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Extractive Spectrophotometric Determination of Osmium (VIII) using p-methylphenylthiourea as a Chromogenic reagent: Mutual separation of Palladium, Osmium and Platinum

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Abstract

Simple, rapid and sensitive solvent extraction and spectrophotometric method for the determination of osmium(VIII) using p-methylphenyl thiourea as an analytical reagent has been developed. P-methylphenyl thiourea extracts osmium(VIII) quantitatively into chloroform from 0.45 mol L-1 perchloric acid medium. The chloroform extract shows an intense peak at 512 nm (λ max). The method is applicable over wide Beers range (upto 60 µg mL^{-1}).The molar absorptivity and sandell's sensitivity for Os (VIII)-PMPT system is 6.83 x 10^{3} L mol^{-1}cm^{-1} and 0.028 µg cm^{-2} respectively. The composition of complex is found to be 1:1(Os (VIII): PMPT) by slope ratio, mole ratio and job's continuous variation methods. Interference by various ions has been studied. The proposed method has been successfully employed for determination of Os(VIII) in synthetic samples. Mutual separation of palladium(II), osmium(VIII) and platinum(IV) is carried out using proposed method.

1. Introduction

Osmium, the densest natural element, has oxidation states ranging from -2 to +8 [1] . It was identified as a black residue remaining after dissolving platinum ores in aquaregia. The most common compound of osmium exhibiting the +8 oxidation state is osmium tetroxide. Osmium is used in alloys. Because of the volatility and extreme toxicity of its oxide, osmium is rarely used in its pure state, and it is instead often alloyed with platinum, iridium and other platinum group metals. Those alloys are utilized in high wear applications, fountain pen tips, electrical contacts, record player needles, and in other applications where extreme durability and hardness are needed [2,3] .Alloys of osmium are also used as hydrogenation catalysts [4], pacemakers and heart valves [5].Osmium 191 isotope is employed in radiopharmaceuticals [6]. Osmium tetroxide, a very volatile, water-soluble and toxic compound, is the main source for the contact to the environment and simplicity formed from osmium. It is used as effective catalysts for olefin hydroxylation and dihydroxylation reactions [7–9]. Large numbers of osmium compounds have been used as a catalyst for olefin metathesis[10], micro enzyme sensors[11] and electroluminescent materials[12].Solvent extraction is one of the most versatile methods used for the removal, separation and concentration of metallic species from aqueous media. It is used for the processing of most of the metals in periodic table because of its high separation efficiency and relatively low cost. Acidic solutions are the typical media for solvent extraction, but ammonical alkaline solutions are sometimes in use, owing to the ability of these metal ions to form complexes with ammonia. Thiourea and its derivatives coordinate to several transition metal ions to form stable complexes. Thiourea is versatile ligands, able to coordinate to metal centres either as neutral ligands, monoanions or dianions[13,14]. Numerous organic reagents have been proposed for the spectrophotometric determination of osmium. Spectrophotometric determination of osmium (VIII) using ethylene thiourea was reported. The method has interference from several cations[15]. Congo Red was used to determine osmium (IV) in intermettalic compounds [16]. method requires heating for 10 minutes. Orange G [17], ethylisobutrazine hydrochloride [18], prochlorperazinebismethanesulfonate[19] have been reported as an analytical reagents for spectrophotometric determination of osmium. Direct and first derivative analysis of osmium (VIII) and osmium (IV) by UV-VIS spectrophotometry using quercetin[20] and anthranilic acid [21] as a chromogenic reagent was reported. Osmium and ruthenium in chloride solution were determined by direct and third order derivative spectrophotometry [22]. Method requires high concentration of hydrochloric acid (9 mol L^{-1}). Catalytic kinetic spectrophotometric method for the determination of trace quantity of osmium is used [23]. Janus Green is oxidized by hydrogen peroxide in borate buffer at pH 9.0 and Os (VIII) catalyzes the reaction. Absorbance of the complex decreases after 150 sec. methylene blue, butyl rhodamine B and nile blue [24], Methylene Blue [25], Diantipyrylphenylmethane Derivatives [26] are also used as a catalytic agents for determination of osmium (VIII).Osmium (VIII) is determined by solid phase extraction method using 5-chloro-2-hydroxythiobenzhydrazide [27]. Method reports the separation of osmium and platinum. The presentprotocol deals with the rapid solvent extraction and visible spectrophotometric determination of osmium (VIII) using p-methylphenylthiourea as a sensitive chromogenic reagent from perchloric acid media. Method also describes the sequential separation of palladium, osmium and platinum. The comparison between earlier methods and present method is elaborated (Table 1). [28–36].

2. Material and Methods

2.1. Instrumentation

Systronics make double-beam UV-visible spectrophotometer model AU-2701 using matching 1 cm quartz cells was used for absorbance measurements. Contech make electronic balance (CA-123) was used for weighing purposes. Graduated glasswares were used and are cleaned by soaking in dilute nitric acid followed by washing with liquid soap and rinsed with distilled water.

