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Solvent extraction, spectrophotometric determination of copper (II) from environmental samples using o-methylphenyl thiourea as a novel reagent

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Abstract

A simple and rapid method has been developed for solvent extraction and spectrophotometric determination of copper (II) using o-methylphenyl thiourea (OMPT) as a sensitive reagent. The basis of proposed method is formation of copper (II)-OMPT complex. Copper (II) was extracted with 0.020 mol L^{-1} OMPT in chloroform from aqueous solution in 0.075 mol L^{-1} potassium iodate. The absorbance of complex was measured at 510 nm. Beer's law was obeyed up to 600 µg mL^{-1} for copper (II). The molar absorptivity and Sandell's sensitivity of the complex were 1.0167×10^3 L mol^{-1} cm^{-1} and 0.0625 µg cm^{-2} respectively. Correlation coefficient of the method was 0.93. The stoichiometry of copper (II)-OMPT complex was 1:1 established from slope ratio, mole ratio and job's continuous variation methods. The stability of copper (II)-OMPT complex was >24 h. The proposed method is free from interferences from large number of foreign ions. The proposed method was successfully applied for separation and determination of copper (II) from real samples (vegetable and environmental samples), binary and ternary synthetic mixtures. Precision of method was checked by finding relative standard deviation for eight determinations that was 0.23%.

Keywords: O-methylphenyl thiourea; environmental samples; solvent extraction; analysis; copper; spectrophotometry.

Introduction

Copper is extensively distributed in environment and it is the third most nutritionally necessary trace element in the body following iron and zinc [1]. The copper is present in all body tissues; however, the liver, the brain, the heart and the kidney contain copper in maximum amount. Copper is transported, absorbed, stored, distributed and excreted in the body. A complex homeostatic process ensures a

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constant and sufficient supply of micronutrient and simultaneously avoids excess level [2]. Copper shortage causes diseases like anemia, low immune function, osteoporosis, wound healing, arthritis and cardiovascular diseases. The excess intake of copper leads to diarrhoea, stomach upset, nausea and it also causes jaundice, Wilson disease and tissue injury etc. [3]. Pure copper is used comprehensively for cables and wires, electric contacts, and a wide variety of conducting parts. The alloys of copper find wide use in automobile radiators, heat exchangers, home heating systems and panels for absorbing solar energy. Besides, they are also used for pipes, valves, fittings in systems carrying drinkable water, process water and other aqueous fluids. Cupric sulphate is used in the manufacture of pigments, pesticides and medicine.

A literature survey reveals that the solvent extraction and spectrophotometric determination of copper was carried out using 2-carboxybenzaldehyde thiosemicarbazone [4], *N*-ethyl-3-carbazolecarbox-aldehyde-3 thiosemicarbazone [5], 25,26,27,28, tetrahydroxy-5,11,17,23-tetra[4-(*N*-hydroxyl-3-phenylprop-2enimidam-ido) phenylazo] calyx(4)arene [6], 1-phenyl-1-hydrazonyl 2oximinopropane-1,2-dione [7], 1-(2'-methy-lanilino)1,1,2,3,3,4,4,-5,5,6,6-undekafluorinehexanetiol-2 [8], *N*,*N*-bis [(E)-(4-fluorophenyl) methyldene] thiocarbonhydrazide [9], 2-[4-chloro-2-methoxyphenylazo]-4,5diphenyl imidazole [10], isonitrosopropiophen-one thiosemicarbazone [11], 3-methoxy-4-hydroxybenzaldehyde-4-bromophenylhydrazone [12], 2-hydroxy-5 methylacetophenone isonicotinoyl hydrazone [13], α-(2-benzimidazolyl)-α', α"-(N-5-nitro-2-pyridylhydrazone)–toluene [14],morph-olene–4– carbodithiote [15], 1 - (2', 4'-dinitro amino phenyl)-4,4,6-trimethyl-14-dihydropyrimidine-2-thiol [16], 2-acetyl-thiophenone thiosemicarbazone [17], 4-vanllideneamino-3-methyl-5-mecapto-1,2,4-triazole [18] and hydrazine carboxymide 2-[(2-hydroxyphenyl) methylene (HC22HPM) [19] which have been reported as a sensitive spectro-photometric reagent for the determination of the copper(II). The comparison of proposed method with other extraction spectrophotometric determination methods is reported in Table 1.

In our laboratory, we have developed extraction and spectrophotometric determination methods for rhodium(III) [20], ruthenium(III) [21], iridium(III) [22], palladium(II) [23] and osmium(IV) [24] using o-methyl phenyl thiourea (OMPT). In the extension of our earlier work, we have developed extraction spectro-photometric determination methods for cerium(IV) [25] palladium(II) [26], osmium(IV) and ruthenium(III) [27] with *o*-methoxy phenyl thiourea (OMePT).

Present article deals with selective and simple method for the extraction spectrophotometric determination of the copper (II) using o-methyl phenyl thiourea as a chromogenic reagent. O-methyl phenyl thiourea forms pink complex with copper (II) in iodate medium which is extractable in chloroform within 1.5 min. and the complex remains stable for more than 24 h.

Table 1. Comparison of present method with other extraction spectrophotometric determination methods of copper (II)

Reagents	λ_{max} (nm)	Condition / pH	Beer's Law (µg mL^{-1}) validity range	Molar Absorptivity (L mol^{-1} cm^{-1})	M:L	Remark	Ref
2-Carboxybenzaldehyde thiosemicarbazone	346	--	0.5–5.0	1.2×10^4	1:1	Sensitive, absorbance in UV region	4
N-Ethyl-3-carbazole carboxaldehyde-3 thiosemicarbazone	380	3.00	0.4–3.6	2.243×10^4	1:1	Absorbance in UV region	5
25,26,27,28,Tetrahydroxy-5,11,17,23-tetra-[4-(N-hydroxyl- 3-phenylprop-2 enimidamido) phenylazo] calyx[4]arene	432	3 mol L^{-1} HNO_3	5–10	0.96×10^4	1:1:1	Require synergent and one hour heating at 25^0c	6
1-Phenyl-1-hydrazonyl-2-oximinopropane-1,2-dione	345	9.4	0.1–1.0	0.35×10^3	1:2		7
1- (2'-methylanilino) -1,1,2,3,3,4, 4,5,5,6,6-undekafluorinehexanetiol-2	450	2.8-5.3	0.2-20	4.5×10^4	1:2	Absorbance in UV region	8
N",N"'-bis[(E)-(4-fluorophenyl) methylidene] thiocarbonohydrazide	375	1.7–3.4	2–14	4.2546×10^4	1:1:2	Low sensitivity	9
2-[4-Chloro-2-methoxyphenylazo]-4,5- diphenyl imidazole	519	8.0	0.5–30	8.459×10^3	1:2	Absorbance in UV region, requires synergent	10
Isonitrosopropiophenone thiosemicarbazone	390	10.0	0.5–6.0	5.8×10^3	1:2	Separation requires 10 minutes	11
3-Methoxy-4-hydroxybenzaldehyde-4-bromophenylhydrazone	462	4.0	0.2–4.0	2.05×10^4	1:1	Absorbance near UV region	12
2-Hydroxy-5methyl acetophenone Isonicotinoyl hydrazone	440	3.4	0.5–4.0	9.3×10^4	1:1	Requires surfactant	13
α-(2-Benzimidazolyl)-α', α"-(N-5-nitro-2- pyridylhydrazone) – toluene	410	6.0	0–2.5	3.81×10^4	1:2	Applications not studied	14
Morpholene-4-carbodithiote	320	4–7	0.2–15	2.46×10^4	1:2:1	Shaking time 5 minutes, requires surfactant	15
1-(2',4'-Dinitro amino phenyl)-4,4,6-trimethyl-14, dihydropyrimidine-2-thiol	445	8.7–10	100–600	8.7×10^4	1:2:2	Absorbance in UV region, requires synergent and surfactant	16
2-Acetylthiophenone thiosemicarbazone	370	5–7	0.2– 6.0	1.83×10^4	1:1	Requires synergent	17
4-Vanllideneamino-3-methyl-5-mercapto-1,2,4-triazole	430	8.5	4–32	9.92×10^2	1:2		18
Hydrazinecarboxymide2-[(2-hydroxyphenyl) methylene (HC22HPM)	359	6.80	1-10	0.33×10^5	1:2	Absorbance in UV region	19
O-methylphenyl thiourea	510	0.075 mol L^{-1} KIO_3	Upto 600	1.0167×10^3	1:1	Non extractive and low sensitivity few diverse ions studied	P M
						Simple, sensetive and precise, 1.5 min equilibration time, No heating required, large beer's range, complex stability > 24 h, applicable for analysis of environmental samples	

PM: Present method

Experimental

Apparatus

A double beam UV-Visible spectrophotometer (Systronics make model AU-2701) with matched 10 mm quartz cells was used for absorbance measurements. Contech make electronic balance model CA-123 was used for weighing purpose. Calibrated glassware were used and cleaned by soaking in dilute nitric acid followed by washing with soap water and rinsed two times with distilled water.

Reagents

Standard copper (II) solution

A standard stock solution of copper (II) was prepared dissolving 1.964 g copper sulphate pentahydrate in 25 mL 2.0 N sulphuric acid and diluted to 500 mL in a calibrated flask with distilled water. This solution was standardized by the reported method [28]. A working standard solution of copper (II) 200 µg mL^{-1} was prepared by diluting the standard stock solution with distilled water.

O-methylphenyl thiourea solution

O-methylphenyl thiourea (OMPT) was synthesized as per method reported by Frank and Smith [29]. A 0.020 mol L^{-1} solution was prepared by dissolving 0.166 g OMPT in 20 mL ethanol and diluted with ethanol in a 50 mL calibrated volumetric flask.

Solution of foreign ions

Standard solutions of different metal ions used for interference study were prepared after dissolving exactly weighed quantities of their respective salts in distilled water or dilute hydrochloric acid. Standard solutions of anions were prepared after dissolving their respective alkaline metal salts in distilled water. Different synthetic mixtures were prepared by combining their definite compositions.

Recommended procedure

An aliquot of solution containing 200 µg copper (II), 0.075 mol L^{-1} potassium iodate and 1 mL 0.020 mol L^{-1} OMPT in ethanol were transferred to a 25 mL volumetric flask. This mixture was equilibrated with 10 mL chloroform for 1.5 min. After equilibration and separation of two phases, the chloroform layer containing copper (II)-OMPT complex was transferred to a dry beaker and traces of water was removed using 1.0 g anhydrous sodium sulphate. This solution was transferred to a 10 mL volumetric flask and made up to mark with chloroform. The copper (II)-OMPT complex was measured at λ_{max} 510 nm against reagent blank.

Results and discussion

Absorption spectra

Copper (II)-OMPT complex shows absorbance in the range of 450 nm to 600 nm. The wavelength of maximum absorbance (λ_{max}) is 510 nm. The reagent blank shows no absorption at the wavelength 510 nm (Figure 1). Physico-chemical characteristics of the copper (II)-OMPT complex are reported in Table 2.

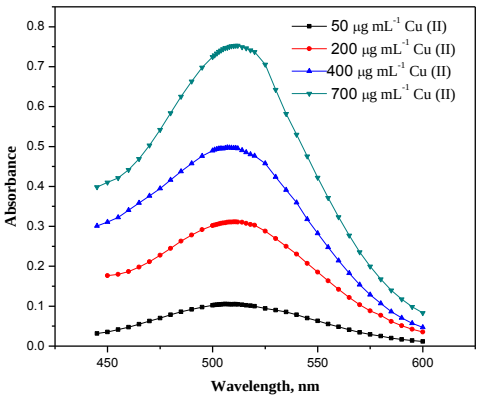

Figure 1. Absorption spectra of Cu (II)-OMPT complex
OMPT: 0.020 mol L^{-1} ; KIO_3: 0.075 mol L^{-1},shaking time 1.5 min.

Table 2. Spectral and physico-chemical characteristics of copper (II)-OMPT complex

Characteristics	**Parameters**
Potassium iodate conc.	0. 075 mol L^{-1}
Reagent concentration	0. 020 mol L^{-1}
Equilibration time	1.5 min
Extraction solvent	chloroform
λ_{max}	510 nm
Molar absorptivity	1. 0167×10^3 $Lmol^{-1}cm^{-1}$
Sandell's sensitivity	0. 0625 µg cm^{-2}
Beer's law range	up to 600 µg ml^{-1}
Ringbom's optimum range	150 to 600 µg ml^{-1}
Limit of detection	0. 08 µg mL^{-1}
Relative standard deviation	0. 23%
Stiochiometry	1:1(Copper(II):OMPT)
Stability of complex	> 24 h
Correlation coefficient	0. 93

Effect of reagent concentration

The concentration of o-methyl phenyl thiourea in ethanol was varied in the range of 0.0025 - 0.040 mol L^{-1} to study effect of reagent concentration for extraction of 200 µg copper (II). 1 mL, 0.020 mol L^{-1} reagent was sufficient for complete complex formation. In a method, there was no adverse effect on excess of reagent (Figure 2).

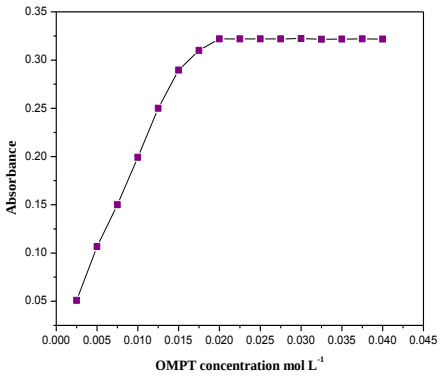

Figure 2. Reagent concentration variation
copper (II): 200 µg mL^{-1}; KIO_3: 0.075 mol L^{-1} shaking time 1.5 min.

Effect of potassium iodate concentration

Copper (II)-OMPT complex formation takes place in iodate media and depends upon the potassium iodate concentration. To study the effect of potassium iodate concentration, it was varied from 0. 0125 to 0.125 mol L^{-1}. The complete complexation and quantitative extraction of copper (II) was obtained at 0. 075 mol L^{-1} potassium iodate (Figure 3).

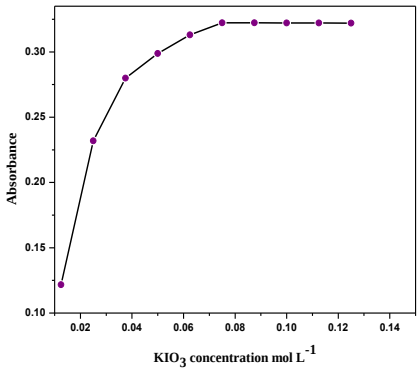

Figure 3. Potassium iodate concentration variation copper (II): 200 µg mL^{-1} ; OMPT: 0. 020 mol L^{-1}; λ_{max}: 510; shaking time 1.5 min.

Effect of equilibration time and stability of complex

The study of change in absorbance with variation in equilibration time was carried out over 0.5 min to 5.0 min. It has been observed that extraction was completed in 1.5 min and there was no any adverse effect of prolonged equilibration time on extraction of copper (II)-OMPT complex up to 5 min. Hence 1.5 min equilibration time was fixed for further study. The stability of complex was studied with the absorbance value measurement at regular time intervals of 1.0 h each at room temperature. The copper (II)-OMPT complex was stable for more than 24 h.

Analytical figures of merit

Validity of Beer's law

The complex obeys Beer's law over the concentration range up to 600 µg mL^{-1} (Figure 4). Ringbom's plot has the range of linearity in the absorbance and concentration of 150 to 600 µg mL^{-1} with a slope value of 0.7412 (Figure 5).

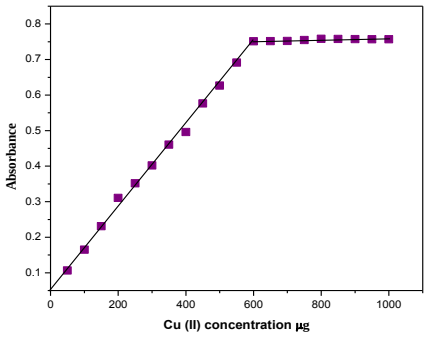

Figure 4. Beers law OMPT : 0.020 mol L^{-1}; KIO_3: 0.075 mol L^{-1}, λmax: 510 nm; shaking time 1.5 min.

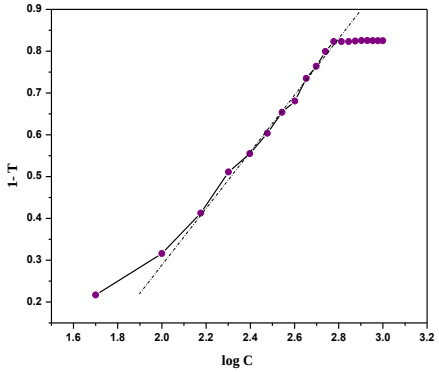

Figure 5. Ringboms plot OMPT : 0 020 mol L^{-1}; KIO_3: 0.075 mol L^{-1}, λ_{max}: 510 nm; shaking time 1.5 min.

Molar absorptivity, Sandell's sensitivity and correlation coefficient

The molar absorptivity and Sandell's sensitivity of the complex are $1.0167x10^3$ L mol^{-1} cm^{-1} and 0.0625 µg cm^{-2} respectively. The correlation coefficient values of complex with an independent variable as concentration in µg mL^{-1} and dependent variable as absorbance was found to be 0.93.

Stoichiometry of copper (II)-OMPT complex

The plot of log D $_{[Cu(II)]}$ against log $C_{(OMPT)}$ at 0.075 mol L^{-1} potassium iodate concentration gives the slope value of 1.40 (Figure 6). Hence the probable composition of the extracted species was 1:1 (Cu (II): OMPT). This composition of complex was confirmed by mole ratio (Figure7) and Job's continuous variation method (Figure 8).

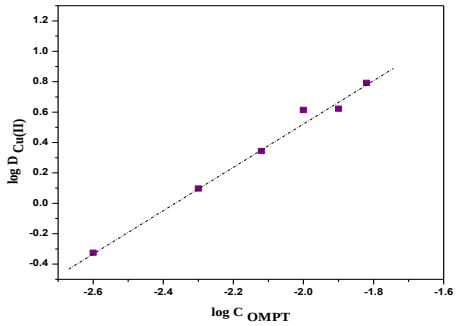

Figure 6. Log – log plot copper (II); 200 µg mL^{-1}; KIO_3: 0.075mol L^{-1}; λ_{max}: 510 nm; shaking time1.5 min.

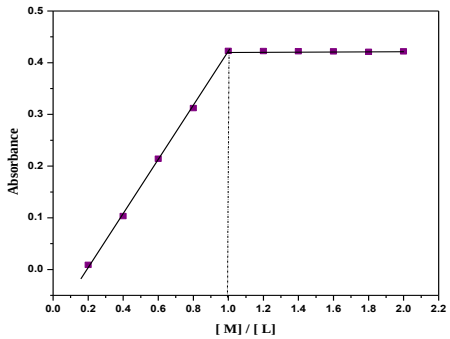

Figure 7. Mole ratio plot for Cu (II)-OMPT complex KIO_3: 0.075 mol L^{-1}, λmax: 510 nm, shaking time: 1.5 min.

Table 3. Effect of foreign ions

Foreign Ions	Added as	Tolerance limit mg
Mn(II)	$MnCl_2.6H_2O$	0. 10
Cd(II)	$CdCl_2.2H_2O$	1. 00
Fe(III)	$(NH_4)Fe(SO_4)_2..12H_2O$	0. 025
Hg(II)	$HgCl_2$	0. 50
Ni(II)	$NiCl_2.6H_2O$	0. 25
Ce(IV)	$Ce\ (SO_4)_2.4H_2O$	0. 50
Al(III)	$AlCl_3.\ 6H_2O$	0. 50
Cr(III)	$CrCl_3$	0. 10
Zn(II)	$ZnSO_4.7H_2O$	0. 25
La(III)	$LaCl_3.7H_2O$	0. 15
Li(I)	LiCl	0. 50
Ti(III)	$(Ti_2SO_4)_3$	0. 10
Mg(II)	$MgCl_2.6H_2O$	0. 50
Ga(III)	$GaCl_3$	0. 005
Mo(VI)	$(NH_4)_5MO_7.2H_2O$	0. 10
W(VI)	$Na_2WO_42H_2O$	0. 25
Zr(IV)	$ZrOCl_2\ .8H_2O$	0. 10
Pb(II)	$PbCl_2$	0. 25
V(V)	V_2O_5	1. 0
Co(II)	$CoCl_2.6H_2O$	0. 10
Ba(II)	$BaCl_2\ .6H_2O$	0. 01
Ca(II)	$CaCl_2.2H_2O$	0. 25
Tl(III)	Tl_2O_3	0. 20
Se(IV)	SeO_2	0. 96
U(VI)	$UO_2(CH_3COO)_2$	0. 05
Fluoride	NaF	5. 00
Sulphate	K_2SO_4	5. 00
Tartarate	$(CHOH.\ H_2O)$	5. 00
Citrate	$(C_6H_8O_7.\ H_2O)$	5. 00
Succinate	$(CH_3COONa)_2.6H_2O$	5. 00
Acetate	$(CH_3COONa).3H_2O$	5. 00

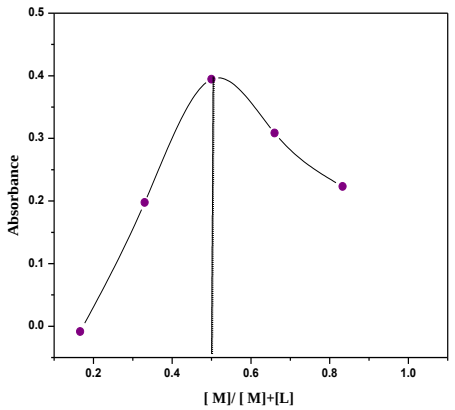

Figure 8. Job's continuous variation method KIO_3: 0.075 mol L^{-1}, λmax: 510 nm, shaking time: 1.5 min.

