of Traces of Metals. Interscience Publishers, Inc., New York, pp 671,426,608,888,600 (1965).