2.2. Reagents

A standard stock solution of osmium(VIII) was prepared by dissolving 1.0 g osmium tetroxide (OsO_4) (Loba. Chem.) in 1.0 mol L^{-1} hydrochloric acid and diluted to 250 mL in a calibrated flask with double distilled water and standardized by a gravimetric method [37]. A working standard solution of osmium(VIII) (50 µg mL^{-1}) was prepared by suitable dilution of the standard stock solution with distilled water. The chromogenic reagent p-methylphenylthiourea (PMPT) was synthesized according to the reported method [38]. The 0.1 mol L^{-1} stock solution of reagent was prepared by dissolving 0.415g of PMPT in 25.0 mL ethanol. The working reagent solution of PMPT (0.02 mol L^{-1}) was prepared in ethanol by suitable dilution of stock solution.Solutions of various metal ions used for interference study were prepared by dissolving their respective salts in distilled water or hydrochloric acid and diluted suitably. Solutions of anions were prepared by dissolving respective alkali metal salts in double distilled water. Double distilled water, organic solvents and analytical reagent grade chemicals were used throught, unless otherwise stated.

2.3. Recommended Method

To an aliquot of solution containing 50 µg of osmium(VIII) and 2 mL 0.02 mol L^{-1} PMPT in 20 % ethyl alcohol taken in 10 mL calibrated flask ,enough perchloric acid was added to maintain the acidity of 0.45 mol L^{-1} on dilution up to mark with distilled water. Pink colored Osmium(VIII)–PMPT complex was formed immediately at room temperature. The complex was equilibrated with 10 mL chloroform for 5 seconds, dried over 1.0 g anhydrous sodium sulphate and absorbance of organic phase containing osmium(VIII)–PMPT complex wasmeasured at 512 nm against reagent blank containing all components other than the osmium.

Table 1: Comparision of reported methods with present method

Name of reagent	**Aqueous Phase**	**Solvent**	**λ_{max} , nm**	**Beers Range, µg mL^{-1}**	**Molar absorptivity, L mol^{-1} cm^{-1}**	**Comment**	**Ref.**
bis 1,6 (2 – mercapto 4,4,6, trimethlyl pyrimidine) – hexane (MTPH)	1 mol L^{-1} $HClO_4$	chloroform	540	5 -30	3.1 x 10^3	Heating for 3 min.	[28]
Carminic acid	pH 10	Water	540	0.1 to 1.5 (ng mL^{-1})	NR	Co(II) and Mn (II) interferes	[29]
TropaeolinO	pH 5.2	Water	540	0.57-28.67	NR	Heating at 90^0C for 30 min.	[30]
TropaeolinOOO-I	pH 8.0	Water	364	0.01-1.15	NR		
Eriochrome Black T	pH 10.0	Water	400	2.8-142.7	NR		
Morin	pH 9.5	Water	485	0.07-0.72	NR		
Quercetin	pH 10.0	Water	440	0.18-1.45	NR		
Tiron	pH 9.5	Water	440	0.19-17.8	NR		
Thionine dye	pH 9.0	Water	600	0.1-220 (ng mL^{-1})	NR	All reagents thermostated at 25^0C for 30 min.	[31]
Tin (II) chloride	2.0 mol L^{-1}HCl	Water	385	7.5-90.0	2.4 x 10^3	1.5 h heating	[32]
Trioctylamine-iodide	0.04 mol L^{-1}HCl + 0.1 mol L^{-1} iodide	Water	654	0.0-30.0	7.6 x 10^3	No interference study	[33]
Pyrogallol red	Neutral	Water	540	0.005-100 (ng mL^{-1})	NR	No interferences	[34]
m-Acetylchlorophosphonazo	-	water	580	0.001-0.016	NR	Reaction temperature 80^0 C	[35]
3-methyl-2,6-dimercapto-1,4-thiopyrone	pH 7.4–9.3	Amyl acetate	401.9	Upto 60	NR	2h stability	[36]
p-methylphenylthiourea	0.45 mol L^{-1} $HClO_4$	chloroform	512		6.83 x 10^3	>8 days stability, instant complexation	PM

PM-Present Method NR-Not Report

3. Results and discussion

3.1. Absorption Spectra

The absorption curves of the osmium(VIII)-PMPT complex in chloroform shows maximum absorption at 512 nm, while the reagent blank does not absorb at that wavelength. (Figure1). Constant nature of spectral curves confirms the formation of only one complex under the working conditions. Hence all the absorbance measurements were done at 512nm against the reagent blank for further spectrophotometric study of osmium(VIII). The spectral and physico-chemical characteristic of the osmium(VIII)–PMPT complex isgiven in Table 2.