Precision and accuracy

To access reproducibility of the results and the accuracy of the method, absorbance measurements of eight identical solutions containing 200 µg copper (II) were carried out as per recommended method. Average of these eight determinations and the relative standard deviation was determined. The relative standard deviation was 0.23 %. The results indicate that the developed method was accurate and precise.

Effect of interfering ions

The selectivity of method was checked by testing different foreign ions. The tolerance limit was fixed for the ions which do not cause deviation more than ± 2 % in the absorbance value for copper (II)-OMPT complex (Table 3).

Applications

Separation and determination of copper (II) from binary synthetic mixtures

Binary synthetic mixtures were analyzed by the proposed method for separation and determination of copper (II) content in presence of different associated metal ions viz: Ni(II), W(VI), Pb(II), and Zn(II) (Table 4). The number of repetitions (n) was 6. After applying the recommended method, copper (II) was separated from the added associated metal ions (left behind in aqueous phase). The copper (II)-OMPT complex extracted in chloroform was measured at 510 nm. After quantitative separation of copper (II), the aqueous phase containing the added associated metal ions was evaporated to moist dryness, followed by addition of 1.0 mL concentrated hydrochloric acid and again evaporated to moist dryness. The residue containing added metal ions was cooled, dissolved in water and these metal ions were determined by reported methods spectrophotometrically [30] (Table 4).

Separation and determination of copper (II) from ternary synthetic mixtures

To a 25 mL volumetric flask containing 200 µg copper (II), other associated metal ions were added in varying proportions gives ternary mixtures. Potassium iodate was added to this ternary synthetic mixtures and the content was diluted up to mark giving the mixture at 0.075 mol L^{-1} potassium iodate. Copper (II) was extracted from mixture as copper(II)-OMPT complex and measured at 510 nm. The results are reported in Table 5.

Table 4. Separation and determination of copper(II) from binary synthetic mixtures copper (II): 200 µg mL^{-1}; KIO_3: 0. 075 mol L^{-1}; OMPT: 0.020 mol L^{1}; λ_{max}: 510 nm; shaking time 1.5 min.

Metal ion	Amount taken (µg)	Recovery[a] (%)	RSD (%)	Chromagenic ligand	Ref.
Cu(II)	200	99. 17	0. 06	OMPT	--
Ni(II)	75	99. 91	0. 07	DMG	30
Cu(II)	200	98. 84	0. 40	OMPT	--
W(VI)	25	99. 89	0. 08	thiocyanate	30
Cu(II)	200	99. 55	0. 20	OMPT	--
Pb(II)	20	99. 83	0. 26	dithiozone	30
Cu(II)	200	94. 74	0. 20	OMPT	--
Zn(II)	50	99. 85	0. 13	dithiozone	30

a: average of six determinations

Table 5. Separation and determination of copper (II) from ternary synthetic mixtures copper (II): 200 µg mL^{-1}; KIO_3: 0.075 mol L^{-1}; OMPT: 0.020 mol L^{-1}; λ_{max}: 510 nm; shaking time 1.5 min.

Composition (µg)	Recovery [a] (%)	RSD (%)
Cu (II) 200; Co(II)30; Pb(II) 40	99. 55	0. 19
Cu (II) 200; Pb(II) 40; Mg(II) 30	99. 58	0. 18
Cu (II) 200; Mg(II) 30; Mo(V) 30	99. 55	0. 29
Cu (II) 200; Mg(II) 30; Co(II)30	99. 44	0. 37

a: average of six determinations

Analysis of copper (II) from environmental sample

Sea water sample

Take 200 mL sea water in 500 mL beaker and heat it on hot plate to moist dryness, add 5 mL concentrated HCl and again heat to moist dryness. Dissolve the residue in very dilute HCl and finally dilute to 50 mL with distilled water. An aliquot of this solution was analyzed for determination of copper as per proposed method. (Table 6).

Table 6. Determination of copper in sea water copper (II): 200 µg mL^{-1}; KIO_3: 0.075 mol L^{-1}; OMPT: 0.020 mol L^{-1}; λ_{max}: 510 nm; shaking time 1.5 min.

Sr. No.	Sea water sample	Quantity taken	copper found µg mL^{-1}	RSD (%)
1	Thialand Sea water sample	5 mL	6. 47	1. 27

a: average of four determinations

Vegetable sample

The vegetable samples (Cauliflower leaves) were prepared in triplicate by ashing 1.0 g portions of oven-dried ground plant tissue in porcelain crucibles for 2.5 h at 500 °C, and dissolving the residue in 2 mL of 6 mol L^{-1} hydrochloric acid. The resulting solutions were evaporated and the residues were again redissolved in 10 mL of 2 mol L^{-1} hydrochloric acid. The resulting solutions were heated and filtered. The residues were then washed again with 10 mL of the 2 mol L^{-1} hydrochloric acid solution and 10 mL of water, the filtrates were collected into 50 mL volumetric flasks and analysed by the proposed method (Table 7).

Table 7. Determination of copper in vegetable sample copper (II): 200 µg mL^{-1}; KIO_3: 0.075 mol L^{-1}; OMPT: 0.020 mol L^{-1}; λ_{max}: 510 nm; shaking time 1.5 min.

Sr. No.	Vegetable sample	Quantity taken	Copper found µg gm^{-1}	RSD (%)
1	Cauliflower Plant leaves. (Oven dried ground plant tissue ash.)	1. 0 gm	743. 5	1. 41

a: average of four determinations

Conclusion

O-methylphenyl thiourea(OMPT) has been proved to be a potent analytical reagent for solvent extraction, spectrophotometric determination of copper (II). The proposed reagent has higher sensitivity and easy determination and is a less expensive

and less tedious procedure at trace level. Considering the comparison between reported extraction spectrophotometric determination methods and the reported one for copper (II), the proposed method has positive merits.

Salient features of the proposed method are as follows:

1. The proposed method is simple, precise and sensitive.
2. It permits highly stable complex formation (>24h), wide Beer's range (up to 600 µg ml^{-1}), lower limit of detection at microgram level (0.08 µg mL^{-1}), direct determination without heating.
3. No sophisticated instrument required and quantitative separation achieved using a simple equipment separatory funnel.
4. A clear phase separation and single stage extraction with direct spectrophotometric determination is possible.
5. The method is reproducible with relative standard deviation of 0.23%, Sandell's sensitivity of 0.0625 µg cm^{-2} and correlation coefficient of 0.93.
6. The method permits enhanced applicability with analysis of binary and ternary synthetic mixtures, analysis of real (environmental and vegetable) samples.

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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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- ✓ Sequential separation.

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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 catalysts 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	3.1×10^3	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	2.4×10^3	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	7.6×10^3	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		6.83×10^3	>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.

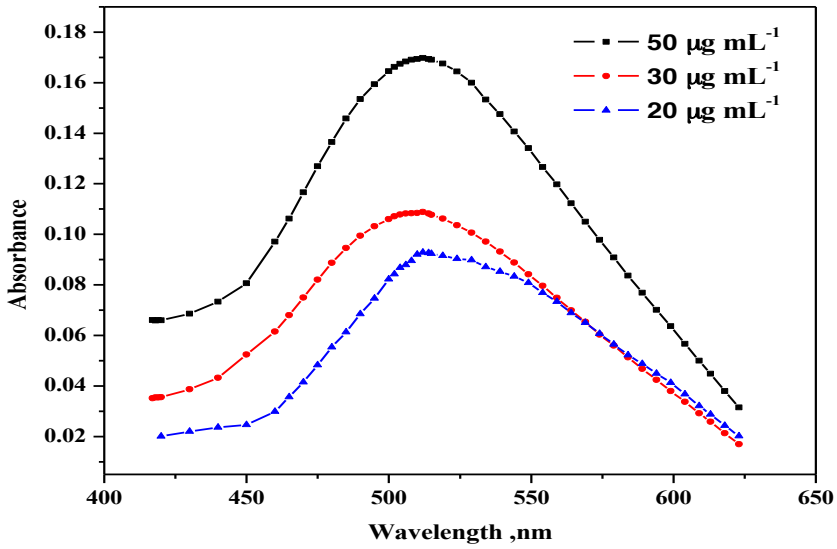


Figure 1 : Absorption spectra of Os (VIII) –PMPT complex

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.

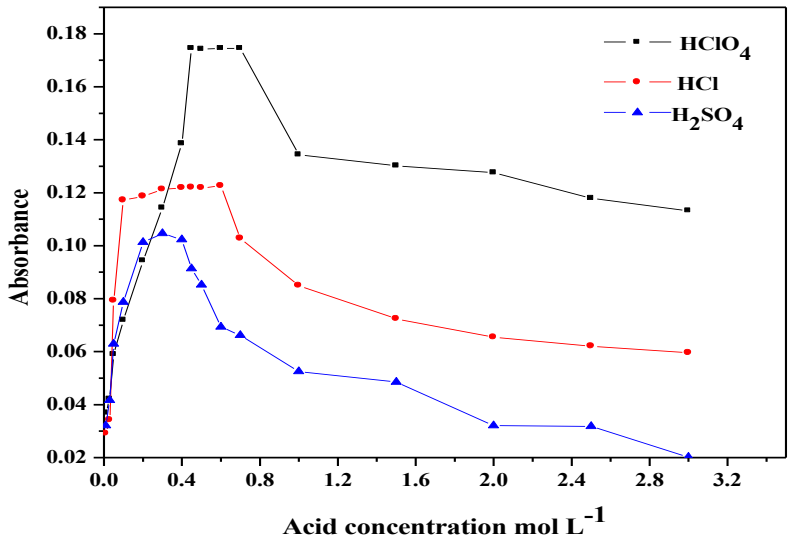


Figure 2: Effect of acid concentration on Os (VIII) - PMPT complex

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)

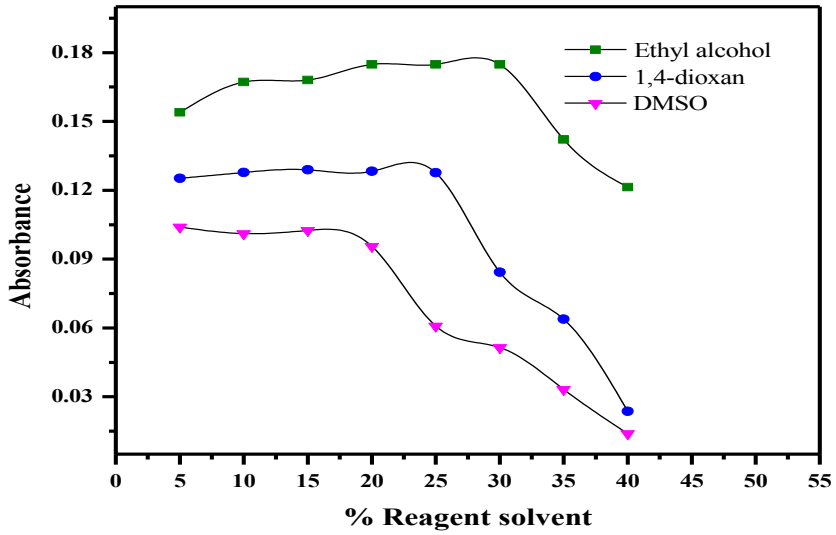


Figure 3 : Effect of reagent solvent (%) on Os (VIII) - PMPT complex

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.

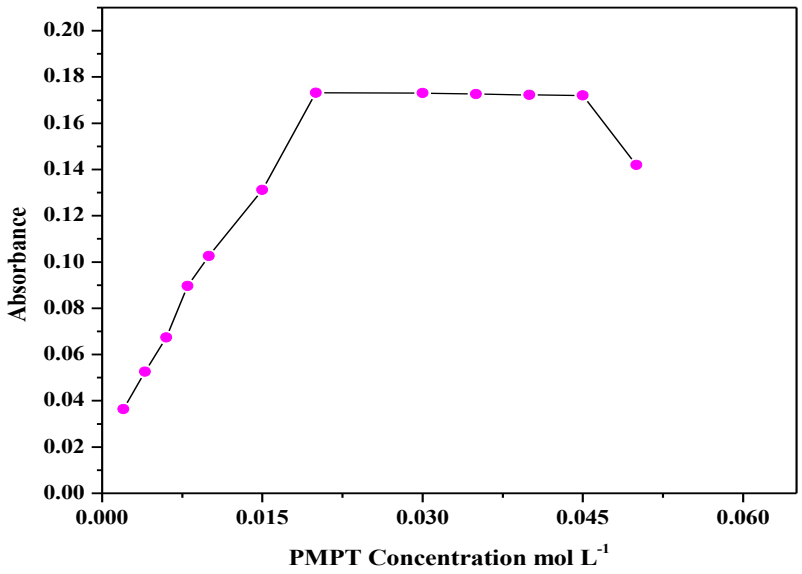


Figure 4: Effect of reagent (PMPT) concentration on Os (VIII) - PMPT complex

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).

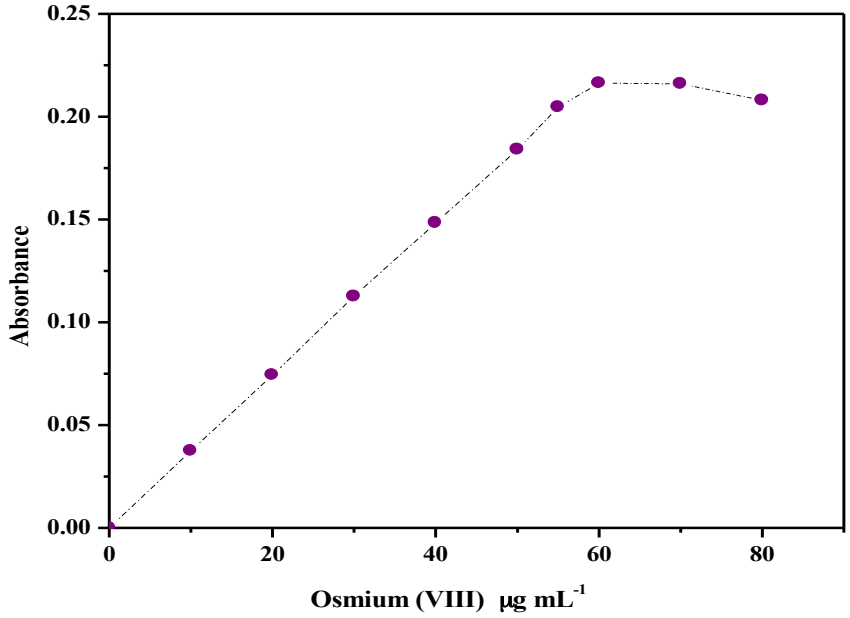


Figure 5: Beers Law range for Os (VIII) –PMPT complex

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.

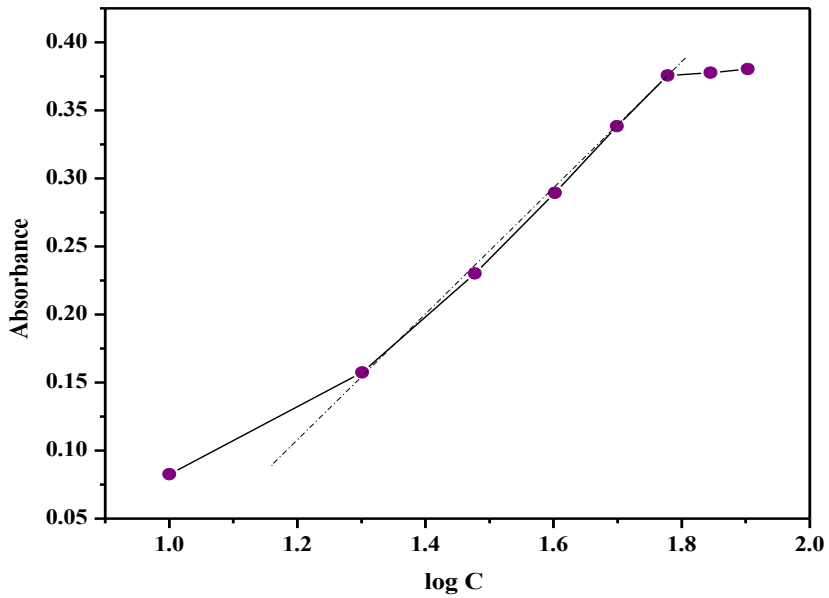


Figure 6: Ringbom plot for Os (VIII) –PMPT complex

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).

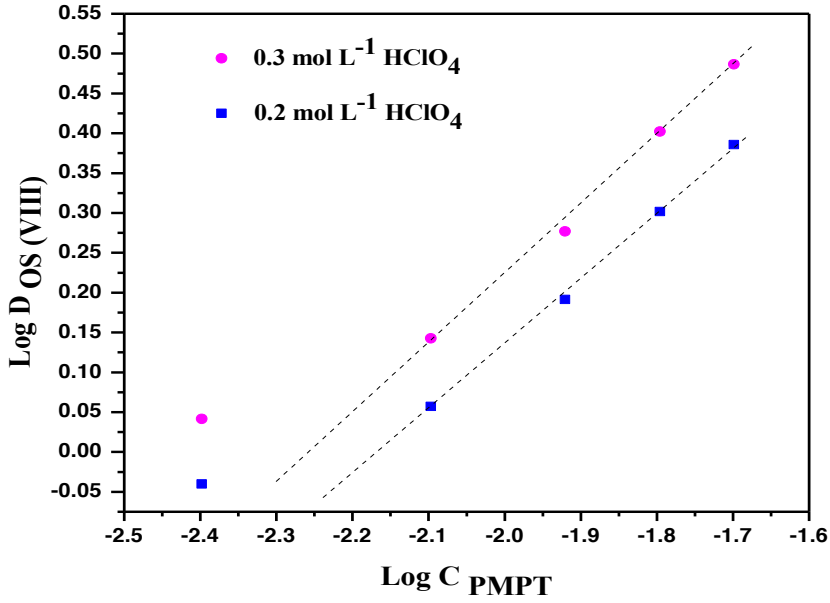


Figure 7: Plot of log D Os (VIII) Vs log C PMPT

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.

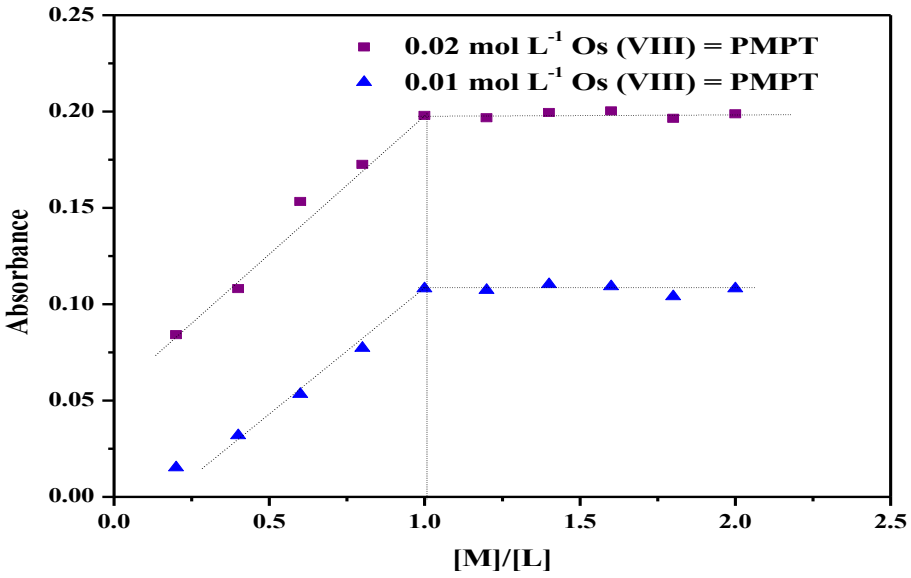


Figure 8: Mole ratio plot for Os (VIII) – PMPT complex

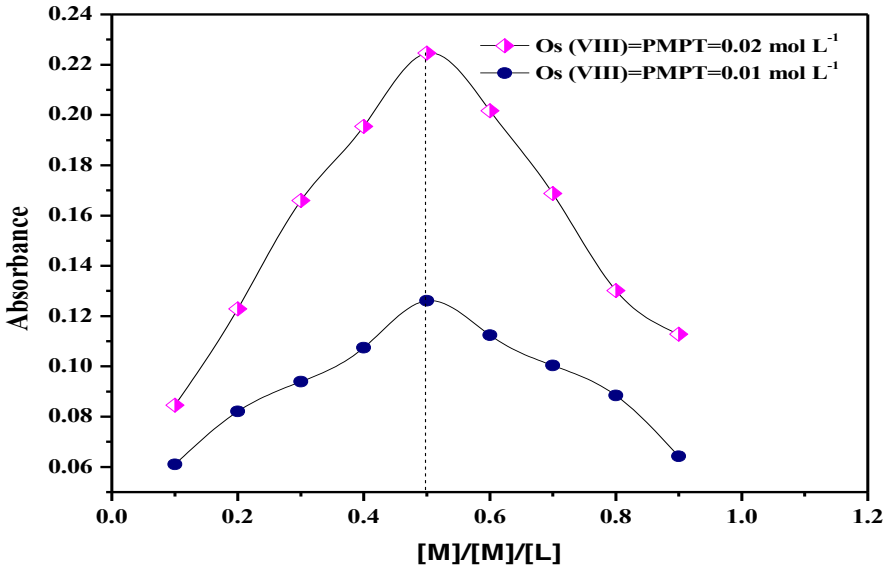


Figure 9: Jobs continuous variation method

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.