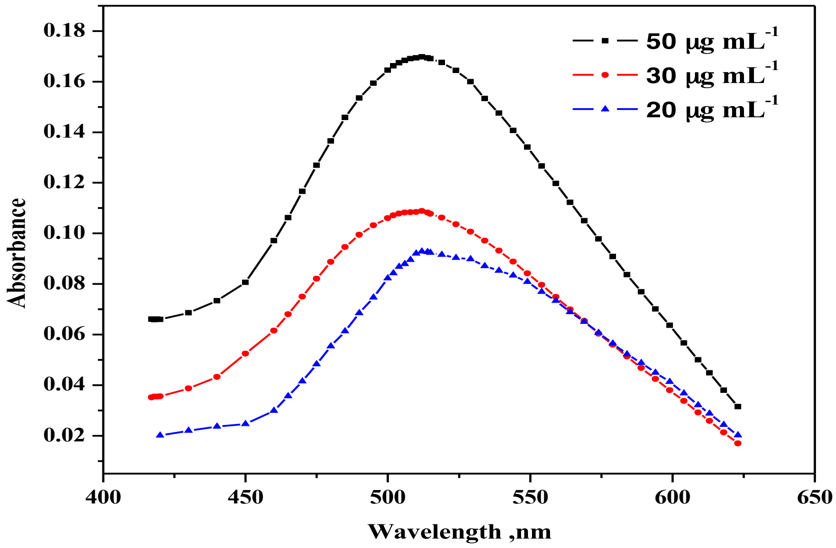


Figure 1 : Absorption spectra of Os (VIII) –PMPT complex

Table 2: Spectral and physico-chemical characteristics of osmium (VIII) - PMPT complex

Parameter	Specification
Perchloric acid concentrate	0.45 mol L^{-1}
Extraction solvent	Chloroform
Reagent concentration	0.02 mol L^{-1}
Equilibration time	5 seconds
λmax	512 nm
Molar Absorptivity	6.83 x 10^3 L $mol^{-1}cm^{-1}$
Sandell’s sensitivity	0.028 μg cm^{-2}
Beers Law range	up to 60 μg mL^{-1}
Ringbom’s optimum range	20 to 60 μg mL^{-1}
Correlation coefficient	0.99
Relative Standard Deviation	0.15 %
Stiochiometry of the complex	1:1 (Os(VIII):PMPT)
Stability of complex	>8 days
Limit of detection(LOD)	0.044 μg mL^{-1}

3.2. Effect of Acid concentration

Osmium(VIII)-PMPT complex formation was studied in different mineral acids viz., hydrochloric acid, sulphuric acid, nitric acid and perchloric acid. Complex formation takes place in all mineral acids studied except nitric acid. Complete complex formation with maximum absorption was takes place in perchloric acid medium in the concentration range from 0.01 to 1.0 mol L^{-1} using 0.02 mol L^{-1}reagent in ethyl alcohol. Absorbance increases as perchloric acid concentration increases from 0.02 mol $L^{-1}$to 0.45 mol L^{-1}. Further increase in acidity there was no increase in absorbance. (Figure 2). Therefore 0.45 mol L^{-1}perchloric acid was fixed for further work.

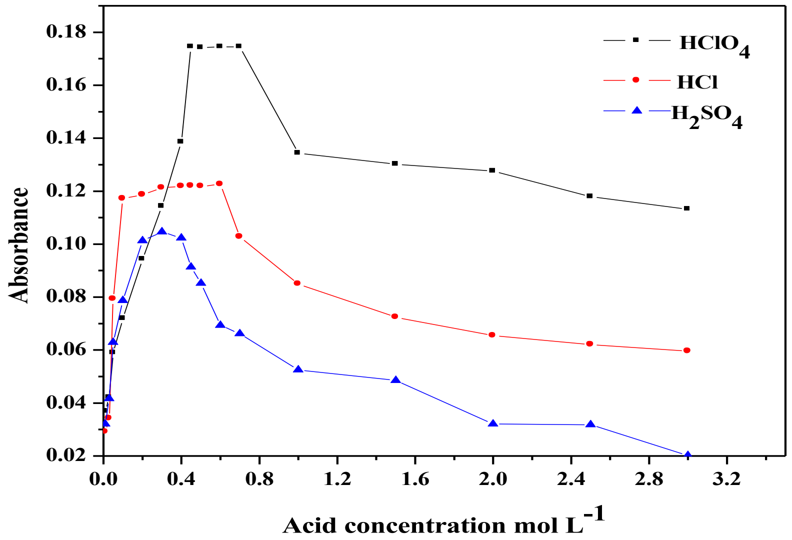


Figure 2: Effect of acid concentration on Os (VIII) - PMPT complex

3.3. Effect of reagent solvent on complex formation

The p-methylphenylthiourea (PMPT) solution in ethyl alcohol, 1, 4-dioxane and dimethyl sulphoxide was used for complex formation. Its concentration was varied in terms of percentage from 1 % to 40 % (V/V) keeping remaining parameters unchanged. Complete complex formation with maximum absorption takes place in ethyl alcohol in the concentration range of 2 to 40% (V/V) .To ensure complete complexation 20 % (V/V) ethyl alcohol was used as a reagent solvent. (Figure 3)

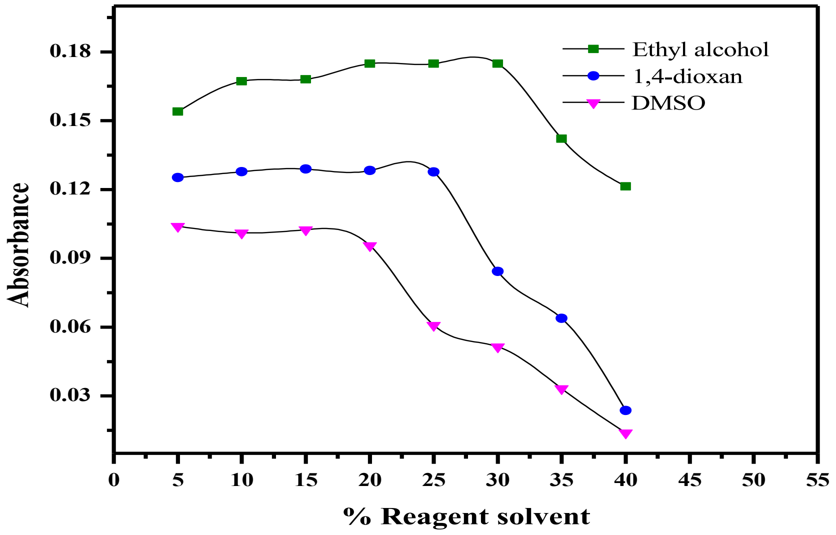


Figure 3 : Effect of reagent solvent (%) on Os (VIII) - PMPT complex

3.4. Effect of Reagent Concentration

The complex formation by 50 µg osmium was studied by varying PMPT concentration from 2 x 10^{-3} mol L^{-1} to 0.05 mol L^{-1} in 20% ethyl alcohol. It was observed that the absorbance of osmium(VIII)-PMPT complex increases with increase in reagent concentration from 2 x 10^{-3}mol L^{-1} to 0.02 mol L^{-1}. After this range absorbance becomes constant up to 0.045 mol L^{-1} (Figure 4). Hence 0.02mol L^{-1} PMPT was fixed for further study.

3.5. *Effect of Equilibration Time and Stability of the Complex*

Osmium(VIII)–PMPT complex was quantitatively extracted into chloroform within 5 seconds after the addition of chloroform. To ensure quantitative extraction, 5mL portion of chloroform was added to aqueous layer and it was equilibrated for 5 sec. No appearance of pink color to chloroform layer confirms the complete extraction of osmium(VIII)–PMPT complex in a single extraction. Further equilibration does not have undesirable effect on complex. The absorbance of complex, studied hourly remained stable for more than 8 days.

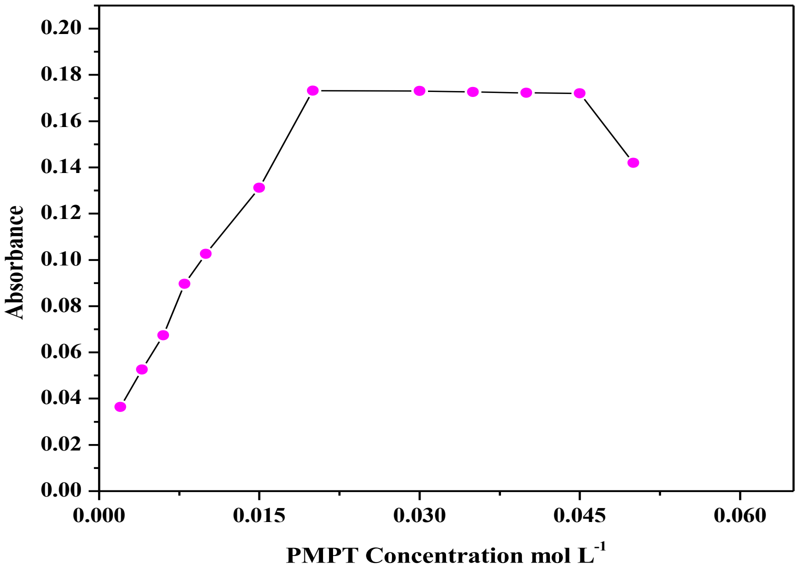


Figure 4: Effect of reagent (PMPT) concentration on Os (VIII) - PMPT complex

3.6. Effect of order of addition of reagents on formation of the Complex

The order of addition of metal ion solution, perchloric acid and reagent has no adverse effect on the absorbance of [Os(VIII)-PMPT] complex.

3.7. Analytical figures of merrit

The series of solutions, 0.45 mol L^{-1} in $HClO_4$ containing different amounts of osmium(VIII) in the range 0-100 µg were used for the study the validity of the Beer's law. The color was developed as per proposed method using 0.02 mol L^{-1}reagent in 20 % ethyl alcohol. After extraction into chloroform, pink colored complexwas measured at 512 nm against reagent blank. The plot of absorbance versus concentration of osmium(VIII) in µg (Figure 5) showed that the beer's law was valid over 60.0 µg mL^{-1} of osmium(VIII).