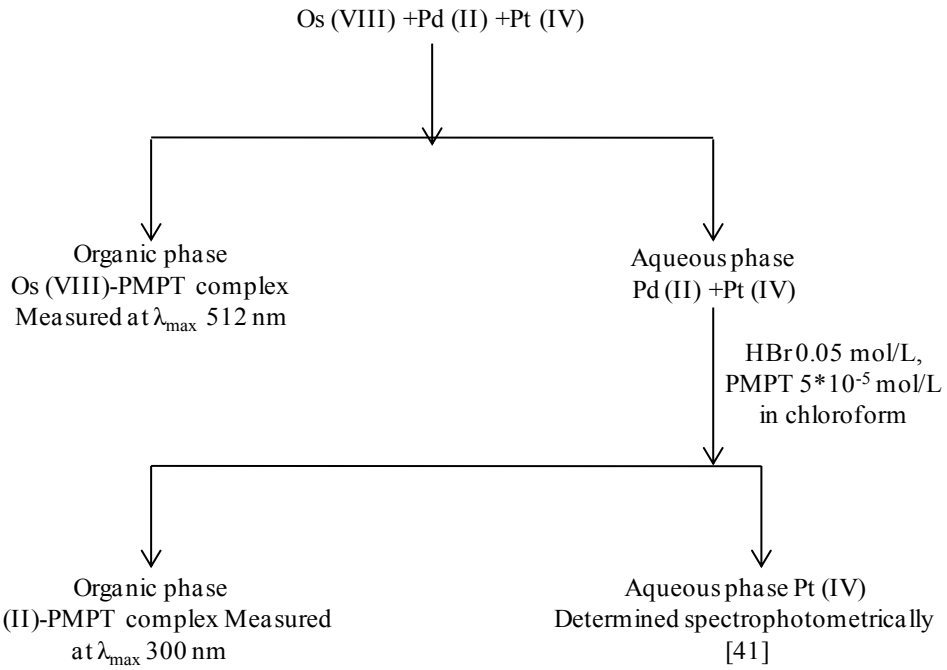
Ternary mixture composition (µg)	Recovery [a] (%)	RSD (%)
Os (VIII) 50;Mn(II) 20; Ni(II) 40	99.49	0.67
Os (VIII) 50;Zn(II) 50; Co(II) 30	99.84	0.46
Os (VIII) 50;Pb(II) 40; Mo(VI) 30	99.31	0.53
Os (VIII) 50;Ni(II) 40; Hg(II) 50	99.97	0.49
Os (VIII) 50; Co(II) 30; Fe(III) 50	99.24	0.48
Os (VIII) 50;Mg(II) 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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SOLVENT EXTRACTION, SPECTROPHOTOMETRIC DETERMINATION AND SEPARATION OF RHODIUM(III) FROM SYNTHETIC ALLOY SAMPLES USING P-METHYLPHENYL THIOUREA

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Abstract : A selective and sensitive solvent extraction and spectrophotometric study of the rhodium(III) - p-methylphenyl thiourea (*PMPT*) system is presented. The optimum conditions of complexation were determined by study of acid concentration, reagent concentration, equilibration period, heating time and effect of solvent on the equilibration. Rhodium(III) forms 1:2 complex with *PMPT* in 20 % ethanol and extracted into chloroform. Conformity to Beer's law at 298 nm was observed up to 40 µg mL^{-1} of rhodium. Molar absorptivity and Sandell's sensitivity were found to be 1.65 x 10^3 L mol^{-1} cm^{-1} and 0.066 µg cm^{-2} respectively. The detection limits was 0.079 µg mL^{-1} of rhodium(III). Proposed method was successfully applied to the separation and determination of rhodium from synthetic alloys samples, binary and ternary mixtures.

Key Words **- p-methylphenyl thiourea, solvent extraction, alloy, rhodium(III).**

I. INTRODUCTION

Rhodium is a rare, silvery-white, hard, corrosion resistant, precious and chemically inert platinum group metal. ^{103}Rh is the only naturally occurring isotope of rhodium. Rhodium is found in platinum or nickel ores together with the platinum group metals. The main use of rhodium is as the catalysts in the three-way catalytic converters in automobiles. Rhodium is usually alloyed with platinum or palladium and finds applications in high-temperature and corrosion-resistive coatings. Wilkinson's catalyst, well known rhodium-halogen compound which is used in the hydroformylation or hydrogenation of alkenes(Osborn, Jardine, Young, & Wilkinson, 1966). Rhodium forms chelating complex with the drug promethazine hydrochloride and is used for the determination of promethazine hydrochloride from pharmaceutical samples (AL-Ayash, Jasim, & Zair, 2008).Various rhodium compounds exhibits anti-tumer activity(Katsaros & Anagnostopoulou, 2002; Ruiz et al., 2012). A new field of rhodium nanoparticals has been emerged in recent years and its possible future is highlighted(Lin, Chen, & Su, 2013; Motoyama, Takasaki, Yoon, Mochida, & Nagashima, 2009; Yuan, Yan, & Dyson, 2012).Catalytic performance of rhodium has been reported for various reactions like hydroformylation(Cobley, Ellis, Guy Orpen, & Pringle, 2000) ,hydrogenation(Ojeda, López Granados, Rojas, Terreros, & Fierro, 2003), reduction(Terada & Toda, 2012; Wu, Tang, Pettman, & Xiao, 2013), oxidative cycloaddition(Hyster & Rovis, 2010; Shibata & Tanaka, 2012), amidation(Deng et al., 2012), C-H activation(Song, Wang, & Li, 2012) and C-C bond formation(Fagnou & Lautens, 2003).

Due to low natural abundance, significant properties, prominent catalytic role and numerous applications, development of a sensitive, cost effective and selective method for separation and determination of rhodium from various matrices is of vital importance.

Various analytical methods were reported for the determination of rhodium. Some of them were flame atomic absorption spectrometry(Ghaseminezhad, Afzali, & Taher, 2009; Suvardhan et al., 2007),ICP-AES(Panahi et al., 2009),ICP-OES(Tavakoli et al., 2008), Laser induced-thermal lens spectrometry(Shokoufi & Shemirani, 2007) and Differential pulse polarography(Puri, Dubey, Gupta, & Puri, 1997).Tediuos procedures, high cost of instruments are the demerits of these methods.

Comparatively, solvent extraction is the most efficient technique for separation of metals which offers simplicity, high speed and applicable to both tracer and macro quantities of metal ions.

Variety of extractants were used for the separation of rhodium like 2-Dodecylaminopyridine(Shep, Bagal, & Arbad, 2017), Aliquat 336(Levitin & Schmuckler, 2003), TBP(Zou, Chen, & Pan, 1998). These methods give quantitative separation at trace level but require external chromogenic reagents for spectrophotometric determination, stripping agents and backwashing.

Variety of complexing reagents were reported for the spectrophotometric determination of rhodium(III). 1, 2, 3-Cyclohexanetrione dioxime forms 1:2 complex with rhodium. Absorbance measurement requires standing time of 10 min. The method also lacks the interference study and applications(Ganescu et al., 2002). Spectrophotometric Determination of Rhodium with Phenanthraquinone Monothiosemicarbazone is reported. Method requires heating of content for 90 min.(Sinha & Tomar, 2017).

Extractive spectrophotometric determination using various extractants is more advantageous with ease of methodology, minimum interferences and maximum applications. Red colored 2-[(5-bromo-2-pyridylazo)]-5-diethylaminophenol-rhodium complex was extracted into dichloromethane. Method is sensitive but narrow beers range limits its applicability(Thakur, Khande, & Deb, 2005). 2-(5- bromo-2-oxoindolin-3-ylidene) hydrazine carbothioamide extracts rhodium(III) into n-amyl alcohol(Borgave & Barhate, 2016). Method requires digestion of contents in water bath for 10 min. N - (O- Hydroxy benzylidene) pyridine - 2 - amine extracts rhodium into n-amyl alcohol in the pH range 4.5-5.7(Gupta & Barhate, 2012).Method needs digestion for 20-25 min. Comparison of present method with previously reported methods was summarized (Table 1) (El-Sayed, 1995; Kawamura, Igarashi, & Yotsuyanagi, 2006; Keyvanfard & Ensafi, 2003; Panahi, Kalal, Menderjani, & Moniri, 2011; Sánchez Rojas, Ojeda, & Pavón, 2004; Tofan, 2011; Xu, Chen, & Hu, 1994).

In the present method, p-methylphenyl thiourea has been used for solvent extraction and spectrophotometric determination of rhodium(III) quantitatively into the chloroform. The method is rapid, simple and selective for the determination of rhodium in presence of associated metal ions. The developed method is successfully applied for quantitative determination of rhodium from synthetic alloy samples, binary and ternary mixtures.

Table 1 Comparison of present method with reported methods

Reagent	Aqueous phase	Solvent	λ_{max}, nm	Beers Range (µg mL^{-1})	ε, (L mol^{-1}cm^{-1})	Remark	Reference
Alizarin-boric acid	pH-2.5 acetate buffer	Water	470	0.1-18.0	5.68 x 10^3	Standing time 1h	(Panahi et al., 2011)
5,10,15,20-Tetrakis(4-N-methylpyridyl)prophine	pH-3.9 acetate buffer	Water	432	0.09-6.2	NR	Heating at100°C for 15 min	(Kawamura et al., 2006)
4-(5-Chloro-2-pyridylazo)-1,3-diaminobenzene	pH-4.0 acetate buffer	Water	555	2.0-10.0	NR	Few diverse ions studied	(Xu et al., 1994)
O-Toulidine	pH-3.9 phosphate buffer	Water	628	1.0-400.0 (ng mL^{-1})	NR	Reagents thermostated at 35°C for 15 min	(Keyvanfard & Ensafi, 2003)
5-(3,4-Methoxybenzylidene)rhodanine	pH-4.2 acetate buffer	Water	445	0.26-4.2	5.13 x 10^4	30 min heating at 85°C	(El-Sayed, 1995)
Disodium-1-nitroso-2-hydroxynaphthalene-3,6-disulfonate	--	--	--	0.5-2.0	3.03 x 10^4	Solid support Dowex 1x1 used	(Tofan, 2011)
1,5-bis(2-pyridyl)-3-sulphophenyl methylene thiocarbonohydrazide	4.0 mol L^{-1} HNO_3	Water	--	0-50.0 (ng mL^{-1})	NR	Solid support Dowex 1x1 used	(Sánchez Rojas et al., 2004)
p-methylphenyl thiourea	0.5 mol L^{-1} HCl	Chloroform	298	0-40	1.65 x 10^3	Short equilibration time Synthetic Applications	PM

PM-Present method NR-Not Reported

II. MATERIALS AND METHOD

2.1 Instrumentation

Absorbance measurements were done with Systronics make double-beam UV-visible spectrophotometer model AU-2701 using matching 1 cm quartz cells. An electronic balance Contech, model CA-123 was used for weighing purposes. Calibrated glasswares were used and were cleaned by soaking in acidified potassium dichromate solution followed by washing with liquid soap and rinsed with distilled water.

2.2 Reagents

A standard stock solution of rhodium(III) was prepared by dissolving 1.0 g rhodium trichloride ($RhCl_3$) (Loba. Chem.) in 1.0 mol L^{-1} hydrochloric acid and diluted to 250 mL in a calibrated flask with double distilled water and was standardized by a gravimetric method (Furman, 1962). A working standard solution of rhodium(III) (30 µg mL^{-1}) was prepared by diluting the standard stock solution with double distilled water.

P-methylphenyl thiourea (*PMPT*) was synthesized according to the reported method (Jadhav, Khillare, Rai, & Durrani, 2010). The 0.1 mol L^{-1} stock solution of reagent was prepared by dissolving 0.415 g of reagent in 10 mL ethanol and was made up to 25 mL volumetric flask with ethanol. The working reagent solution of *PMPT* (0.001 mol L^{-1}) was prepared in ethanol by suitable dilution of stock solution.

Solutions of different metal ions used for interference study were prepared by dissolving exactly weighed quantities of their respective salts in distilled water or hydrochloric acid and diluted suitably. Solutions of anions were prepared by dissolving respective alkali metal salts in distilled water.

Various synthetic mixtures containing rhodium(III) and other associated metal ions were prepared by combining their definite compotitions.

Recommended Method

An aliquot of solution containing 30 µg of rhodium(III) and AR grade concentrated hydrochloric acid were transferred to 10 ml volumetric flask to maintain the acidity of 0.5 mol L^{-1} on dilution up to the mark with distilled water. After addition of 0.001 mol L^{-1} *PMPT* in 20% (V/V) ethanol, the content was heated in water bath at 70°C for 5 minutes. The mixture was cooled to room temperature and faint

yellow colored complex was equilibrated with 10 ml chloroform for 10 seconds in a 125 mL separatory funnel. The two layers were allowed to separate. The organic layer containing rhodium(III)-*PMPT* complex was dried over 1.0 g anhydrous sodium sulphate and diluted up to the mark in 10 mL volumetric flask with chloroform. The absorbance of rhodium(III)-*PMPT* complex was measured at 298 nm against the reagent blank prepared in a same manner without rhodium.

III. RESULT AND DISSUCTION

3.1 Absorption Spectra

The absorption spectrums of the rhodium(III) - *PMPT* complex in chloroform at different concentrations of rhodium(III) shows maximum absorption at 298 nm, while the reagent blank shows negligible absorbance at that wavelength. (Figure 1). Constant nature of spectral curves confirms the formation of only one complex under the working conditions. Thus all further spectral measurements of *Rh(III)-PMPT* system were done at 298 nm .The spectral and physico-chemical characteristics of the rhodium(III)–*PMPT* complex are summarised in Table 2.

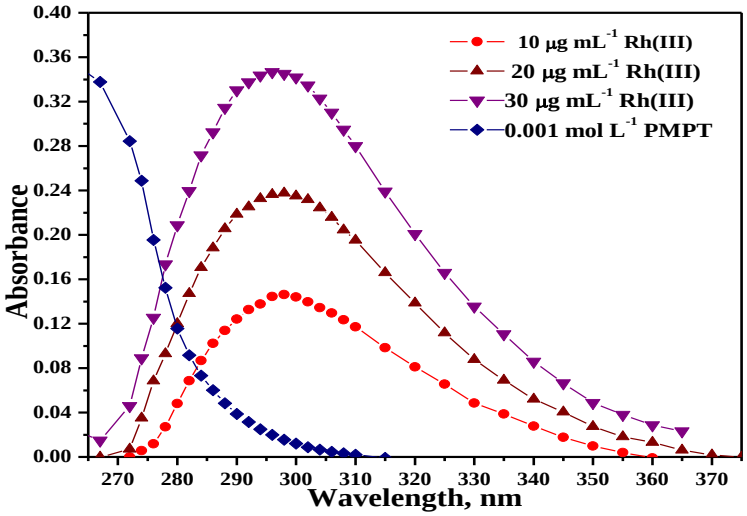

Figure 1. Absorption spectrum for *Rh*(III)-*PMPT*

Table 2 Spectral and physico-chemical characteristics of rhodium(III) - *PMPT* complex

Parameter	**Specification**
Hydrochloric acid concentration	0.5 mol L^{-1}
Reagent solvent	Ethyl alcohol
Extraction solvent	Chloroform
Reagent concentration	0.001 mol L^{-1}
Equilibration time	10 seconds
λmax	298 nm
Molar Absorptivity	1.65 x 10^3 L $mol^{-1}cm^{-1}$
Sandell's sensitivity	0.066 µg cm^{-2}
Beers Law range	up to 40 µg mL^{-1}
Ringbom's optimum range	20 to 40 µg mL^{-1}
Correlation coefficient	0.99
Relative Standard Deviation	0.58 %
Stiochiometry of the complex	1:2 (Rh (III):*PMPT*)
Stability of complex	>24 hr
Limit of detection(LOD)	0.079 µg mL^{-1}

3.2 Effect of acid concentration on complex formation

Rhodium(III)-*PMPT* complex formation was studied in different mineral acids viz., Hydrochloric acid, sulphuric acid, nitric acid, perchloric acid and hydrobromic acid. Complex formation takes place in hydrochloric acid and hydrobromic acid. The absorbance value increases with increase in hydrochloric acid concentration from 0.05 mol L^{-1} to 0.5 mol L^{-1} using 0.001 mol L^{-1} reagent in ethyl alcohol. With further increase in acid concentration the absorbance remains unchanged. (Figure 2). Hence 0.5 mol L^{-1} hydrochloric acid was fixed for further work.

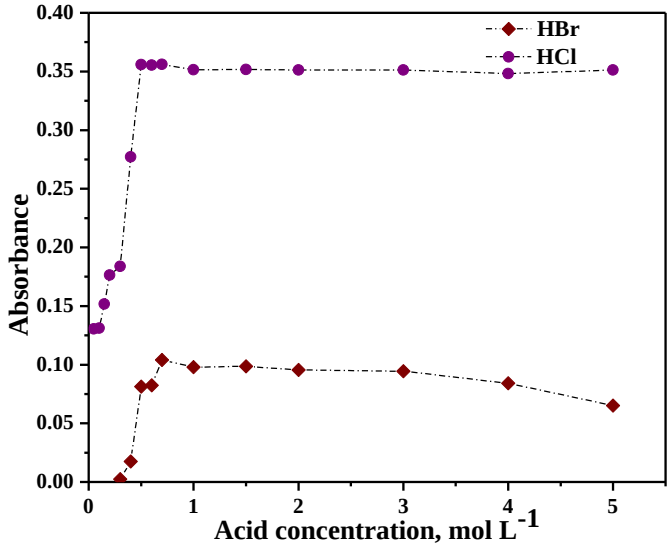

Figure 2. Effect of acid concentration on *Rh*(III)-*PMPT* complex

3.3 Effect of reagent solvent on complex formation

The p-methylphenyl thiourea solution in ethyl alcohol was used for complex formation. Its concentration was varied in terms of percentage from 1 % to 70 % (V/V) keeping all other parameters constant. Complete complex formation takes place in 2.0 to 20% ethyl alcohol .To ensure complete complexation 20 % (V/V) ethyl alcohol in aqueous phase was used as a reagent solvent. (Figure 3)

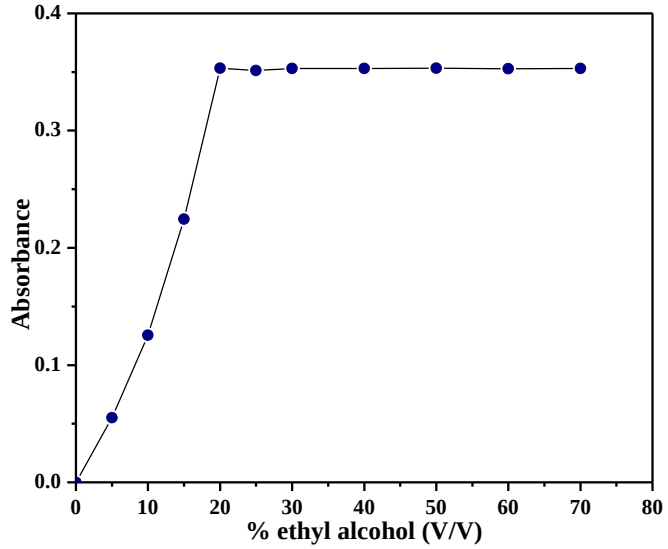

Figure 3. Effect of variation of reagent solvent on Rh(III)-*PMPT* complex

3.4 Effect of Reagent Concentration

The complex formation by 30 µg rhodium was studied by varying *PMPT* concentration from 1 x 10^{-4} mol L^{-1} to 0.01 mol L^{-1} in 20% ethyl alcohol. It was observed that the absorbance of rhodium(III)-*PMPT* complex increases with increase in reagent concentration from 1 x 10^{-4} mol L^{-1} to 0.001 mol L^{-1}. After this range absorbance becomes constant up to 0.01 mol L^{-1} (Figure 4). Hence 0.001 mol L^{-1} *PMPT* in 20% ethyl alcohol (V/V) was fixed for further study.