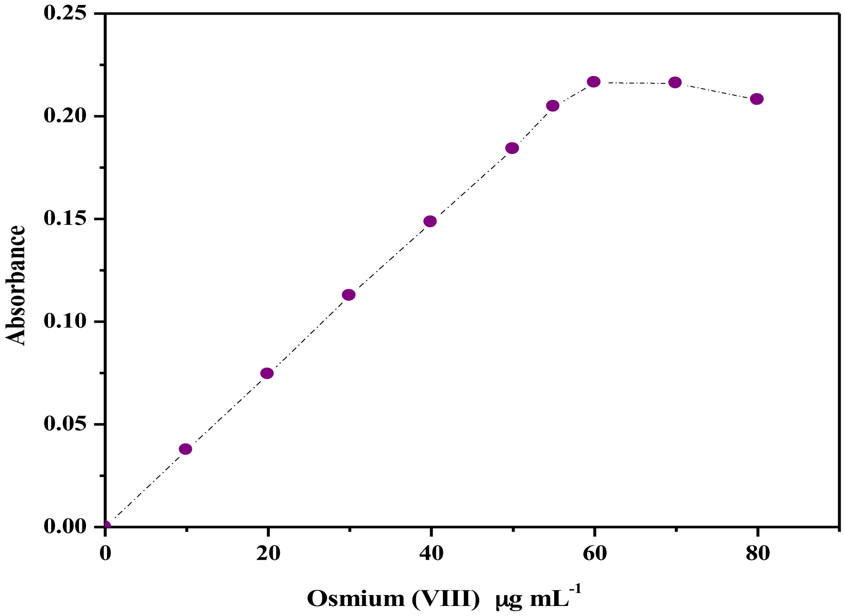


Figure 5: Beers Law range for Os (VIII) –PMPT complex

The molar absorptivity and sandell's sensitivity were 6.83 x 10^3 L mol^{-1} cm^{-1} and 0.028 µg cm^{-2}, respectively. The optimum concentration range in the determination of osmium defined by Ringbom's plot (Figure 6) was found to be 20 to 60 µg cm^{-3}. The correlation coefficient of Os(VIII)-PMPT complex with an independent variable as concentration in µgmL^{-1} and a dependent variable as absorbance was found to be 0.99, indicating a clear linearity between these variables. The slope and intercept for the best fitted lines were 0.0034 and 0.0077 respectively. Therefore thecontent of osmium(VIII) in real samples can be determined using the straight line equation, y = 0.0034 x + 0.0077.

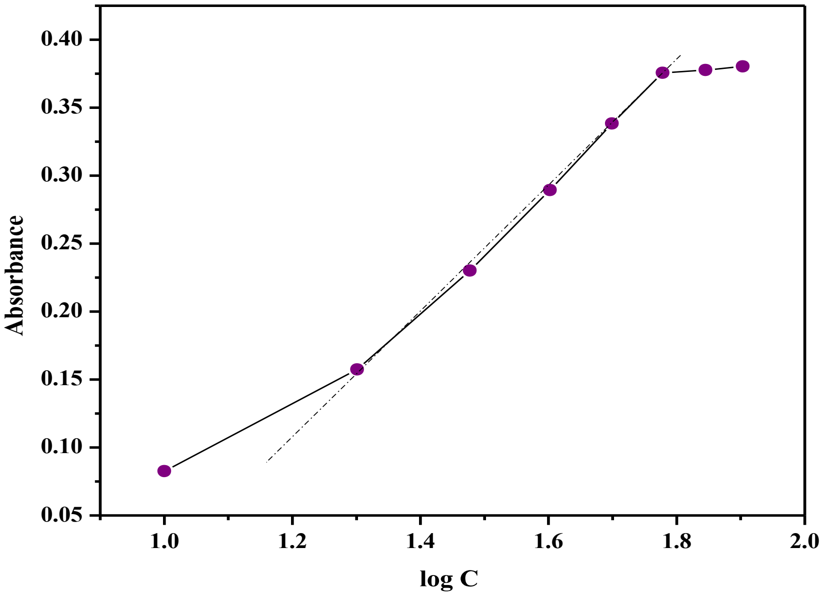


Figure 6: Ringbom plot for Os (VIII) –PMPT complex

3.8. *Stiochiometry of complex*

The possiblestiochiometry of the extracted complex was studied by the slope ratio method, mole ratio method and job's method of continuous variation. The plot of log $D_{Os\ (VIII)}$ against log C_{PMPT} at 0.2 mol L^{-1} and 0.3 mol L^{-1}perchloric acid concentration were linear with slope values 0.85 and 0.87 respectively (Figure 7).