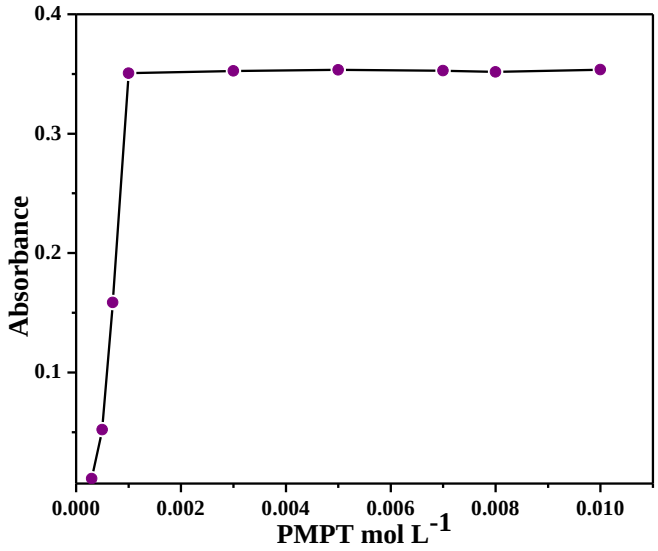

Figure 4. Effect of reagent concentration on Rh(III)-*PMPT* complex

3.5 Effect of Equilibration Time and Stability of the Complex

Rhodium(III)–*PMPT* complex was quantitatively extracted into chloroform within 10 seconds equilibration after the addition of chloroform. Further equilibration does not have undesirable effect on complex. To ensure quantitative extraction, 5mL portion of chloroform was added to aqueous layer and it was equilibrated for 10 sec. faint yellow colour does not appears to chloroform layer which confirms the quantitative extraction of rhodium(III)–*PMPT* complex in a single step. The absorbance of complex, studied hourly remained stable for more than 24 hours.

3.6 Analytical figures of merit

The series of solutions, 0.5 mol L^{-1} in hydrochloric acid containing different amounts of rhodium(III) in the range 0-100 µg were used for the study the validity of the Beer's law. The colour was developed as per proposed method using 0.001 mol L^{-1} reagent in 20 % ethyl alcohol. The faint yellow coloured complex was extracted into chloroform and measured at 298 nm against reagent blank. The plot of absorbance versus concentration of rhodium(III) in µg (Figure 5) showed that the beer's law was valid upto 40.0 µg mL^{-1} of rhodium(III).

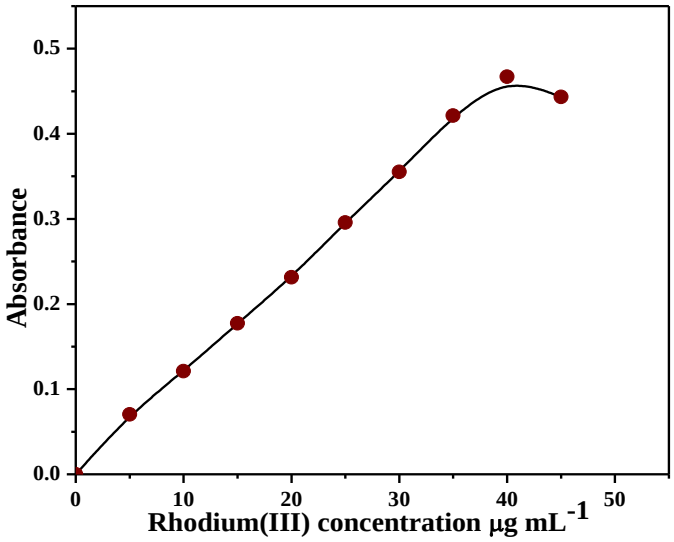

Figure 5. Beers law range for Rh(III)-PMPT complex

The molar absorptivity and sandell's sensitivity were 1.65 x 10^3 L mol^{-1} cm^{-1} and 0.066 µg cm^{-2}, respectively. The optimum concentration range in the determination of rhodium(III) defined by Ringbom's plot was found to be 20 to 40 µg mL^{-1} (Figure 6).

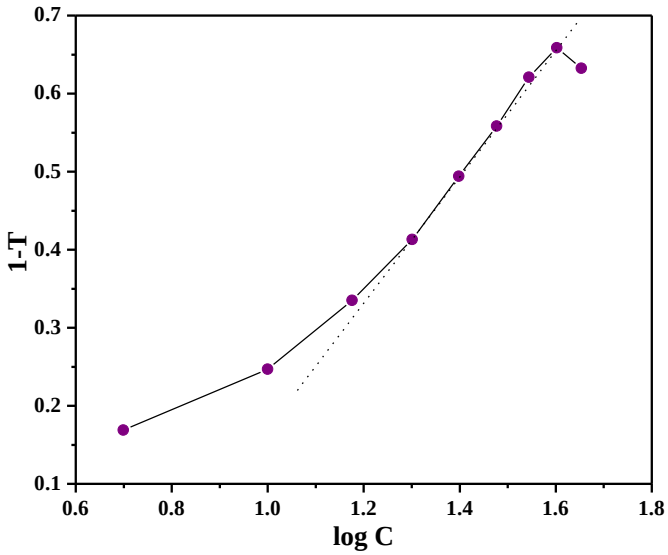

Figure 6. Ringboms plot for Rh(III)-*PMPT* complex

The correlation coefficient of *Rh*(III)-*PMPT* complex with an independent variable as concentration in µg mL^{-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 the rhodium(III) content in real samples can be determined using the straight line equation, y = 0.0034 x + 0.0077.

3.7 Stiochiometry of complex

The probable composition of the *Rh(III)-PMPT* was studied by the slope ratio method. The plot of log $D_{Rh(III)}$ against log C_{PMPT} at 0.2 mol L^{-1} and 0.3 mol L^{-1} hydrochloric acid concentration were linear with slope values 2.41 and 2.13 respectively (Figure 7). Hence the probable stiochiometry of the *Rh*(III): *PMPT* complex was 1:2.

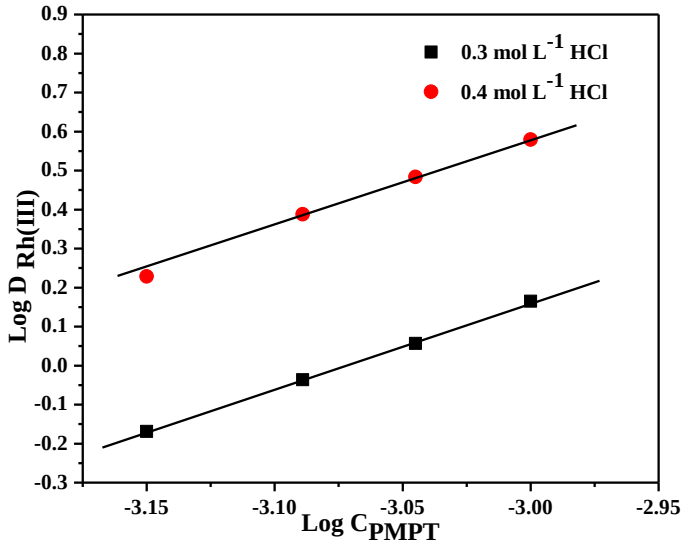

Figure 7. Plot of log C_{PMPT} Vs log $D_{Rh(III)}$ for *Rh*(III)-*PMPT* complex

3.8 Interference Study

Effect of various diverse ions on quantitative extraction of rhodium(III) was studied to ascertain the applicability of proposed method. Variable amounts of diverse ions were added to a solution containing 30 µg rhodium(III). Extractive spectrophotometric determination of rhodium(III) with *PMPT* was carried out according to proposed method. Initially diverse ions were added to rhodium(III) solution in excess. 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). Interference of Fe(II) and Fe(III) was eliminated by using EDTA as a masking agent while that of palladium(II) and iridium(III) was removed by their prior extraction.

Table 3 Effect of foreign ions on extraction of Rh (III)-*PMPT* complex

Foreign ion	Added as	Tolerance limit, mg	Foreign ion	Added as	Tolerance limit, mg
Mn (II)	$MnCl_2.6H_2O$	0.2	Fe(III)[b]	$(NH_4)Fe(SO_4)_2.12H_2O$	1.0
Al(III)	$AlCl_3.6H_2O$	0.3	As (III)	As_2O_3	5.0
W (VI)	$Na_2WO_4.2\ H_2O$	2.0	Au (III)	$HAuClO_4.\ H_2O$	0.1
Sn (II)	$SnCl_2.2\ H_2O$	0.5	Ca (II)	$CaCl_2.2\ H_2O$	10
Li (I)	LiCl	15	Os (VIII)	OsO_4	0.5
Co (II)	$CoCl_2.6\ H_2O$	0.1	Pt (IV)	H_2PtCl_6	0.3
Ni (II)	$NiCl_2.6\ H_2O$	0.3	Pd (II)[a]	$PdCl_2$	0.5
Pb (II)	$PbCl_2$	0.7	Ir (III)[a]	$IrCl_3$	0.8
Mg (II)	$MgCl_2.6\ H_2O$	10	Ru(III)	$RuCl_3$	0.4
Cr (III)	$CrCl_3$	0.8	Sb (III)	$RuCl_3.6\ H_2O$	1.0
Zn (II)	$ZnSO_4.7\ H_2O$	5.0	Ba (II)	$BaCl_2.6\ H_2O$	6.5
Zr (II)	$ZrOCl_2.8H_2O$	5.0	Hg (II)	$HgCl_2$	3.2
Ag(I)	$AgNO_3$	0.1	Ti (III)	$(Ti_2SO_4)_3$	1.0
Cd (II)	$CdCl_2.2\ H_2O$	7.5	E.D.T.A	Na_2EDTA	75
La (III)	$LaCl_3.7\ H_2O$	1.5	Sulphate	K_2SO_4	70
Se (IV)	SeO_2	1.0	Succinate	$(CH_3COONa)_2.6\ H_2O$	100
Ce (IV)	$Ce(SO_4)_2.4\ H_2O$	0.5	Tartrate	$(CHOH:COOH)_2$	60
Fe (II)[b]	$(NH_4)Fe(SO_4)_2.12H_2O$	0.3	Fluoride	NaF	80
Tl (III)	Tl_2O_3	0.2	Bromide	KBr	100
U (VI)	$UO_2(CH_3COO)_2$	0.5	Oxalate	$(COOH)_2.2\ H_2O$	100
Sr (III)	$SrCl_3.6\ H_2O$	8.0	Citrate	$C_6H_8O_7.\ H_2O$	60
V (V)	V_2O_5	5.0	Phosphate	Na_3PO_4	70
Bi (III)	$BiCl_3$	0.1	Malonate	$CH_2(COONa)_2$	90

a: prior extraction b: masked with 75 mg EDTA

3.9 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 0.58 %. This indicates that the developed method was accurate and precise. The limit of detection (LOD) was found to be 0.079 µg mL^{-1}.

IV. APPLICATIONS

4.1 Separation and determination of rhodium(III) from binary synthetic mixtures

Recommended method was successfully applied for the separation and spectrophotometric determination of rhodium(III) from the associated metal ions like Cd(II) , Pb(II), Ni(II), W(VI), Zn(II) and Hg(II). Rhodium(III) was separated from associated ions by proposed method. After quantitative extraction and spectrophotometric determination of rhodium(III) 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 (Sandell, 1958). (Table 4)

Table 4 Separation and determination of rhodium(III) from binary synthetic mixture

Metal ions	Amount taken (µg)	Recovery [a] (%)	RSD (%)	Chromogenic Ligand	Reference
Rh (III)	30	99.8	0.19	*PMPT*	----
Cd (II)	50	99.8	0.11	Dithiozone	(Sandell, 1958)
Rh (III)	30	99.6	0.35	*PMPT*	----
Pb (II)	40	99.0	0.30	Dithiozone	(Sandell, 1958)
Rh (III)	30	99.6	0.26	*PMPT*	----
Ni (II)	25	99.4	0.33	*DMG*	(Sandell, 1958)
Rh (III)	30	99.7	0.23	*PMPT*	----
W (VI)	50	99.7	1.65	Thiocyanate	(Sandell, 1958)
Rh (III)	30	99.7	0.22	*PMPT*	----
Zn (II)	50	99.7	0.18	Dithiozone	(Sandell, 1958)
Rh (III)	30	99.7	0.14	*PMPT*	----
Hg (II)	60	99.7	0.17	Dithiozone	(Sandell, 1958)

a : average of five determinations

4.2 Separation and determination of rhodium(III) from ternary synthetic mixtures

Ternary synthetic mixtures with known amount of different associated metal ions and 30 µg rhodium(III) was taken in 10 mL calibrated volumetric flask and rhodium(III) was separated quantitatively and determined as *Rh*(III)-*PMPT* complex by recommended method. Results were in good agreement with the expected amounts (Table 5).

Table 5 Separation and determination of rhodium(III) from ternary synthetic mixture

Composition (µg)	Recovery [a] (%)	RSD, (%)
Rh (III) 30 ; Ni (II) 25; Zn (II) 50	99.86	0.21
Rh (III) 30 ; Pb (II) 40; Cd (II) 50	99.89	0.22
Rh (III) 30 ; Hg (II) 60; Zn (II) 50	99.91	0.26
Rh (III) 30 ; Pb (II) 40; W(VI) 50	99.82	0.09
Rh (III) 30 ; Ni (II) 25; Cd (II) 50	99.42	0.85

a : average of five determinations

4.3 Separation of rhodium(III) from synthetic mixtures corresponding to alloys

Various synthetic mixtures were prepared according to the certified composition viz. Pseudo-palladium alloy, Nickel-Rhodium alloy and Iron-Rhodium alloy The recommended procedure was applied for the extraction and determination of rhodium(III). The quantitative amount of rhodium(III) was recovered.(Table 6)

Table 6 Separation and determination of rhodium(III) from synthetic alloy samples.

Name and composition of alloy	Amount of Rhodium (III)		Recovery [a], %	RSD, %
	taken, (µg)	found, (µg)		
Pseudo-palladium alloy Rh(III) 50%, Ag(I) 50%	30	29.96	99.86	0.11
Nickel-Rhodium alloy Rh(III) 16%, Ni(II) 84%	30	29.85	99.50	0.84
Iron-Rhodium alloy Rh(III) 75%, Fe(III)[b] 25%	30	29.96	99.87	0.19

a: average of five determinations b: masked with 75 mg E.D.T.A

V. CONCLUSION

P-methylphenyl thiourea is proved to be sensitive reagent for the solvent extraction and spectrophotometric determination of rhodium(III). The developed method is rapid and selective. Low hydrochloric acid concentration (0.5 mol L^{-1}), minimum volume of extractant for determination (10 mL) and high stability of the complex prove the method is beneficial for rapid determination of rhodium with low cost. The numerical values of relative standard deviation (0.58%) and correlation coefficient (0.99) proves the accuracy and reproducibility of method. Analysis of rhodium from binary, ternary synthetic mixtures and from synthetic mixtures corresponding to alloys explains the extensive applicability of the method.

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BIOSORPTION EFFICIENCY OF SYZYGIUM CUMINI BARK FOR REMOVAL OF ZINC FROM INDUSTRIAL EFFLUENT

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Abstract: The rapid industrialization and increased population is found to increase the effluents and wastewater into the aquatic system. Heavy metal ions are the poisonous, found in industrial effluent and they are main cause of hazard to human life. Zinc is a toxic metal and having high concentration in effluents of various industries. Hence the objective of the present study is to investigate the efficiency of *Syzygium cumini* bark as an adsorbent for the removal of zinc. The parameters investigated in this study are adsorbent dosage, contact time, pH, temperature and variable initial zinc concentrations. The maximum adsorption was observed at pH 8 with 2.5 gm adsorbent in 60 minutes. The FTIR spectrum shows the peaks at 1025 cm^{-1} larger and broad at 1614 cm^{-1}, 2361 cm^{-1}, 2915 cm^{-1}, 3000 cm^{-1} wave numbers. Increasing intensity of major peaks probably due to absorption of zinc.

Keywords: Bio-adsorbent, Zinc, Syzygium cumini bark, FTIR

I. INTRODUCTION

Industrialization is the major cause of inclusion of heavy metals in to the environment especially in the water bodies. Waste water commonly contains metal ions Cu, Ni, Cd, Fe, Zn, Pb which are not biodegradable and hence are of vital concern [1]. Zinc is one of these toxic metals and often found in high concentration in effluents, discharged from industries involved in acid mine drainage, galvanizing plants, electroplating, pulp and paper and municipal waste waters [2-3]. Therefore there is a significant interest regarding zinc removal from waste waters [4]. Zinc metal ions are involved in the food chain and finally get accumulated in the living organisms causing diseases and disorders [3].

Zinc toxicity for human is 100-500 mg/day [5-6]. According to world health organization the maximum acceptable concentration of zinc in drinking water is 5 mg/L [7]. The release of large quantities of heavy metals into the natural environment has resulted in a number of environmental problems. A conventional method for removing zinc ions from industrial waste water includes coagulation–flocculation, chemical precipitation, ion-exchange, reverse osmosis, solvent extraction [8]. These conventional methods for removal of metals from wastewater however are often cost prohibitive and having inadequate efficiencies of low metal concentrations. The search for new technologies involving the removal of zinc has directed the attention to biosorption based on metal binding capacities of various biological materials [9-14]. The major advantage of biosorption over other traditional method includes low cost, high efficiency, possibility of regeneration of biosorbent and metal recovery, rapid and eco-friendly behavior. As most of the low cost biosorbents have the limitation of low sorptive capacity hence, there is a need to explore low cost biosorbent having high absorption capacity. Several publications utilized locally available adsorbents [9] [15-16] and agricultural byproducts [17] for heavy metal removal. However, to cover this problem more investigations will be needed to deal with other locally available and cheap biosorbents to remove zinc from industrial contaminated waters. The objective of this study is to develop inexpensive and effective biosorbent which is easily available in large quantities. The efficiency of *Syzygium cumini* bark is studied for adsorption of zinc. *Syzygium cumini* is commonly known as Jamun. Jamun belongs to the family *Myrtaceae. Syzygium cumini* is widely used medicinal plant in the treatment of particularly in diabetes. The plant is rich in compounds containing anthocyanins, glucosides, ellagic acid, isoquercetin, kaemferol and myrcetin [18]. Phytochemicals isolated from *S. cumini* bark has been found to contain betulinic acid, friedelin, epi-friedelanol, beta-sistosterol, eugenin and fatty acid esters of epi-friedelanol [19], ellgaic acid [20], flavonoids and tannins [21]. The presence of gallo and ellagi-tannins may be responsible for the astringents property of stem bark.

Literature survey reveals that, the adsorption study of zinc with *Syzygium cumini* bark, as a biosorbent has been investigated.The effect of variable adsorbent dosage, contact time, pH, temperature and initial ion concentration were investigated. Adsorption of zinc was conformed by taking FTIR spectrum of adsorbent before and after adsorption.

II. MATERIAL AND METHODS

2.1. Sample collection and preparation

The bark scraping of *Syzygium cumini* were collected from local area and washed repeatedly with water to remove dust and soluble impurities. It was dried in natural sunlight for 6 days and then it was pulverized, sieved to obtain uniform size upto 300 µm. It was stored in an air tight box for further use.

2.2. Screening of Biosorbent

The experiments were carried out in conical flasks by agitating a preweighed amount of the *Syzygium cumini* bark powdered adsorbent with the aqueous zinc solutions for a pre-determined period at 10-40^{0}C in ice bath/ thermoregulatory oven. The biosorbent doses were maintained 0.5 to 2.5 gm and pH of solution was adjusted 3 to 8 using 0.01 N HCl and 0.01 N NaOH solution. The time duration studied 15- 90 minutes was maintained for impact of time at zinc concentration of 5 mg/ml and biosorbent dose of 2.5 gm. The concentration of zinc (II) ions in the solution was determined complexometrically.

2.3. Characterization of the Biosorbent

FTIR spectrophotometer was employed to determine the type of functional groups present on the adsorbent, before and after adsorption and thus to find out the groups responsible for metal adsorption. Pellets of adsorbent were made with 1% KBR and 4000 to 650 cm^{-1} wavelength was used on using Thermo scientific instruments.

III. RESULTS AND DISCUSSION

In the present study, *Syzygium cumini* bark has been used for removal of zinc (II) from paper industry effluent. The adsorption of zinc was initially performed with various concentrations of zinc to optimize the concentration of zinc to be used for the study. The result indicates that, adsorbent prepared from *Syzygium cumini* bark has better adsorption capacity. This study was conducted in real time effluents to study the efficiency of removal. The results obtained indicating that the adsorption depends on various experimental conditions such as amount of adsorbent, equilibrium time, pH, temperature, initial ion concentration.

3.1. Effect of Adsorbent Dosages

The effect of adsorbent dose is studied and the results obtained are summarized in fig. 1. 25 ml solution containing zinc is transferred in 100 ml conical flasks treated with 0.5, 1.0, 1.5, 2.0, 2.5 gm of biosorbent (*Syzygium cumini* bark powder). The solution is kept in orbital shaker for about 60 minutes. The concentration of unabsorbed zinc was determined in the solution after filtering through Whatman no.41. The filtrate was titrated with EDTA. The percentage biosorption of zinc was found maximum with increased adsorbent dose of 2.5 gm. The initial increase may be due to increase in surface area of the sorbent. Thus making it probable that the zinc ions are adsorbed onto the adsorption sites [22]. The maximum removal of zinc was 74 % at 2.5 gm biosorbent, thereafter increasing the adsorbent dosage percentage removal decreases.

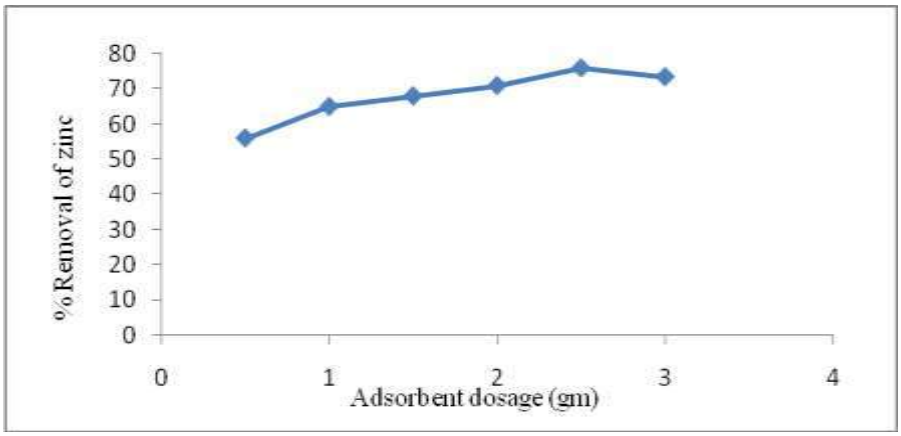

Figure 1. Effect of *syzygium cumini* bark on zinc biosorption

3.2. Effect of Contact Time

The contact time plays crucial role in adsorption of metal species onto the surface of adsorbent. The effect of contact time upto 60 minutes on zinc adsorption was studied using biosorbent dose of 2.5 gm and zinc concentration of 5 mg/ml in each flasks and allowed to stand for different time intervals. These conical flasks were kept in orbital shaker for agitations at 150 rpm.The adsorbent were separated by filtration and amount of zinc unabsorbed was determined by titrating with 0.01 M EDTA solution. The effect of time on percentage removal of zinc ion was shown in fig. 2. Maximum adsorption takes place in first hour of contact time and longer contact time has negligible effect on removal of zinc. The maximum removal was 91% at 60 minutes.

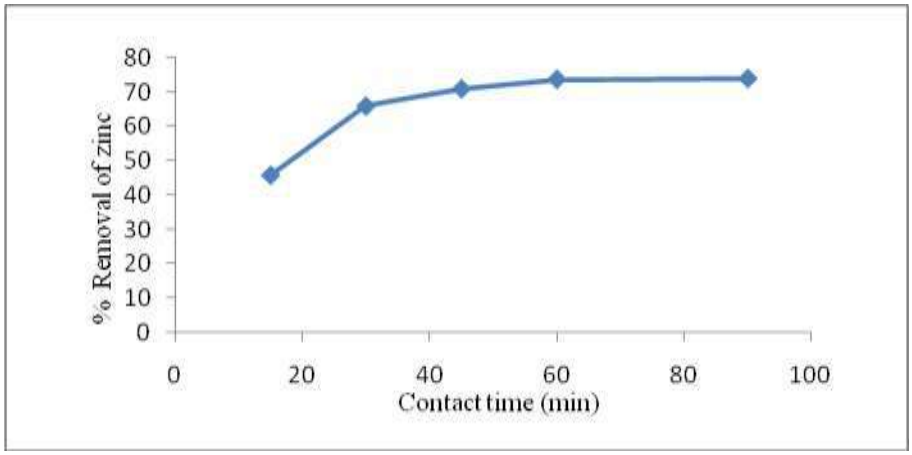

Figure 2. Effect of contact time on zinc on syzygium cumini bark of biosorption

3.3. Effect of pH

The biosorption of zinc is depicted in fig. 3. pH is one of the main factor that influences surface change of the adsorbent, degree of ionization and speciation on adsorbate [23]. At low pH, there is an occupation of the negative sites by the H^+ and H_3O^+ which leads to the reduction of the vacancies for the metal ions and it causes decrease in the metal ion adsorption [24]. It has been observed that with increased pH, the percentage of adsorption of zinc increased, maximum adsorption was obtained at pH 8. The acidic medium has been found to show biosorption upto 54 % which increases upto 90 %.

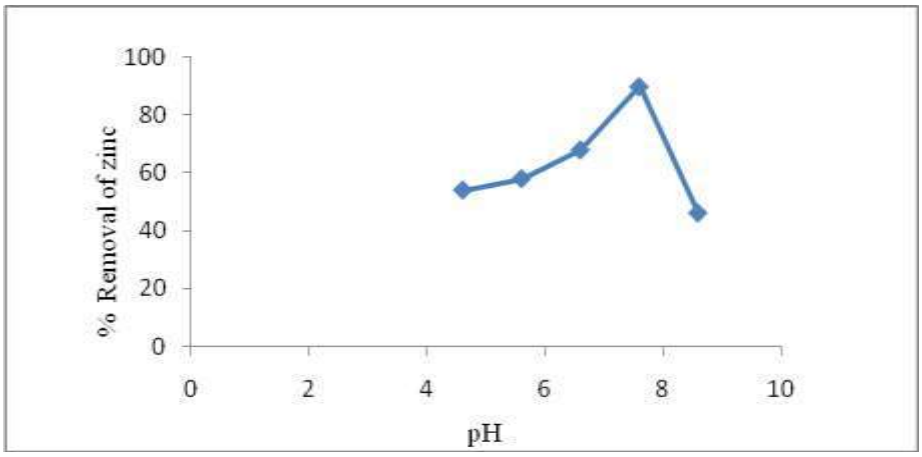

Figure 3. Effect of pH on zinc biosorption using *syzygium cumini* bark

3.4. Effect of Temperature

The biosorption of zinc by *Syzygium cumini* bark was studied at different temperatures with constant concentration of the zinc of 5 mg/ml using 2.5 gm biosorbent, maintained at 10, 20, 30, 40 and 50^{0}C. The solutions were kept for 60 minutes with gentle shaking at periodical intervals and the remaining concentration of zinc was measured in the solution after filtration. The percentage biosorption of zinc was found maximum 94 % at optimum temperature 40^{0}C and minimum 38^{0}C at 10^{0}C (fig.4). Further increase in temperature (Beyond 40^{0}C), there is no increase in percentage removal of zinc. The increase in adsorption with increase in temperature was due to change in pore size, desolvation of zinc ions and increase in intra particle diffusion [14].

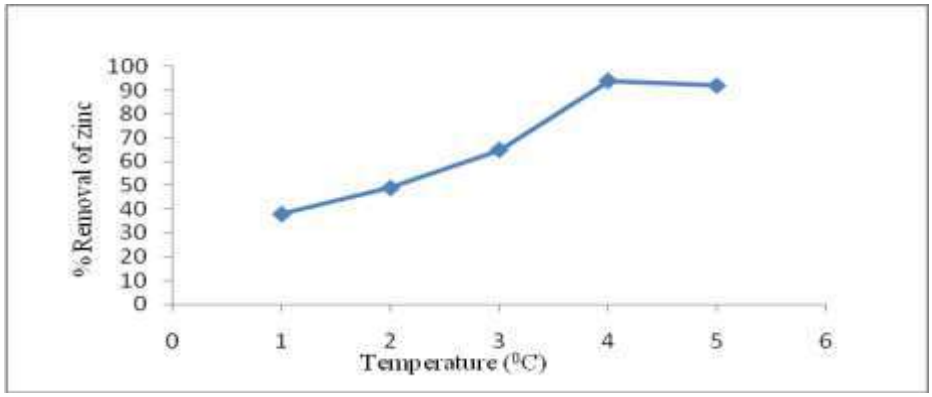

Figure 4. Effect of temperature on zinc biosorption using *syzygium cumini* bark

3.5. Effect of Initial ion Concentration

The effect of change in adsorption efficiency with initial concentration as shown in fig. 5. Initial ion concentration was varied from 1 to 5 mg/ml were treated with biosorbent 2.5 gm in each flasks. The percentage adsorption increase upto 84 % for 5 mg/ml zinc in solution, with increase in the concentration, the percentage removal of zinc decreases. At higher concentration, metal ion diffuse to the adsorbent surface by intraparticle diffusion and the hydrolyzed ions diffuse at a slower rate decreasing the percentage removal [25].

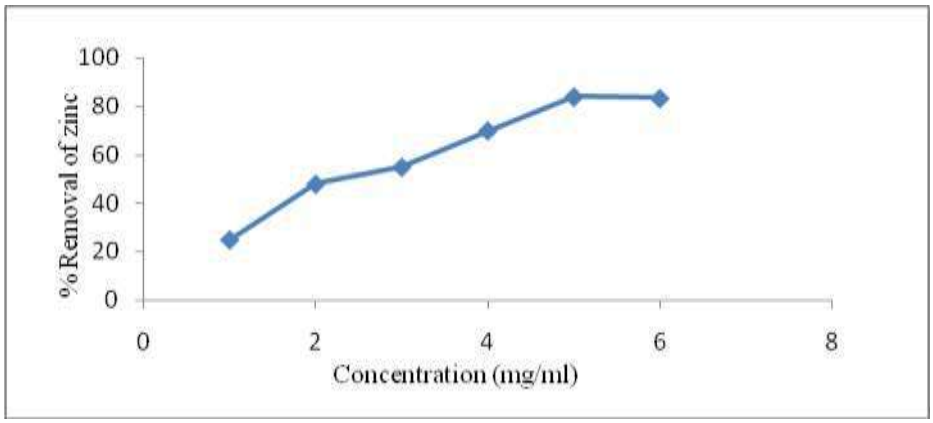

Figure 5. Effect of increasing concentration of zinc on syzygium *cumini* bark biosorption

3.6. FTIR spectra of *Syzygium cumini* bark

FTIR spectra of *S.cumini* bark before and after biosorption with zinc was carried out using Thermo scientific spectrophotometer in fig. 6 and 7. The strong peaks observed in *Syzygium cumini* bark at wave numbers 1024 cm^{-1} (-CN stretching viberations of the protein fractions), 1457.41cm^{-1} (symmetric bending of CH_3 of acetyl moiety), 1540.84 cm^{-1} (amide bond), 1617.08 cm^{-1} (C=0 chelate stretching), 2361 cm^{-1} (vibrations of $–NH_2$), 2915cm^{-1}, 2980.33 cm^{-1} (C-H stretching) and 3418.60 cm^{-1} (bonded –OH group, -NH stretching), 668.01 cm^{-1} (C-X). The peaks after biosorption with zinc became more prominent, slight shifted and larger at 1025 cm^{-1}, broad at 1614cm^{-1}, 2361 cm^{-1}, 2915 cm^{-1}, 3000 cm^{-1} wave numbers respectively. The increasing in intensity of major peaks after zinc adsorption is probably due to chelating effect of zinc ion with the functional groups of biosorbents.

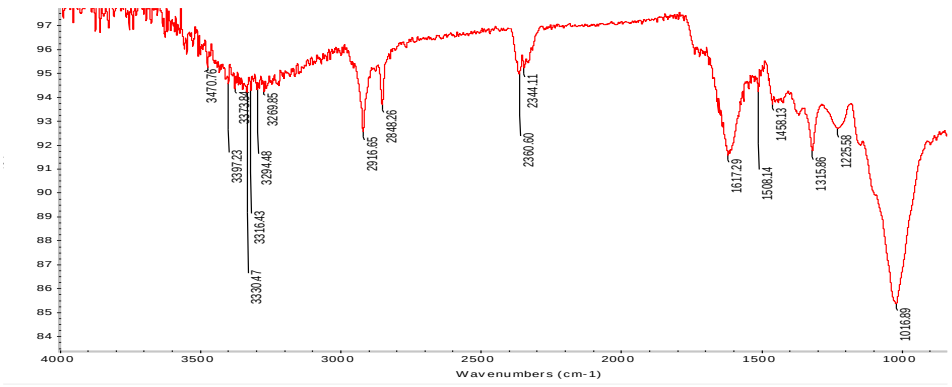

Figure 6. FTIR of *syzygium cumini* before zinc biosorption

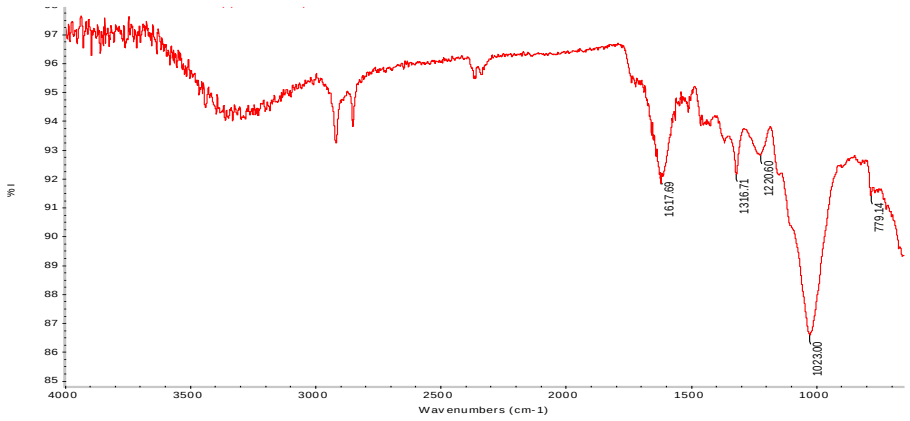

Figure 7. FTIR of *syzygium cumini* after zinc biosorption

IV. CONCLUSION

The present study investigates the adsorption of zinc by bark of *Syzygium cumini*, as *Syzygium cumini* bark powder has successful application as an adsorbent and it shows high efficiency for the removal of zinc from industrial effluent. FTIR spectra showed that the functional groups like carbonyl and hydroxyl ions played an important role in biosorption of zinc. The optimal conditions for the zinc removal were studied, It is observed that the maximum removal of zinc occurs at 5 mg/ml at pH 8 with an adsorbent dose of 2.5 gm and maximum agitation time 60 minutes. The findings of the study revealed that *Syzygium cumini* bark is easily available and its utility as an biosorbent will be economical and can replace the expensive adsorbents in the adsorption process.

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RESEARCH ARTICLE

Green Synthesis of Copper Nanoparticles Using *Syzygium Cumin*, Leaf Extract, Characterization and Antimicrobial Activity

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Abstract: The use of plant material for synthesis of nanoparticles is a green technology. This green technique was used for synthesis of copper nanoparticles by biologically reducing copper sulphate solution with aqueous *Syzygium Cumin* leaf extract at pH 5.0. The formation of copper nanoparticles was indicated by the colour change from yellow to brown. The UV-Visible spectrum of copper nanoparticles gave surface Plasmon resonance (SPR) of 190 nm. The synthesized nanoparticles were characterized using scanning electron microscopy (SEM), x-ray, diffraction (XRD) and FTIR, These biologically synthesized copper nanoparticles were tested for antimicrobial activity against human pathogens *viz. Bacillus subtilis* and *E-coli*. Presence of elemental copper was revealed by EDAX. These biologically synthesized copper nanoparticles were found to be effective in controlling growth of human pathogens *viz., Bacillus subtilis* and *E-coli*.

Keywords: *Syzygium cumini*, SEM, XRD, EDAX, FTIR, UV-Vis, *Bacillus subtilis* and *E- coli*

Introduction

Nanoscience and nanotechnology include the areas of synthesis, characterization, exploration, application of nanostructure and nanosize materials[1]. Nanoparticles have been extensively studied over the last decade due to its characteristics like chemical, physical, electronic, electrical, mechanical, magnetic, thermal, dielectric, optical and biological properties[1]. In recent years, the biocidal properties of copper nanoparticles (CuNPs) have wide application in treating wounds. CuNPs are used through processed bandages with affordable cost of preparation as well as exceptional physical and chemical properties[2,3]. Preparation of nanoparticle is primarily based on their smaller size and their high surface to volume ratio. Now a day's metal and metal oxide nanoparticles are receiving increasing attention in a large variety of application. They have industrial usage such as gas sensors,

solar cells, catalytic processes *etc.,*[4,5]. Several methodologies have been proposed with interesting approaches to control the nonmaterial properties such as size and shape, these include metal vapor co-deposition, electrochemical reduction, gas phase evaporation method, thermal decomposition, radiolytic reduction and chemical reduction *etc*.,[6,7]. Although various physical and chemical methods have been extensively used to produce nanosized copper particle such as micro-emulsion method[8] arc submerged. Nanoparticle synthesis system[9], flame based aerosol methods[10], sonochemical[11], hydrothermal[12] and solid state techniques[13]. The use of toxic chemicals for the synthesis of nanoparticle limits their applications in clinical fields. Therefore, developments of clean, biocompatible, nontoxic and eco-friendly methods for nanoparticles synthesis are advantageous. The interest in this field has shifted toward 'green' chemistry and bio-processor approach. These approaches focus on utilization of environmental-friendly, cost-effective and biocompatible reducing agents for synthesis of copper nanoparticles from various plant extracts have been utilized in the synthesis of nanoparticles. Ascorbic acid present in the *Syzygium cumin* leaves extract is a good reducing and capping agent and aids in the biosynthesis of copper nanoparticles[14]. In this communication we are reporting biomaterial assisted synthesis of copper nanoparticles, reducing the copper ions by the aqueous extract of *Syzygium cumin* leaf extract.

Experimental

0.1 M solution of copper sulphate pentahydrate was prepared by dissolving 2.497 g salt in distilled water and diluted to 100 mL with distilled water.

Preparation of leaf extract

The fresh leaves of *Syzygium cumin* were thoroughly washed with normal water and then followed by distilled water to remove the impurities. The cleaned leaves were kept under sun shade to remove moisture completely and subsequently transferred to 100 mL beaker containing distilled water and allow to boil at 100 °C for 30 min. Then cool it to room temperature. This solution was initially filtered through ordinary filter paper and then by Whatman No.1 filter paper to get clear extract. This solution was diluted to 100 mL with distilled water. The filtrate was stored at room temperature for use.

Green synthesis of copper nanoparticle using leaves extract

The leaf extract about 10 mL was introduced drop wise into 100 mL of 0.1 M solution of $CuSO_4.5H_2O$ (0.025 g/mL) under continuous stirring with help of magnetic stirrer. After the complete addition of leaf extract, the mixture was kept for incubation for 24 h within a particular time; the green colour of extract was changed into dark green, (Figure 1) which indicates the formation of copper nanoparticles. Then supernatant was removed and nanoparticles containing extract was transferred to silica crucible and kept in oven at 99 °C then temp was increased to 300-400 °C. These particles were analysed using FTIR, SEM and EDAX.

Figure 1. Synthesis of copper nanoparticle **A**-Cu solution, **B**-leaf extract, **C-**Cu solution + leaf extract

Results and Discussion

UV-Visible studies

The reduction of copper ions to copper nanoparticles was monitored by recording UV-Visible spectrum of the reaction mixture after diluting a small aliquot of the sample with distilled water. The measurements were recorded on Systronics Au-2701 model UV-Visible dual beam spectrometer operated at resolution (190-900 nm) giving maxima at 190 nm (Figure 2).

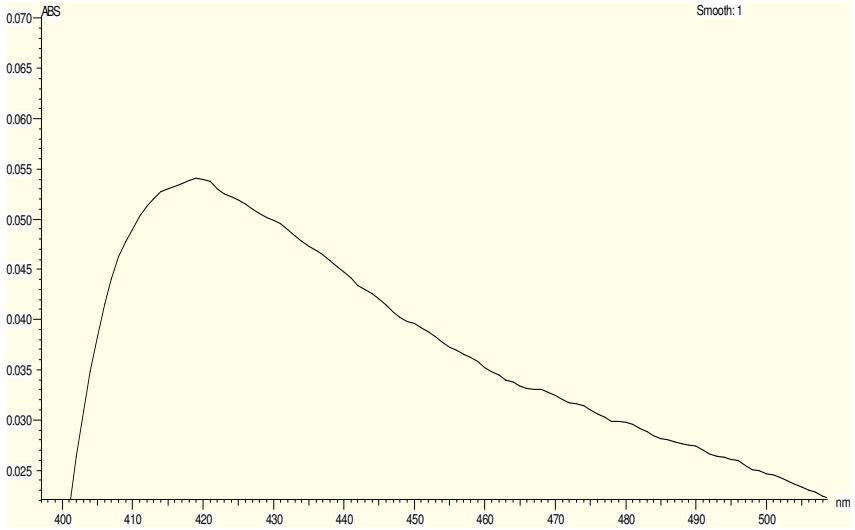


Figure 2. UV-Visible spectra of synthesized CuNP

Fourier transform-Infrared (FT-IR)

The FTIR spectrum was taken to identify and characterize the molecule and their functional group present in synthesized CuNPs are shown in (Figure 3), CuO and Cu_2O vibrational modes are observed[15] at 605.65 cm^{-1}.

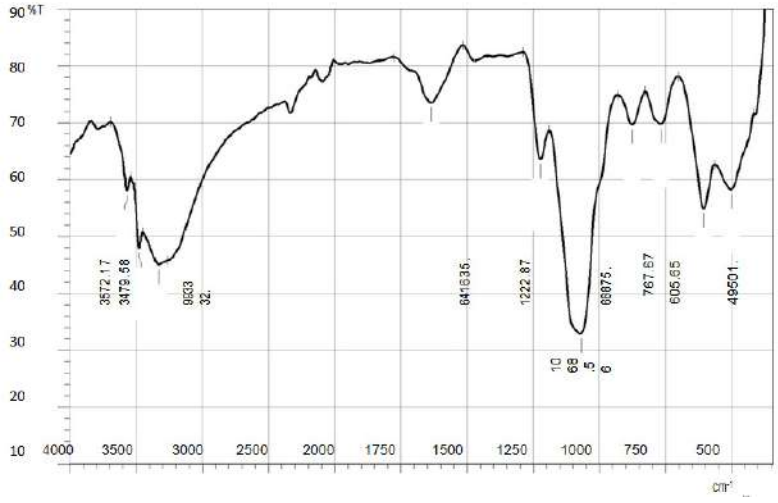


Figure 3. FTIR spectrum of synthesized CuNPs

X-Ray diffraction studies

X-ray diffraction (XRD) measurement of the copper nanoparticles is shown in Figure 4. Spectrum was taken using powder x-ray diffractometer instrument. The crystallite domain size was calculated by using Debye-Scherrer formula. The sample of CuNPs demonstrated a high crystalinity level with diffraction angles of 34.3, 35.3, 38.6, 48.2 and which related to monoclinic end centered with space group C2/c (15) of copper lines indexed at (023), (111), (111)) and (202).