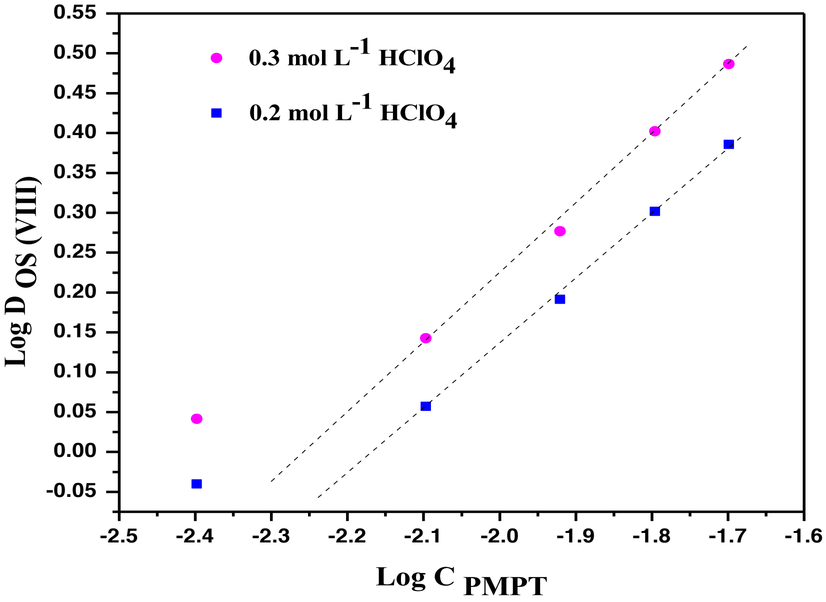


Figure 7: Plot of log D Os (VIII) Vs log C PMPT

Hence the probable composition of the Os(VIII): PMPT complex was therefore 1:1. This composition was also verified by the mole ratio method (Figure 8) job's continuous variation method (Figure 9).

3.9. Interference Study

To consider the possible applications of the proposed method, effect of various foreign ions on quantitative extraction of osmium(VIII) was studied. Variable amounts of foreign ions were added to a solution containing 50 µgosmium(VIII). Extractive spectrophotometric determination of osmium(VIII) with PMPT was carried out according to proposed method. Initially foreign ions were added to osmium solution in large excess; cations 10 mg and anions 200 mg. When interference was large the study was repeated with successively smaller amounts. The tolerance limit was fixed at the amount of added diverse ions that would give an error of ±0.2% in the absorbance values (Table 3). Thus the developed method was found to be free from interference from large number of diverse ions.