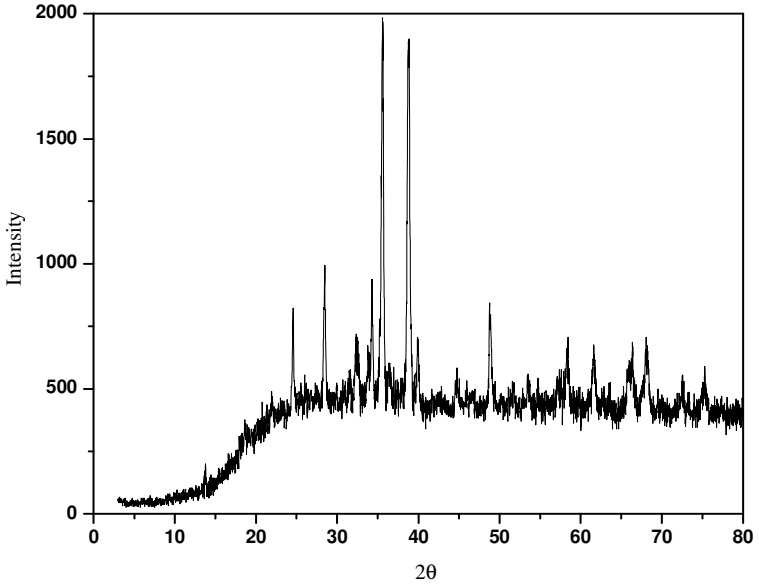
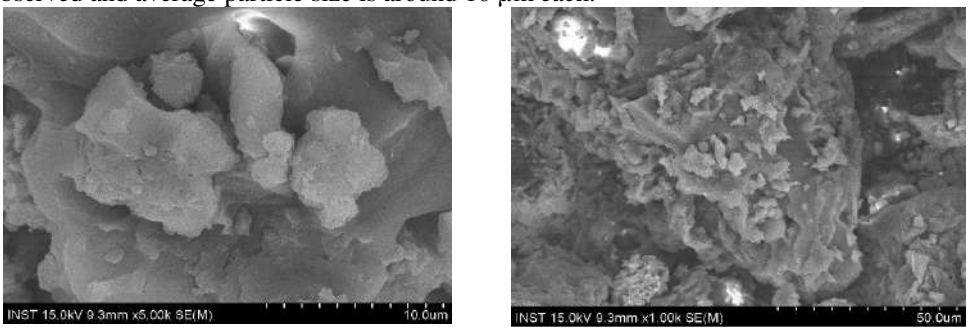


Figure 4. XRD analysis of copper nanoparticles

Scanning electron microscopic analysis

Scanning electron microscopic (SEM) analysis was carried out using S-4800, serial number-HI-9143-004 SEM machine. Thin films of the sample were prepared on a carbon coated copper grid by just a very small amount of the sample on the grid, extra sample was removed using a blotting paper and then the film on the SEM grid were allowed to dry by putting it under a mercury lamp for 5 min. SEM Agglomeration of the Cu nanoparticles observed and average particle size is around 10 µm each.

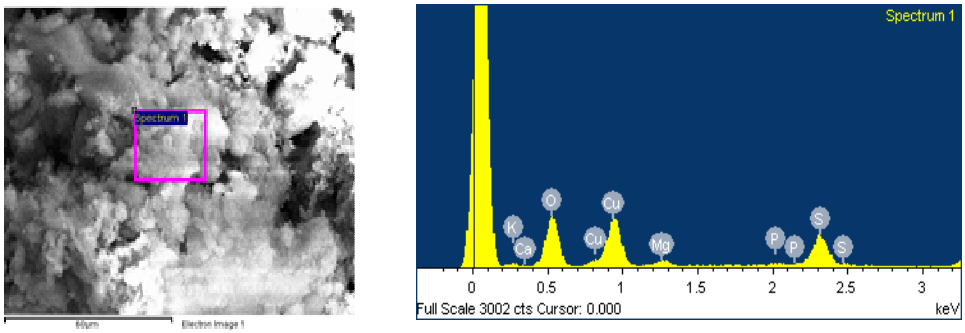


a b

Figure 5. SEM images of copper nanoparticles (a) 10 µm (b) 50 µm

EDAX

The composition of copper nanoparticles was further probed by energy-dispersive x-ray (EDX) analysis. Figure 6 shows the EDX pattern of CuNPs obtained from plant extract, which indicates the presence of Cu and small amount of oxygen. Energy dispersive x-ray spectroscopy (EDX) analysis revealed that pure copper (39.16%) was present in CuNPs.



Element and series	Weight %	Atomic %
OK	38.81	65.5
Mg K	2.61	2.40
P K	0.54	0.47
S K	9.59	8.10
K K	7.15	4.95
Ca K	2.59	1.75
Cu L	39.16	16.68
Total	100.00	

Figure 6. EDX spectrum

Antimicrobial activity

The antimicrobial activity of pathogens was established using well diffusion method. The bactericidal effect of copper nanoparticles has been attributed to their high surface to volume ratio and small size which allows them to interact very closely with microbial membranes. The antimicrobial study of CuNPs was carried out using two pathogenic bacteria such as *E-coli* and *bacillus subtilis*. To cultivate the bacteria, nutrient agar was used. About 20 mL of sterile molten agar was poured into the sterile Petri dishes. After solidification of medium, the Petri dishes were placed on the solidified medium. Then copper nanoparticles with 600 µL concentration was prepared. 40 µL concentration were added into the one of the well of Petri dishes. Petri dishes were incubated for 24 h at 37 °C. Antibacterial capacity of the copper nanoparticles was measured by standard zone of inhibition assay (Figure 7).

(a) *Bacillus subtilis* (b) *E-coli*

Figure 7. Antimicrobial activity of CuNPs

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Impact of Nutri-psycho Counseling on Adjustment Level of Obese School Going Children

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ABSTRACT

Impact of nutri-psycho counseling on adjustment of obese school going children was assessed in Pune, Nashik and Ahmednagar districts of Western Maharashtra. For this study, 180 obese school going children were selected, from which 90 boys and 90 were girls and 60 from each selected district in 6- 16 age group. The adjustment of selected children was assessed by using 'Adjustment Inventory for School Students' (AISS) recommended by A.K.P. Sinha and R.P. Singh. It was found that, the adjustment in relation with emotional, social, and educational was found increased after NP counseling.

Key Words : Obese children, Adjustment, Nutri-psycho counseling

INTRODUCTION

Obesity is a universal problem having different ramifications national, regional and local. The pace at which the obesity epidemic is threatening the world's children and adolescents has raised immediate public health concern. Scholars have studied obesity and overweight in their own perspective. "The term overweight rather than obese is often used in children as it is less stigmatizing." (Bessesen, 2008). Due to availability of square food and affinity of parents the school children are provided more nutritious food than they require, which leads to complex situation of obesity.

Globally, an estimated 43 million preschool children (under age 5) were overweight or obese in 2010, a 60 per cent increase since 1990 which is a serious problem. The problem is affecting various countries not only in rich but also developing and economically backward countries. By understanding their sheer numbers, places, it reveals that the greatest burden lies on the developing countries of Asia and Africa. Of the world's 43 million overweight and obese preschoolers, 35 million live in developing countries (Ramchandran *et al.*, 2002). By 2020, if the current epidemic continues unabated, 9 per cent of all preschoolers will be overweight or obese – nearly 60 million children (de Onis and Blossner, 2010).

In the last few decades children have become less active due to easy access to technological advances. A positive relation has been observed between lack of activity e.g. Time spent on watching television (Dietz and Gortmaker; 1985) or playing computer games impact on an increase in adiposity in the school age children.

Social, psychological and metabolic factors all contribute to the prevalence of overweight. It carries a social stigma and often children are made a figure of fun and are though responsible for their condition. A feeling of personnel shame frequently occurs as a result of such condemnation and rejection particularly in the adolescent who is overweight. Those involved in management should not imply overweight patients are self-indulgent or lack of will power.

Negative outcomes from being overweight during

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childhood include being at higher risk number of chronic and acute conditions as well as negative social and psychological outcomes (Lee, 2009 and Sullivan, 2004) states that these are a great deal of evidence that emotional health underpins at least part of the trend towards obesity. Like adults, children often rely on food fixes to deal with emotions. They may eat more often when they are feeling sad, stresses or bored and they are more likely to do so, if this pattern was demonstrated to them through their parents.

METHODOLOGY

An exploratory research has been conducted in three districts such as Pune, Ahmednagar and Nasik of Western Maharashtra. Total 600 (obese) children among obese children having age between 7 to 12 years including male and female were selected by (purposive) simple random sampling method. About 200 obese children were randomly selected from each district. Out of 600 obese children 224 were male and 376 were female. From this samples, only 60 children from each district were taken from study, in which 30 male and 30 females were there. The obese children were selected by calculating BMI through school information of height and weight of children with prior permission of principal. The adjustment level of obese children was assessed by 'Adjustment Inventory for School Students' (AISS) recommended by A.K.P. Sinha and R.P. Singh. The inventory contains 60 items, 20 items in each area of adjustment. The areas of adjustment are Emotional, Social and Educational. The scoring is done by indicative responses as per given in manual. The collected data were pooled, tabulated and analysed statistically.

RESULTS AND DISCUSSION

The self-esteem of obese children was assessed by 'Adjustment Inventory for School Students' (AISS) recommended by A.K.P. Sinha and R.P. Singh. The impact of nutri-psycho counseling was assessed on children's adjustment of obese children. Their rating assessment after nutritional and psychological counseling was compared with their ratings before NP counseling.

Impact of nutri-psycho counseling on adjustment behavior of selected school going obese boys is shown in Table 1. The adjustment behavior of children is categorized in emotional, social and educational aspects. It is observed from table that emotional adjustment is increased non-significantly at good level. But on average level it was found significantly increased from 60.0 to 74.4 per cent. Unsatisfactory and very unsatisfactory levels were significantly decreased *i.e.* from 18.9 to 8.9 and 7.8 to 1.1 per cent, respectively.

Regarding social adjustment of obese boys that there is significant increase in good and average levels after NP counseling *i.e.* 10.0 to 14.4 and from 62.2 to 70.0 per cent, respectively. Whereas for unsatisfactory level there is significant decrease from 24.4 to 15.6.

It is also seen in educational adjustment found non-significantly increase at good level. The average level was increased significantly *i.e.* from 44.4 to 57.8 per cent. There is significant decrease noted in unsatisfactory and very unsatisfactory level *i.e.* from 25.6 to 21.1 and

Table 1 : Impact of 'NP' Counseling on Adjustment behavior of selected school going obese boys

Areas of adjustment	Level	Boys(90)				'Z' values
		Before		After		
		Frequency	%	Frequency	%	
Emotional	Good	12	13.3	14	15.6	$(1.40)^{NS}$
	Average	54	60.0	67	74.4	(3.38)**
	Unsatisfactory	17	18.9	08	8.9	-(3.20)**
	Very unsatisfactory	07	7.8	01	1.1	-(2.71)*
Social	Good	09	10.0	13	14.4	(2.60)*
	Average	56	62.2	63	70.0	(2.75)*
	Unsatisfactory	22	24.4	14	15.6	-(2.41)*
	Very unsatisfactory	03	3.3	00	--	--
Educational	Good	13	14.4	14	15.6	$(0.14)^{NS}$
	Average	40	44.4	52	57.8	(3.11)**
	Unsatisfactory	23	25.6	19	21.1	-(2.39)*
	Very unsatisfactory	14	15.6	05	5.6	-(2.46)*

*Significant at 5% level; **Significant at 1%level; NS non-significant

from 15.6 to 5.6 per cent, respectively.

The Table 2 reveals the information regarding average statistical analysis of adjustment behavior of selected school going obese boys. It is observed that the mean before and mean after nutri-psycho counseling for emotional, social and educational adjustment were found significantly difference. Hence, it is concluded that the NP counseling helped to improve the psychological status of obese boys significantly.

Impact of NP counseling on adjustment behavior of selected obese girls can be seen from the data presented in Table 3.

It is observed that from Table 3 that emotional adjustment is increased significantly at good level *i.e.* from 25.6 to 30.0. On an average level, it found significantly increased from 58.9 to 65.6 per cent. Unsatisfactory and very unsatisfactory levels were significantly decreased *i.e.* from 12.2 to 4.4 and from 3.3 to 0 per cent, respectively.

Regarding social adjustment of obese girls that there is significant increase in good and average levels after NP counseling *i.e.* from 23.3 to 25.6 and from 65.6 to 68.9 per cent, respectively. Whereas for unsatisfactory level, there is significant decrease from 7.8 to 5.6.

It is also seen in educational adjustment that the significant increase at good level is found (from 21.1 to 23.3). The average level was increased significantly *i.e.* from 50.0 to 57.8 per cent. There is significant decrease found in unsatisfactory and very unsatisfactory level *i.e.* from 20.0 to 13.3 and from 8.9 to 5.6 per cent, respectively.

The Table 4 reveals the information regarding average statistical analysis of adjustment behavior of selected school going obese girls. It is observed that the

Table 2 : Average statistical analysis of adjustment behavior of selected school going obese boys

Parameter	Mean Before	Mean After	Z cal	'p' value	Level of significance	Result	Conclusion
Emotional	1.789	2.044	2.627	0.0086	0.05	Reject H0	Significant
Social	1.789	1.99	2.079	0.0376	0.05	Reject H0	Significant
Educational	1.578	1.83	2.713	0.0067	0.05	Reject H0	Significant

Table 3 : Impact of 'NP' counseling on adjustment behavior of selected school going obese girls

Areas of adjustment	Level	Girls(90)				'Z' Values
		Before		After		
		Frequency	%	Frequency	%	
Emotional	Good	23	25.6	27	30.0	(2.43)*
	Average	53	58.9	59	65.6	(2.55)*
	Unsatisfactory	11	12.2	04	4.4	-(2.36)*
	Very unsatisfactory	03	3.3	00	--	--
Social	Good	21	23.3	23	25.6	(2.31)*
	Average	59	65.6	62	68.9	-(2.26)*
	Unsatisfactory	07	7.8	05	5.6	-(2.30)*
	Very unsatisfactory	03	3.3	00	--	--
Educational	Good	19	21.1	21	23.3	(2.35)*
	Average	45	50.0	52	57.8	(2.48)*
	Unsatisfactory	18	20.0	12	13.3	-(2.25)*
	Very unsatisfactory	08	8.9	05	5.6	-(2.31)*

*Significant at 5% level

Table 4 : Average statistical analysis of adjustment behavior of selected school going obese girls

Parameter	Mean Before	Mean After	Z cal	'p' value	Level of significance	Result	Conclusion
Emotional	2.067	2.255	1.84	0.065	0.05	Accept H0	Not Significant
Social	2.089	2.2	1.091	0.274	0.05	Accept H0	Not Significant
Educational	1.833	1.98	1.58	0.114	0.05	Accept H0	Not Significant

mean before and mean after nutri-psycho counseling for emotional, social and educational adjustment were found significantly difference. Hence, it is concluded that the NP counseling helped to improve the psychological status of obese girls significantly.

It can be concluded that NP counseling has found very positive impact on adjustment behavior of selected school going obese children. There was no significant difference was noticed in the impact of NP counseling on adjustment behavior between obese boys and girls.

Conclusion:

Moreover the impact of NP counseling was also found significantly positive in the improvement of psychological status in relation with adjustment behavior. More significant NP counseling impact on psychological status was found in obese girls than boys.

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IMPACT OF ORAL HYGIENE COUNSELLING ON KNOWLEDGE, ATTITUDE AND PRACTICES OF THE MOTHERS TOWARDS PRESCHOOL CHILDREN

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ABSTRACT

Background:- Children under the age of 5 years generally spend most of their time with parents and guardians, especially mothers, even when they attend pre-schools or nurseries. Mothers, who are the primary role model for them, their health beliefs and attitude towards oral health care, act as a significant predictor of children's oral health. Dental health education given to mothers and aimed at children is more concerned with forming habits, rather than trying to manage established routines. Hence knowledge of mothers has an important role in the maintenance of Oral hygiene status of the children.

Objective:-To evaluate the impact of Oral hygiene counselling intervention on knowledge, attitude and practices of the mothers towards preschool children

Materials & Methods:- Mothers and their preschool children aged 3-5 years belongs to pravaranagar region of Ahmednagar District, Maharashtra State, India were selected for the study. 300 mothers were selected as samples for the counselling intervention programme study. Out of these 300 mothers 153 mothers treated as the experimental group for intervention and the other 147 as the control group. The experimental group received Oral hygiene education through counselling by the researcher, while the control group did not. KAP method was used to measure the impact of counselling.

Result and Discussion:- Oral Hygiene knowledge, attitude and practices of the mothers towards the preschool children in the experimental group and control group was assessed before and after the intervention programme. It is overall concluded as from the results that knowledge, attitude and practice score level of the mothers in the experimental group was appreciable improved and statistically significant at 5 percent level (p-value < 0.05).

Conclusion:-The results of the study revealed that the counselling intervention on Oral hygiene has significantly improved the knowledge, attitude, and practices of the mothers towards preschool children.

Key Words: Knowledge, Attitude, Practices, Oral hygiene, Mother, Preschool children

1. INTRODUCTION

Children under the age of 5 years generally spend most of their time with parents and guardians, especially mothers, even when they attend pre-schools or nurseries. These early years involve "primary socialization" during which the earliest childhood routines and habits are acquired (Holm AK, 1990). These include dietary habits and healthy behaviors established as norms in the home and are dependent on the knowledge and behavior of parents and elder siblings. Studies have reported that poor attitude of parents toward oral health of infants and young children are associated with increased caries prevalence (Hind and Gregory, 1995).Young children's oral health maintenance and outcomes are influenced by their parent's knowledge and beliefs, which affect oral hygiene and healthy eating habits. Parent's knowledge and positive attitude toward good dental care are very important in the preventive cycle. It has been found that the more positive is the parents" attitudes toward dentistry; the better will be the dental health of their children (Kamolmatyakul S and Saiong S, 2007). Mothers, who are the primary role model for them, their health beliefs and attitude towards oral health care, act as a significant predictor of children's oral health (Levin L. and Shenkman A, 2004). Dental health education given to mothers and aimed at children is more concerned with forming habits, rather than trying to manage established routines. This concept has yet another advantage when it comes to intervention. Behavior learnt during the child's first year becomes deeply ingrained and resistant to change (Blinkhorn AS. 1981, Petersen PE 1992).

Considering above background, which highlighted the importance of mother's knowledge regarding Oral hygiene, this study was conducted to find out the Impact of Oral hygiene counselling on knowledge, Attitude and Practices of the mothers towards preschool children.

1.1 OBJECTIVES OF THE STUDY

- To counsel and educate mothers towards Oral hygiene of the preschool children.
- To evaluate the impact of the counselling intervention on Oral hygiene knowledge, attitude and practices of the mothers towards preschool children.

2. MATERIAL AND METHODS

2.1 Target Population

The target population was mothers of preschool children aged 3-5 years.

2.2 Study Population

The study population was mother of preschool children aged 3-5 years living in pravaranagar region of Ahmednagar District, Maharashtra State, India.

2.3 Inclusion Criteria

- Mothers of preschool children aged 3-5 years belong to pravaranagar region of Ahmednagar District.
- Mothers who agreed to participate in the study.

2. 4 Exclusion Criteria

- Mothers who had no children aged below 3 years.
- Mothers, who were unavailable, were excluded from the study.

2.5 Sample Selection

The study was carried out in pravaranagar region, which are situated in Rahata, Shrirampur, Rahuri and Sangamner Talukas of Ahmednagar District of Maharashtra State. The List and names of the preschool children (3-5 years of age) and their mothers had been collected from the various preschools and anganwadi schools of selected villages. 300 mothers were selected as sample for the intervention programme study. Out of these 300 mothers 153 mothers treated as the experimental group for intervention and the other 147 as the control group. The educational level of the mother was considered as the matching variable for both the experimental and the control groups.

2.6 Method of data collection

A pre-test–post-test control group design was chosen. The data was collected before and after the study in both the control and the experimental group. The experimental group received Oral hygiene education through counselling by the researcher, while the control group did not. After the intervention, the final data collection was undertaken in both the experimental and control groups after the 3 months gap period from the completion of Oral hygiene counselling intervention programme. In the present study KAP method was used to measure the impact of counselling. The KAP of mother's toward Oral hygiene questionnaire items were rated and scored. The total score obtained for KAP on Oral hygiene was classified into 3 categories: poor, fair and good.