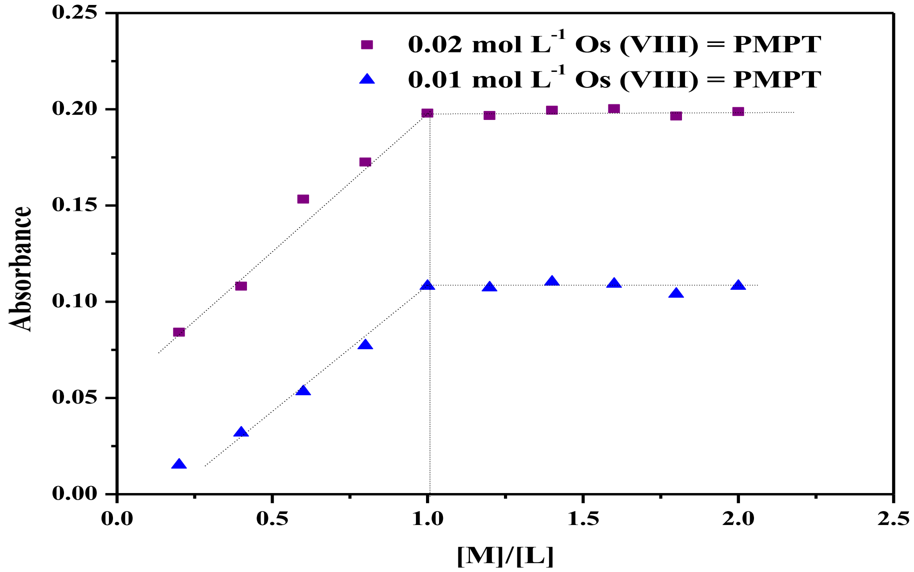


Figure 8: Mole ratio plot for Os (VIII) – PMPT complex

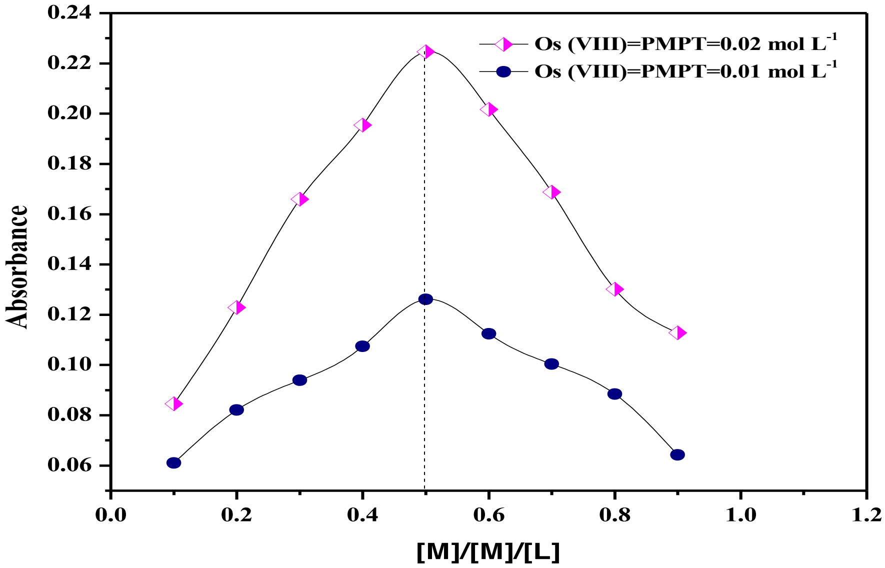


Figure 9: Jobs continuous variation method

Table 3: Effect of diverse ions on extraction of Os (VIII)-PMPT complex

Foreign ion	Added as	Tolerance limit,mg	Foreign ion	Added as	Tolerance limit,mg
Mn (II)	$MnCl_2.6H_2O$	0.50	Au (III)	$HAuClO_4$. H_2O	5.00
Al(III)	$AlCl_3.6H_2O$	0.50	Fe (III)	$(NH_4)Fe(SO_4)_2.12H_2O$	10.0
W (VI)	Na_2WO_4.2 H_2O	0.50	Cu (II)	$CuSO_4$.5 H_2O	0.75
Sn (II)	$SnCl_2$.2 H_2O	1.00	Ca (II)	$CaCl_2$.2 H_2O	3.00
Li (I)	LiCl	25.0	Pd (II)	$PdCl_2$	0.10
Co (II)	$CoCl_2$.6 H_2O	0.50	Rh (III)	$RhCl_3$	0.25
Ni (II)	$NiCl_2$.6 H_2O	1.00	Ru (III)	$RuCl_3$.6 H_2O	0.15
Pb (II)	$PbCl_2$	1.00	In (III)	$InCl_3$.4 H_2O	1.00
Mg (II)	$MgCl_2$.6 H_2O	1.00	Ba (II)	$BaCl_2$.6 H_2O	15.0
Cr (III)	$CrCl_3$	0.10	Ga (III)	$GaCl_3$	5.00
Zn (II)	$ZnSO_4$.7 H_2O	25.0	Hg (II)	$HgCl_2$	1.00
Zr (II)	$ZrOCl_2.8H_2O$	7.00	Ti (III)	$(Ti_2SO_4)_3$	1.00
Ag(I)	$AgNO_3$	0.50	Mo (VI)	$(NH_4)_5MO_7$.2 H_2O	5.00
Cd (II)	$CdCl_2$.2 H_2O	3.50	E.D.T.A	Na_2EDTA	100
La (III)	$LaCl_3$.7 H_2O	3.00	Sulphate	K_2SO_4	80.0
Se (IV)	SeO_2	7.50	Succinate	$(CH_3COONa)_2$.6 H_2O	100
Ce (IV)	$Ce(SO_4)_2$.4 H_2O	0.50	Acetate	$CH_3COONa.3H_2O$	100
Fe (II)	$(NH_4)Fe(SO_4)_2$.12H2O	5.00	Tartrate	$(CHOH:COOH)_2$	100
Tl (III)	Tl_2O_3	0.50	Fluoride	NaF	50.0
U (VI)	$UO_2(CH_3COO)_2$	10.0	Bromide	KBr	100
Sr (III)	$SrCl_3$.6 H_2O	5.00	Oxalate	$(COOH)_2$.2 H_2O	100
V (V)	V_2O_5	0.10	Salicylate	$C_7H_5O_3$	30.0
Bi (III)	$BiCl_3$	1.00	Citrate	$C_6H_8O_7$. H_2O	100

3.10. Accuracy of the method and Limit of Detection

To access the reproducibility and accuracy of the method, absorbance of ten identical sample solutions were measured. The average of these ten measurements and relative standard deviation was determined. The relative standard deviation was found to be 0.15 %. This indicates that the developed method was accurate and precise. The limit of detection was found to be 0.044 µg mL^{-1}.

4. Applications

4.1. Separation and determination of osmium(VIII) from binary synthetic mixtures

Recommended procedure was applied for the separation and spectrophotometric determination of osmium(VIII) from the metal ions like Mn(II), Ni(II), W(VI), Pb(II) and Zn(II). Osmium(VIII) was separated and determined spectrophotometrically from Mn(II), Ni(II), W(VI), Pb(II) and Zn(II) as per recommended method. After separation of osmium(VIII) from synthetic binary mixture, aqueous phase was evaporated to moist dryness followed by 2 mL conc. hydrochloric acid. The residue obtained was cooled, dissolved in water and added metal ions were determined by reported methods [39]. (Table 4)

Table 4: Separation and determination of Osmium (VIII) from binary synthetic mixtures.

Metal ion	Amount taken (µg)	Recovery ^{a} (%)	RSD (%)	Chromogenic reagent	Reference
Os (VIII)	50	99.72	0.11	PMPT	--
Mn(II)	50	99.75	0.34	permanganate	[40]
Os (VIII)	50	99.62	0.35	PMPT	--
Ni(II)	75	99.39	0.34	DMG	[40]
Os (VIII)	50	99.60	0.15	PMPT	--
W(VI)	50	99.38	0.06	thiocyanate	[40]
Os (VIII)	50	99.58	0.11	PMPT	--
Pb(II)	40	99.90	0.05	dithiozone	[40]
Os (VIII)	50	99.35	0.28	PMPT	--
Zn(II)	50	99.73	0.10	dithiozone	[40]

a: average of five determinations

4.2. Separation and determination of osmium(VIII) from ternary synthetic mixtures

Ternary synthetic mixtures with known amount of different associated metal ions and 50 µgosmium(VIII) was taken in 10 mL calibrated flask and osmium(VIII) was separated quantitatively and determined as Os(VIII)-PMPT complex by proposed method. Results were in good agreement with the expected amount (Table 5).