3. RESULT AND DISCUSSION

Table 3.1: Distribution of the Mothers for counselling intervention programme on the basis of educational level

Mothers educational level	Selected Mothers (n=300)		Total (n=300)
	EG (n=153)	CG (n=147)	
Illiterate (unable to read and write)	3	2	5
Primary School	24	23	47
Secondary School	68	68	136
Higher Secondary School	29	28	57
Under graduate (UG)	20	16	36
Graduate /Post graduate(PG)	9	10	19
Total	153	147	300

EG=Experimental Group CG=Control Group n=number

Education is one of the most personal variables likely to have a positive impact on acquisition of knowledge by the respondents and development of attitude and practices by them. Hence in the present study sampled mothers were distributed on the basis of educational level for the Oral hygiene counselling intervention programme. These mothers were further classified into two groups in such a way that they could be matched. Out of these 300 mothers, 153 mothers were randomly selected and treated as the experimental group for intervention and the other 147 as the control group.

Educational level wise distribution of the selected mothers in the sub sample shown in the **table 3.1** indicates that most of 136 mothers had educational status up to secondary level. Followed by 57 had up to higher secondary school level, 47 up to primary school level, 36 up to under graduate (UG) level, 19 up to graduate /post graduate (PG) level. Only 5 mothers were illiterate in the counselling intervention programme.

Impact of Oral Hygiene Counselling Intervention Programme.

Table 3.2: Impact of Counselling Intervention on Oral Hygiene Knowledge of the Mothers

Oral Hygiene Knowledge Score Level	EG (n=153)					CG (n=147)			
	Pre Test		Post Test		Chi-square (alternative)	Pre Test		Post Test	
	n	%	n	%		n	%	n	%
Good >8	20	13	91	59	69.272* (less)	25	17	26	18
Fair >4 to 8	103	67	58	38	25.377*(greater)	99	67	98	67
Poor < 4	30	20	4	3	20.68*(greater)	23	16	23	15
Total	153	100	153	100		147	100	147	100

Table 3.3: Impact of Counselling Intervention on the Attitude of Mothers towards Oral Hygiene of the preschool children

Attitude towards Oral Hygiene Score Level	EG (n=153)					CG (n=147)			
	Pre Test		Post Test		Chi-square (alternative)	Pre Test		Post Test	
	n	%	n	%		n	%	n	%
Good>14	20	13	97	63	79.928* (less)	25	17	26	18
Fair >7 to 14	103	67	52	34	32.685* (greater)	99	67	98	67
Poor<7	30	20	4	3	20.68* (greater)	23	16	23	15
Total	153	100	153	100		147	100	147	100

Table 3.4 : Impact of Counselling Intervention on Oral Hygiene Practices of the Mothers towards the preschool children

Oral Hygiene Practices Score Level	EG (n=153)					CG (n=147)			
	Pre Test		Post Test		Chi-square (alternative)	Pre Test		Post Test	
	n	%	n	%		n	%	n	%
Good>17	20	13	96	63	78.097* (less)	27	18	26	18
Fair >8 to 17	103	67	53	35	31.398* (greater)	97	66	98	66
Poor <8	30	20	4	2	20.68* (greater)	23	16	23	16
Total	153	100	153	100		147	100	147	100

EG=Experimental Group CG= Control Group n=number

*** Significant at 5% level (p-value < 0.05)**

Preschool children's oral health maintenance and outcomes are influenced by their parent's knowledge and beliefs, which affect oral hygiene and healthy eating habits. Parent's knowledge and positive attitude towards good dental care are very important in the preventive cycle. It has been found that the more positive is the parent's attitudes towards dentistry; the better will be the dental health of their children. Mothers, who are the primary role model for children, their health beliefs and attitude towards oral health care, act as a significant predictor of children's oral health

In the present study Oral health hygiene counselling regarding oral hygiene practices, importance, daily brushing, role of fluoride, restricted the intake of sugary food items, regular dental visits, importance of deciduous teeth was imparted to the mothers of experimental group.

The Oral health hygiene knowledge, attitude and practices level of the mothers in the experimental group and control group was assessed after the intervention programme. Observed data related to oral health hygiene knowledge, attitude and practices level of the mothers has been presented in **table 3.2, 3.3 and 3.4**. The data showed that in the present study maximum number of the poor and fair scorers' mothers had upgraded Oral health hygiene knowledge, attitude and practices score to the upper levels i.e. fair and good levels. This shift was appreciable observed in the experimental group after imparting Oral health hygiene counselling. While in the control group a significant improvement was not observed.

The overall performance was appreciable in the post assessment of the experimental group. The increase in oral health hygiene knowledge attitude and practices score level of the mothers was good and statistically significant at 5 percent level (p-value < 0.05). Thus it is overall concluded as from the Chi-square test, there is an improvement in the experimental groups due to the impact of the Oral hygiene counselling intervention programme.

4. CONCLUSION

Here researcher is interested to test that whether Oral hygiene counselling significantly improved knowledge, attitude and practice score of the mothers towards preschool children after the counselling intervention. From the above results, it is overall concluded as knowledge, attitude and practice score level of the mothers in the experimental group was appreciable improved and statistically significant at 5 percent level (p-value < 0.05). From the Chi-square test, it also concluded that there is an improvement in the experimental groups due to the impact of the Oral hygiene counselling intervention programme.

5. RECOMMENDATIONS

The research confirms the indispensability of Counselling mothers on Oral hygiene especially in the view of pivotal role mother plays in preschool children age group who are our future capable citizens. The research therefore, recommended that, there is need to provide Oral hygiene education to mothers by experts which will go a long way in improving children Oral hygiene status.

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3.2.1 *Number of papers published per teacher in the Journals notified on UGC website during the last five years*

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RESEARCH ARTICLE

Biosynthesis and Characterization of Nickel Nanoparticle Using *Ocimum sanctum* (Tulsi) Leaf Extract

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Abstract: Nickel nanoparticles were synthesized by biosynthesis method with the help *ocimum sanctum* leaf extract. The properties of nickel nanoparticles were characterized by using various techniques *viz*. UV-Visible spectrophotometer, Fourier transform infrared spectrometry(FT-IR) and scanning electron microscopy(SEM) coupled with energy dispersive micro analysis(EDAX) and XRD. The spectroscopic methods confirmed the formation of nickel nanoparticles and the microscopic technique confirmed the shape and size of the nickel nanoparticles as spherical. Antibacterial activity of the synthesized nanoparticles was measured by zone inhibition method. The nickel nanoparticles showed effective antibacterial activity against human pathogenic bacteria such as *Pseudomonas*, *Aeruginosa* and *Escherichia coli*. The usage of plant extract for the biosynthesis of nickel nanoparticle makes the process cost effective, non-hazardous and green method.

Keywords: Nickel nanoparticles, *Ocimum sanctum* leaf extract, Biosynthesis

Introduction

The green synthesis is an eco-friendly pathway for nanoparticle synthesis. The chemical constituents of this herbs includes ursolic acid, eugenol, oleanalic acid, rosmarinic acid, linalool and carvacol. The high eugenol contain in this plant helps to act like a pain killer. These functions are often attributed to tulsi's high content of phenolic compounds and antioxidant properties, with Krishna tulsi (black/purple variety) having a higher phenolic content and antioxidant capacity than white Vana (wild) tulsi[1]. Synthesis of metal nanoparticles has gained significant interest in last twenty years because of their unusual properties and

prospective applications in optical, electronic, catalytic, magnetic materials, thermal properties with corresponding bulk metals. A number of methods have been developed for the preparation of metal nanoparticles such as photo catalytic reduction, radiolytic reduction, solvent extraction reduction, micro emulsion technique, polyol process and alcohol reduction[2]. In recent years there is an emerging interest to synthesize magnetic nanoparticles of Fe, Co and Ni due to their superior magnetic properties and potential uses in many fields including catalysis, memory storage devices and sensors. In the field of medicine they are used for magnetically controlled drug delivery, magnetic resonance imaging and hyperthermia treatment of cancer cells[3–5]. Many physical and chemical methods including co-precipitation[6], sol-gel[7], microemulsion[8], hydrothermal reaction[9], electrospray synthesis[10], and laser ablation[11] are used to synthesize nanoparticles. These methods may produce well defined pure nanoparticles but they have low productivity, high cytotoxicity, low antioxidant potential and low antimicrobial activity and are not environmental friendly[12]. They also find environmental applications in the field of adsorption of hazardous dye and inorganic pollutants and thus play a vital role in the cleanliness of environment[13]. Due to their good antibacterial and anti-inflammatory activities they are used in the field of biomedicine[14-26].

Experimental

For the preparation of nickel solution, 5.59 g of nickel sulphate was dissolved in double distilled water and made up to 250 mL.

Preparation of leaf extract (Ocimum sanctum)

Exactly 5 g of fresh *ocimum sanctum* leaves were taken in clean beaker, and then washed thoroughly with doubled distilled water. The leaves were dried on filter paper to remove the excess water then 100 mL distilled water was added by using measuring cylinder and boiled to get leaf extract. It was stored in umber colour bottle and kept in refrigerator.

Synthesis of nickel nanoparticles

1-2 mL of 5 mg/mL nickel solution was added in a round bottom flask then 20 mL of *osmium sanctum* leaf extract was added with constant stirring again 100 mL of nickel solution (5 mg/mL) was added the brown colour was observed which indicates the formation of nickel nanoparticles (Figure 1). Then synthesized nickel nanoparticles were characterized by UV-Visible spectroscopy. The resulting solution is centrifuged for 20 mins at 5000 rpm, centrifugate of aqueous layer was discarded. The residue obtained was removed with little amount of distilled water. Then it was kept for removal of water in plane surface glass dish, these particles were analyzed using FT-IR, XRD, SEM and Edax.

Figure 1. Synthesis of nickel nanoparticle
A-Std Ni solution, B- Leaf extract, C- Ni solution + Leaf extract

Results and Discussion

UV-Visible spectra

UV-Visible spectra of colloidal nickel nanoparticle shown in Figure 2. It shows well defined surface Plasmon resonance at about 656 nm. The UV-Visible spectra also show that particle are uniformly distributed and round in nature. The SPR characteristic peak is due to oscillation of conduction band electron of nickel. The broadening of peak is due to wide size distribution in solution. The nickel nanoparticle suspended in water and UV-Visible peak of this solution was observed at 656 nm wavelength. The position and shape of Plasmon absorption of nobel metal nano cluster is strongly dependant on size, shape, dielectric medium, surface absorbed species and surrounding matrix.

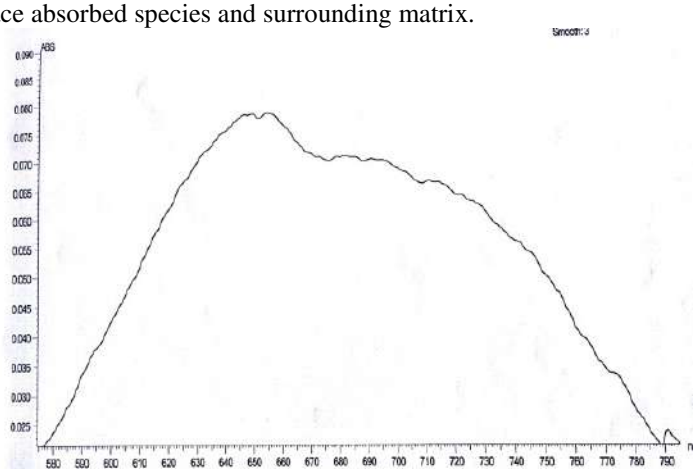


Figure 2. UV-Vis spectra of synthesis Ni-nanoparticle

FT-IR

The result of FT-IR analysis of nickel particles is depicted in Figure 3a. The spectra of nickel particles showed transmission peak at 3500, 2500, 1700, 1150 and 1100 cm^{-1}. The peak at 1100 indicate saturated alkanes, the peak at 1150 indicate alcohol, phenol. The peak at 1700 indicates amide, the peak 2500 indicates carboxylic acid, the peak at 3500 indicates the hydrogen bonded alcohol and phenol. Figure 3b shows that the FT-IR spectra of biosynthesized nickel nanoparticles and carried out to identify the possible interaction between protein and nickel nanoparticles. The result of FT-IR study showed sharp absorption peak located at 1100 and 3500 cm^{-1}.

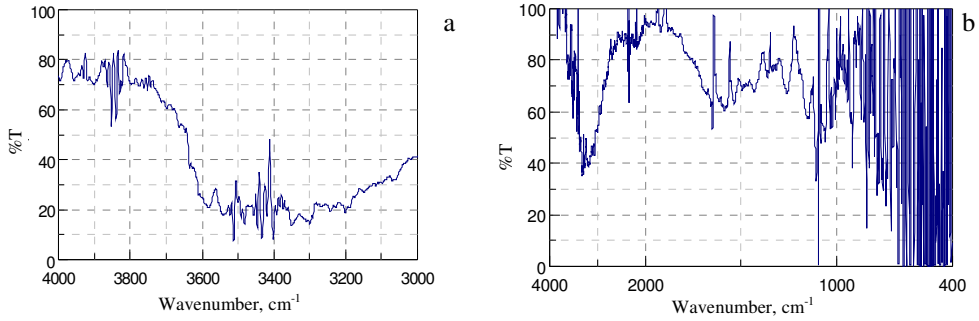


Figure 3. FT- IR spectra of (a) nicke particles (b) nickel nanoparticle

XRD analysis

Analysis through x-ray diffraction was carried out to confirm the crystalline nature of nickel nanoparticles. The dry powders of nickel nanoparticles were used for XRD analysis (Figure 4). The diffracted intensities were recorded from 20 to 80 ^{o}C at 2Ɵ angles. The comparison of our XRD spectrum with the standard confirmed that nickel nanoparticles form were in the form of nano crystals as different diffraction lines were observed at 2Ɵ angle 15, 16, 24.5 and 26 respectively. The average particles size of the nickel nanoparticles synthesized by present bio synthesis method can be calculated by using Debye-Scherer's equation, the average particle size of synthesized nickel nanoparticle is 4.5 nm.

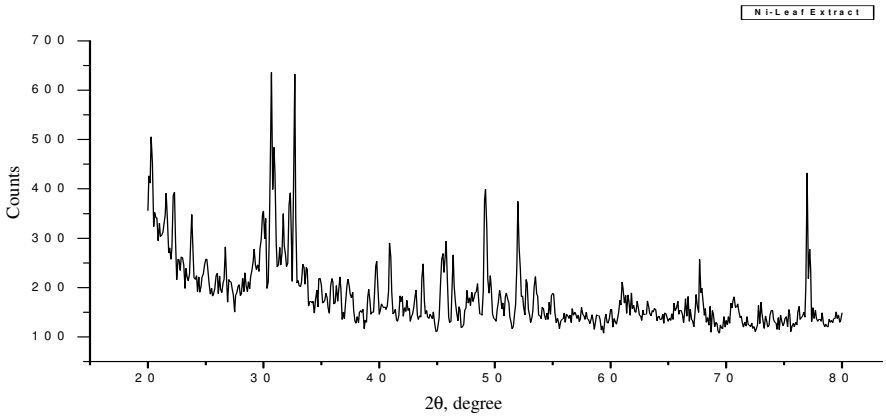
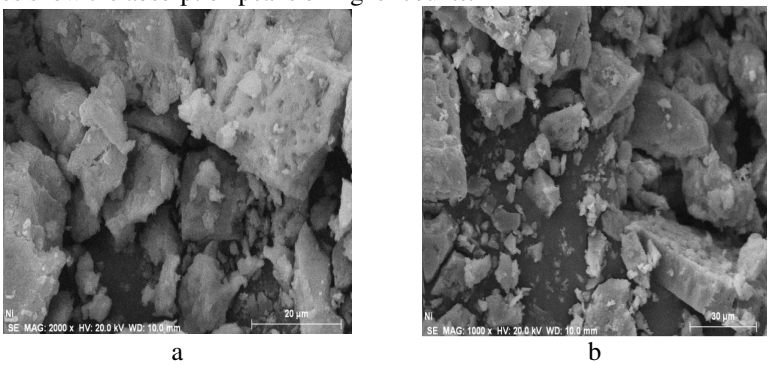


Figure 4. XRD image for nickel nanoparticle

SEM-EDAX analysis

SEM analysis provided the morphology and size details of the nanoparticles. Figure 5 shows that high density of nanoparticles synthesized by plant extract of *ocimum sanctum*, the interaction such as hydrogen bonding and electrostatic interaction between the bioorganic capable to form molecular bond is a reason for synthesis of nickel nanoparticles using plant extract. The nickel nanoparticles are rectangular, trigonal and spherical in shape with uniform distribution. However the average size of an individual particle is estimated to be 20-30 µm. The quantitative and qualitative analysis of element may be concern in the formation of nickel nanoparticles and were identified by EDAX analysis (Figure 6). Due to the surface Plasmon resonance, the nickel nanoparticles show the absorption peaks of higher counts.



a b

Figure 5. SEM image for nickel nanoparticles (a) 20 µm and (b) 30 µm

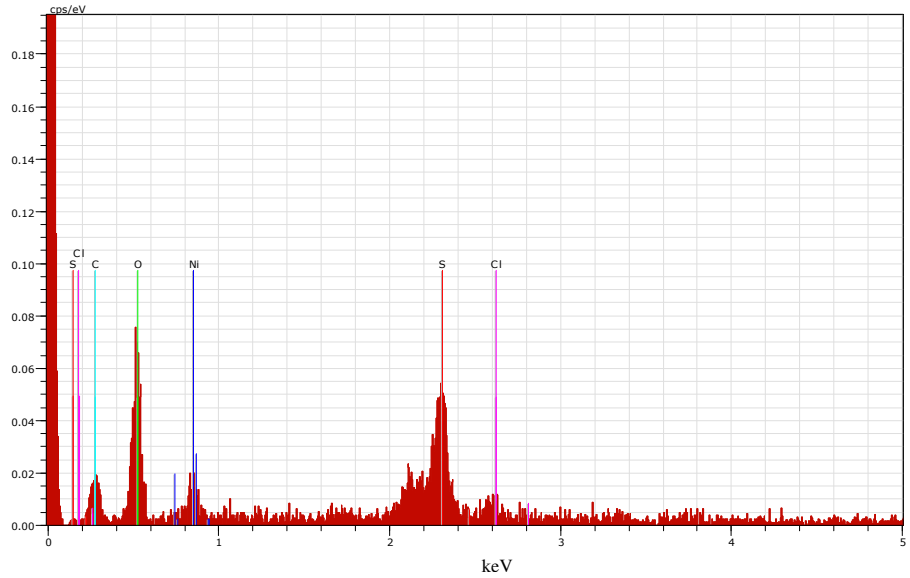


Figure 6. E-DAX image of nickel nanoparticles

Spectrum: Ni

El	AN	Series	unn. [wt.%]	C norm. [wt.%]	C Atom. [at.%]	C Error[%]
O	8	K- series	37.29	52.83	65.29	9.7
Ni	28	K- series	18.04	25.57	8.61	0.9
C	6	K- series	8.80	12.47	20.53	4.6
S	16	K- series	5.70	8.07	4.98	0.3
CI	17	K- series	0.75	1.06	0.59	0.1
			Total: 70.58	100.00	100.00	

Antimicrobial activity

The Figure 7 shows the nanoparticle synthesized from nickel are capable of showing antimicrobial activity against *E-coli* and *Pseudomonas* bacteria. The zone of inhibition for these organisms was found to be 2.1 mm and 1.3 mm respectively. The synthesized nickel nanoparticles prepared from *ocimum sanctum* leaf extract showed antimicrobial activity against tridox, curry. However the antimicrobial activity of nickel nanoparticles depends on the type of bacteria along with the size of nickel nanoparticles and also the formation of pits in the cell wall of microorganism. The nickel nanoparticles affects fugus cell by attacking their membrane thus distrusting the membrane potential. The biological synthesized nickel nanoparticles prepared by direct reduction method showed antimicrobial activity against *E-coli* and *pseudomonas*. The highest antimicrobial activity was observed against curry and tridox.

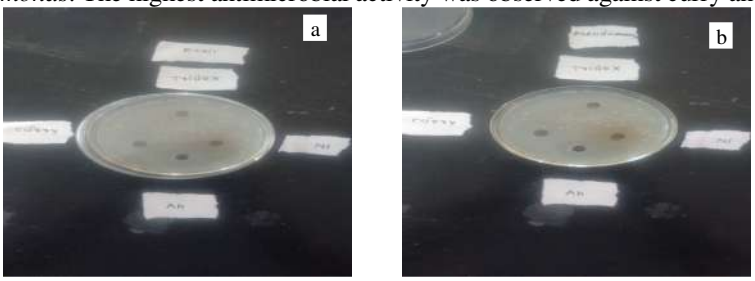


Figure 7. Antimicrobial activity of nickel nanoparticle (a) E-coli and (b) *Pseudomonas*

Conclusion

In this study simple approach was attempted to obtain a green eco-friendly, non-toxic way for synthesis of nickel nanoparticle. The primary confirmation for nickel nanoparticle was due to colour changes and UV/Vis absorption spectra of nickel nanoparticles formed peak at 656 nm. The SEM study was identified that the shape of nickel nanoparticle appeared like irregular spherical shape with rough surface. Edax study was to find out percentage of nickel, oxygen, carbon and chlorine antimicrobial activity of nickel nanoparticle shows better zone of inhibition against two bacterial pathogens *i.e*. *Pseudomonas* and *E.coli*. Green synthesis method is rapid, convenient and less time consuming environmentally safe method for the synthesis of nickel nanoparticles.