Table 5: Separation and determination of osmium (VIII) from ternary synthetic mixtures.

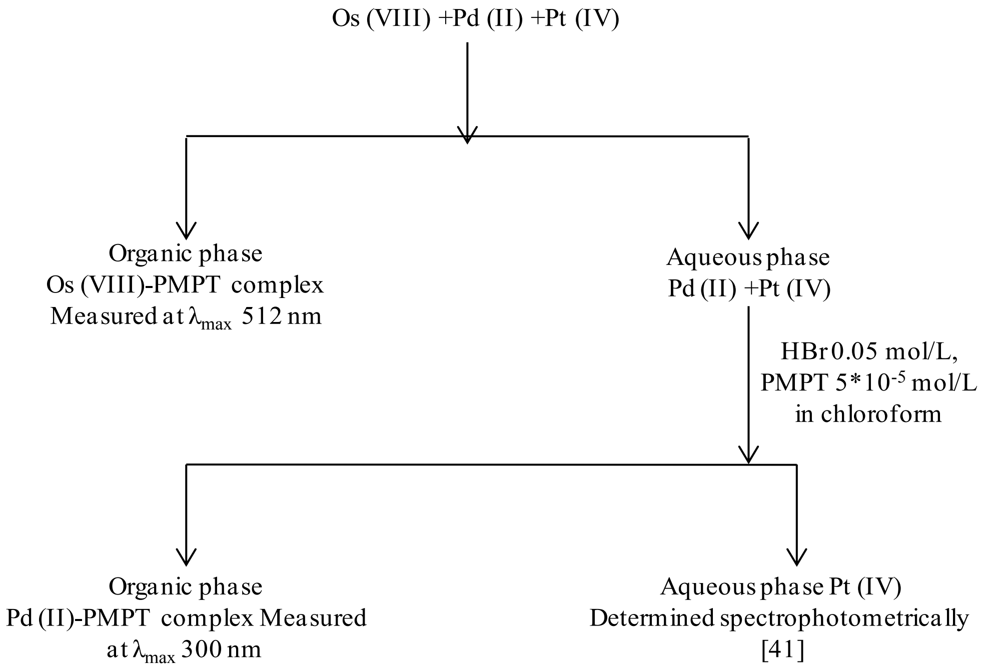
Ternary mixture composition (µg)	Recovery [a] (%)	RSD (%)
Os (VIII) 50;Mn(II) 20; Ni(II) 40	99.49	0.67
Os (VIII) 50;Zn(II) 50; Co(II) 30	99.84	0.46
Os (VIII) 50;Pb(II) 40; Mo(VI) 30	99.31	0.53
Os (VIII) 50;Ni(II) 40; Hg(II) 50	99.97	0.49
Os (VIII) 50; Co(II) 30; Fe(III) 50	99.24	0.48
Os (VIII) 50;Mg(II) 30; Cd(II) 50	99.74	0.17
Os (VIII) 50; Mo(VI) 30; Cd(II) 50	99.7	0.23

a: average of five determinations

4.3. *Mutual separation of osmium(VIII), Palladium(II) and platinum(IV)*

Proposed protocol was applied for the mutual separation and spectrophotometric determination of osmium(VIII), palladium(II) and platinum(IV) from their synthetic mixtures (Scheme 1). Osmium(VIII) was extracted into chloroform from synthetic mixture using, 0.02 mol L^{-1} PMPT in 20 % ethyl alcohol from 0.45 mol L^{-1} perchloric acid media at room temperature.

Scheme 1:mutual separation of osmium(VIII), Palladium(II) and platinum(IV)



Aqueous phase containing palladium(II) and platinum(IV) was evaporated to moist dryness; residue was dissolved in 10 mL water, enough hydrobromic acid was added to make solution at 0.05 mol L^{-1} with respect to hydrobromic acid and diluted to 25 mL using distilled water. This solution was extracted with 10 mL, 5 x 10^{-5}mol L^{-1} PMPT in chloroform for 10 sec. Pd(II) - PMPT complex was measured at 300 nm. The raffinate containing platinum(IV) was evaporated to moist dryness, cooled and dissolved in 10 mL distilled water. Platinum(IV) was determined by reported method [40] (Table 6).

Table 6: Sequential separation of Palladium (II), Osmium (VIII) and Platinum (IV)

Mixture	Amount taken (μg)	Chromogenic ligand	Recovery [a]	RSD %
Os (VIII)+ Pd (II)+Pt (IV)	Os (50)	PMPT	99.79	0.096
	Pd (30)	PMPT	99.24	0.095
	Pt (30)	OMPT	99.38	0.44

a: average of five determinations

Conclusion

p-methylphenylthiourea is proved to be sensitive reagent for the solvent extraction and spectrophotometric determination of osmium(VIII). The developed method is rapid and selective. Analysis of osmium from binary, ternary synthetic mixtures and mutual separation of osmium(VIII), palladium(II) and platinum(IV) explains extensive applicability of the method. Low perchloric acid concentration (0.45 mol L−1), minimum volume of extractant for determination (10 ml), instant complex formation at room temperature with no need of heating or standing and high stability of the complex proves the method is beneficial for rapid determination of osmium with low cost.

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