Acknowledgment

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Green synthesis of cobalt nanoparticles, its characterization and antimicrobial activities

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Abstract

In the present study, cobalt nanoparticles were synthesized by an recyclable and cost effective method using ocimum sanctum extract and characterized using various techniques such as UV-visible spectrophotometry, Fourier transform infrared spectrometry(FT-IR) and Scanning electron microscopy(SEM) coupled with Energy dispersive micro analysis(EDAX) and XRD. The spectroscopic methods confirmed the formation of cobalt nanoparticles and the microscopic technique confirmed the shape and size of the cobalt nanoparticles as spherical. Antibacterial activity of the synthesized nanoparticles was measured by zone inhibition method. The cobalt nanoparticles showed effective antibacterial activity against human pathogenic bacteria such as Pseudomonas Aeruginosa and Escherichia coli. The usage of plant extract for the preparation of Cobalt nanoparticle makes the process cost effective, non-hazardous and green method.

Keywords: cobalt nanoparticles, ocimum sanctum leaf extract.

INTRODUCTION

Nanoparticle research is presently an area of strong scientific interest due to a wide variety of potential application in biomedical, optical and electronic fields. Cobalt is considered to be the first catalyst made from nonprecious metal with properties closely matching with those of platinum[1]. The shape and size of the nanoparticles influence the physical characterization of these novel materials. Nanoparticles are the nano-sized particles[2-3] which have found various applications in the fields of medicine[4-7], biology [8-11], catalysis[12-14]etc. The nanoparticles can be synthesized by physical, chemical or biological methods. Cobalt nanoparticles can be synthesized by various approaches like ultrasonic spray pyrolysis, DC magnetron sputtering[15], thermal decomposition[16],electrochemical[17] and Liquid-Phase Reduction[18] process and also by biological methods such as microbial synthesis [19] of nanoparticles. Recently, many studies have proven that the plant extracts act as a potential originator for the synthesis of the nanomaterials in harmless ways. The plants are used successfully in the synthesis of several greener nanoparticles such as cobalt, copper, silver, gold, palladium, platinum, zinc oxide and magnetite. Plant mediated biological synthesis of nanoparticles is gaining importance due to its simplicity, cost effective and eco-friendliness [20-21]. Cobalt nanoparticles could be efficient nanoparticles as they possess good catalytic[22-23] and high performance permanent magnetic properties[24-25] and also possess biomedical[26] and cytotoxic[27] activity.

Here we have taken into account green chemistry concept and synthesized cobalt nanoparticles by using osmium santum leaves extract. Osmium sanctum (tulsi) is cultivated for spiritual and therapeutic purposes

and essential oil. It is widely known across South Asia as medicinal plant and herbal tea and commonly used in Ayurveda's.

EXPERIMENTAL

Experimental set up is very simple it consists of magnetic stirrer. The 100 ml round bottom flask is fitted with metallic stand. Flask is kept on magneric stirrer for constant stirring.

MATERIAL AND METHOD

Experimental Details:

Preparation of 50 mg/ml cobalt solution

For the preparation of cobalt solution we use the cobalt chloride 50.46 gm of $CoCl_2$ dissolved in double distilled water and dilute to 250ml of water.

Preparation of leaf extract (Ocimum sanctum)

Exactly 30 gm of ocimum sanctum leaves were taken in clean beaker then washed thoroughly with doubled distilled water. The leaves were dried on filter paper to remove the excess water then add 100 ml distilled water by using volumetric flask and boiled to get leaf extract and stored in umber colour bottle and keep in refrigerator.

Synthesis of cobalt nano particles:

Add 20 ml 50 mg/ml cobalt solution in a round bottom flask then add 1-2 ml of osmium sanctum leaf extract with constant stirring again add 60 ml of leaf extract the dark bluish colour was observed which indicates the formation of cobalt nanoparticles Fig.1. Then synthesized cobalt nanoparticles were characterized by UV visible spectroscopy. Then keep the flask for 24 hrs for setting the particles. After 24 hrs the resulting solution is centrifuged for 20 mins at 500 rpm, then centrifuge and discard the aqueous layer and remove the residue with little amount of distilled water then keep it for dehydration in plane surface glass dish with covering. After 2-3 days dehydration is completed then collects the particles which are present on surface of glass.

Characterization of cobalt nanoparticles:

Dark bluish colored indicates cobalt nanoparticles are synthesized and detected by using UV-Visible spectroscopy, Morphology of cobalt nanoparticles using Scanning electron microscopy (SEM), X-ray diffraction spectroscopy (XRD) and Elemental analysis was performed by Electron Diffraction X-ray analysis (EDX).

Fig.1 A: Cobalt solution; B: plant Extract; C: Cobalt Nanoparticles

RESULT AND DISCUSSION

UV visible spectroscopic analysis of cobalt nanoparticles:

The UV visible spectroscopy is most widely used technique to investigation the optical properties of the particles. The colours changes from Pink to dark bluish colour which indicates formation of cobalt nano particles.UV visible spectroscopy analysis was done in the range of 200-800 nm and maximum absorbance was observed at 646 nm region for the formation of cobalt nano particles Fig. 2

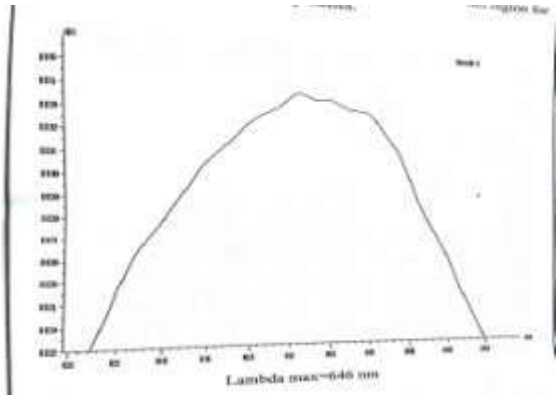

Fig. 2. UV-Visible spectrum of Co-NPs

FTIR of cobalt nanoparticles

FTIR measurements were carried out to identify the possible biomolecules responsible for the reduction of cobalt and capping of cobalt nanoparticles. The FTIR spectrum of cobalt nanoparticles represents the major absorption bands as the bands 1100-1150 cm^{-1} represents C-O stretching. The bands 1640-1650 cm^{-1} indicates C=C stretching. The bands 1050-1080cm^{-1} assigned phenolic or alcoholic group. Fig. 3.

Bands on these results the presence of phenolic compound and protein were believed to be responsible for the formation and stabilization of synthesized cobalt nanoparticles.

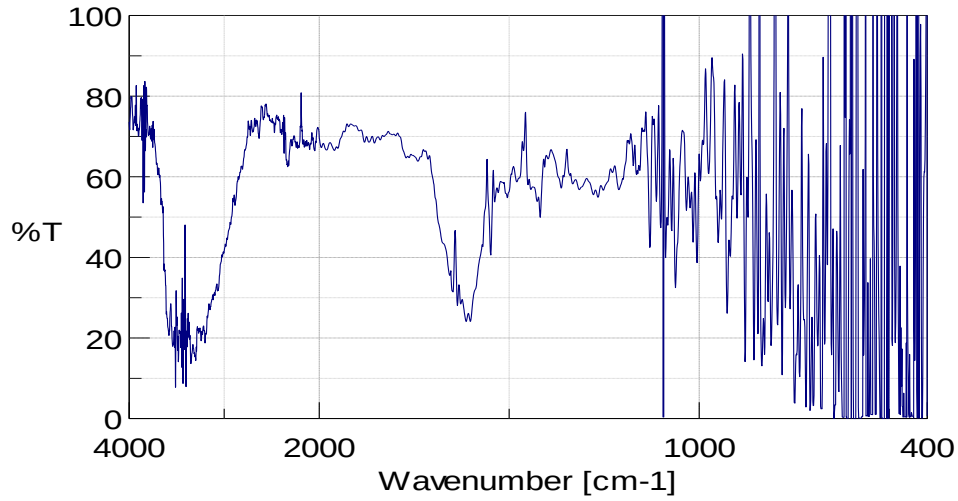

Fig. 3 FTIR Spectrum of Co-NPs

XRD Analysis of cobalt nanoparticles:

Analysis through X-ray diffraction was carried out to confirm the crystalline nature off cobalt nano particles Fig. 4. The dry powders of cobalt nanoparticles were used for XRD analysis. The diffracted intensities were recorded from 20^0C to 100^0C.At 2Θ angles. The comparison of our XRD spectrum with the standard confirmed that cobalt nanoparticles form were in the form of nano crystals as different diffraction lines were observed at 2Θ angle 15,16,20.5,22.5 respectively. The average particles size of the cobalt nanoparticles synthesized by present bio synthesis method can be calculated by using Debye-Scherer's equation.

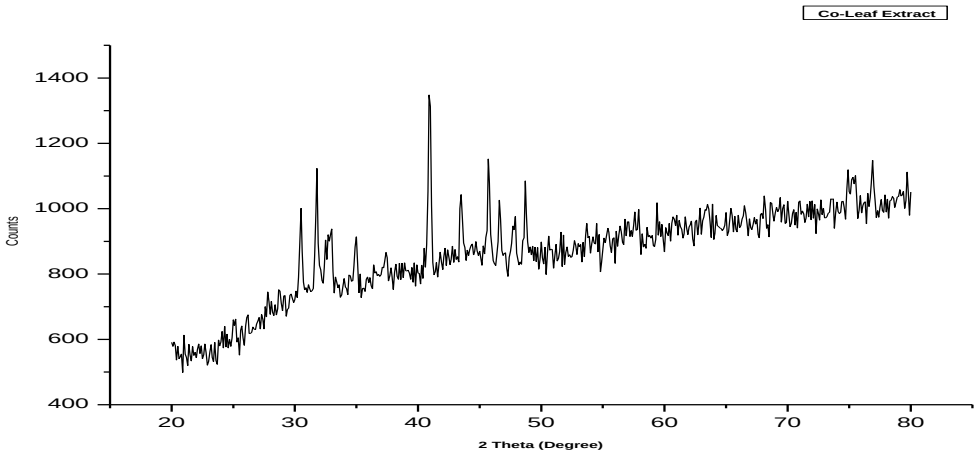

Fig. 4 XRD Spectrum of Co-NPs

Scanning electron microscopy

Analysis of the sample performed using SEM method. Scanning electron microscopy provided the morphology and size details of the cobalt nanoparticles. It was identified that shapes of cobalt nano particles appeared like irregular spherical shape with rough surface Fig. 5.

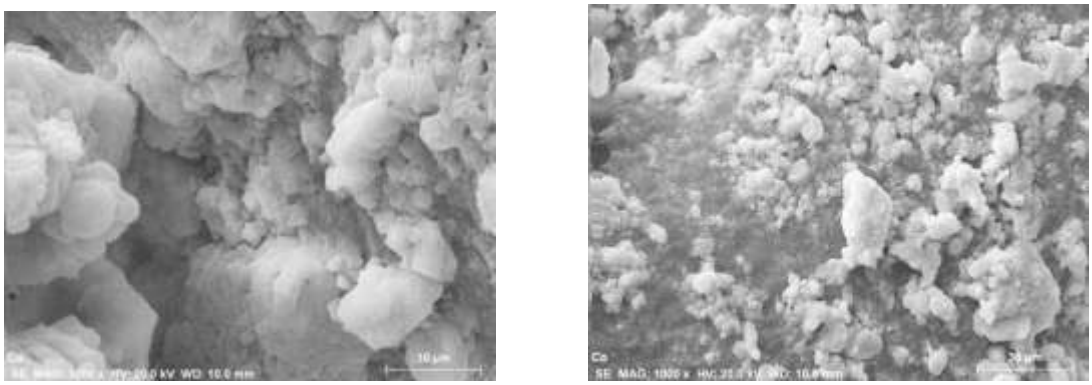

Fig. 5 SEM Image

Energy dispersive micro analysis (EDAX)

The element analysis of cobalt nano particles was studied using energy dispersive micro analysis (Edax). The analysis revealed highest proportion of cobalt in the nano particles followed by carbon, oxygen and chloride. Fig. 6.

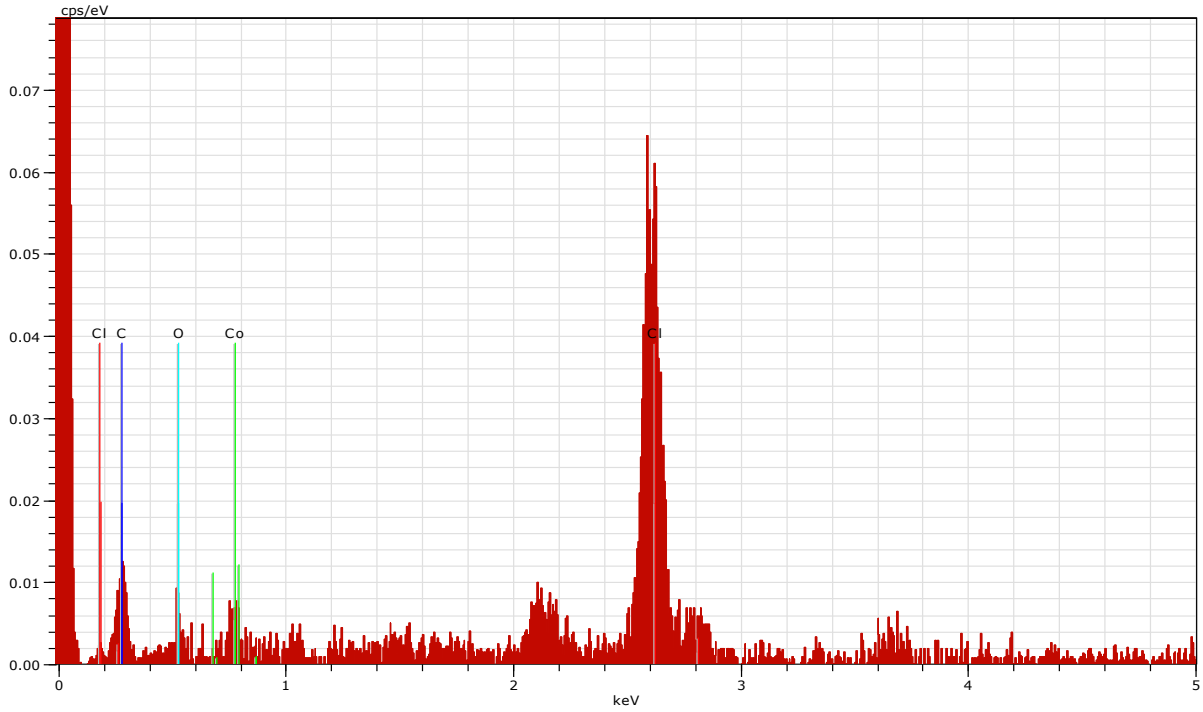

Fig. 6 Energy dispersive micro analysis (EDAX)

Spectrum: Co

El	AN	Series	unn. C [wt.%]	norm. C [wt.%]	Atom. C [at.%]	Error [%]
Co	27	K-series	15.18	28.03	9.86	0.9
O	8	K-series	14.51	26.80	34.73	8.3
C	6	K-series	13.75	25.40	43.85	8.4
Cl	17	K-series	10.70	19.77	11.56	0.6
		Total:	54.14	100.00	100.00	

Antimicrobial Activity of Cobalt Nano particles

Antibacterial activity of cobalt nano particles were checked against two bacterial pathogens such as Pseudomonas Aeruginosa Fig. 7 and Escherichia coli Fig. 8, Cobalt complex was shown better result in the form of zone of inhibition in culture plates for these organism were found to be 2.1 mm and 1.6 mm respectively.

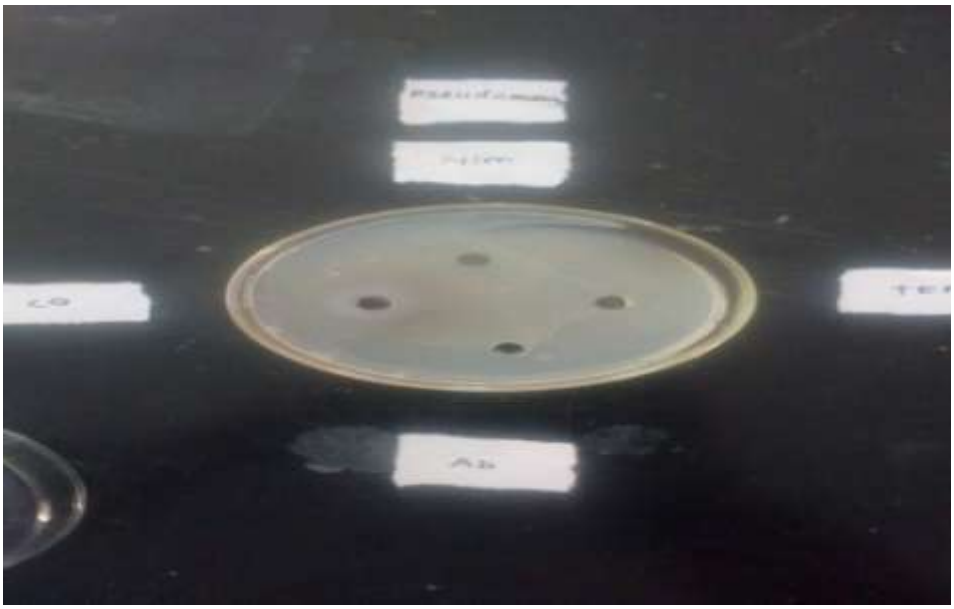

Fig. 7 Pseudomonas Aeruginosa

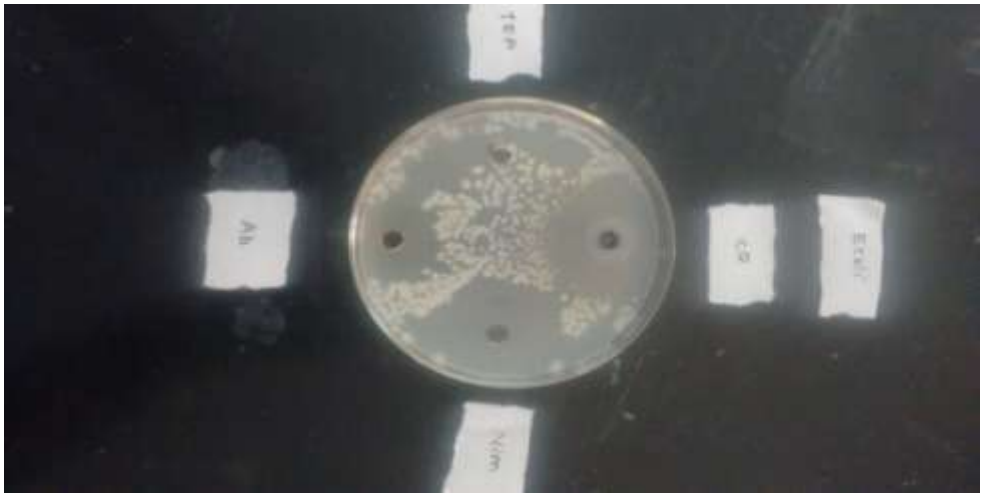

Fig. 8 Escherichia coli

CONCLUSION

In this study simple approach was attempted to obtain a green eco-friendly, non-toxic way for synthesis of cobalt nanoparticle. The primary confirmation for cobalt nanoparticle was due to colour changes and UV/Vis absorption spectra of cobalt nanoparticles formed peak at 646 nm.The SEM study was identified that the shape of cobalt nanoparticle appeared like irregular spherical shape with rough surface. Edax study was to find out percentage of cobalt, oxygen, carbon and Chlorine antimicrobial activity of cobalt nanoparticle shows better zone of inhibition against two bacterial pathogen i.e. Pseudomonas and E.coli.Green synthesis method is rapid, convenient and less time consuming environmentally safe method for the synthesis of cobalt nanoparticles.

Acknowledgement

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Tridax Procumben Leaf Extract Mediated Green Synthesis of Iron Oxide Nanoparticles: Spectroscopic and Microscopic Studies

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ABSTRACT

An ecofriendly green synthesis of iron oxide nanoparticles were rapidly synthesized by reduction of Ferric chloride using Tridax Procumbens leaf extract. UV-visible spectra showed the maximum absorbance of 450 nm due to the surface Plasmon viberations in the iron oxide nanoparticles formation. The average particle size of the synthesized iron oxide nanoparticles was estimated to be 4-5nm using Scherrer's equation. The formation of Fe3O4 nanoparticles as well as their morphological dimensions in the SEM study revealed that the particles were aggregated

KEYWORDS: Iron oxide nanoparticles, Tridax Procumbens leaf extract.

INTRODUCTION

Nanoparticles are ultrafine particles with their size ranging from 1-200 nm.Nanoparticles have attracted considerable attraction due to their unusual and fascinating properties with various applications, over their bulk counterparts[1-2]. Synthesis of metal nanoparticles using plant extract is very cost effective so can be used as an economic and valid alternative for the large scale production of metal nanoparticles[3].The bioreduction of metal nanoparticles by combination of biomolecules found in plant extract such as enzymes, proteins, aminoacids, vitamins, polysaccharides typically obtained by contact of a broth of plant with metal salts, has been intensively investigated in recent years[4]. Iron as a nanoparticles has been somewhat neglected. This is unfortunate, but understandable, extreme reactivity has traditionally made iron nanoparticles difficult to study and inconvenient for practical applications. Recent work has begun to take advantages of irons potential and work in this field appears to be blossoming[5] . Iron oxide nanoparticles have attracted intensive research interest because of their important applications in cancer therapy, drug delivery magnetic resonance imaging (MRI) and waste water treatment[6].The biosynthesis of iron oxide nanoparticles of different sizes and shapes has been reported using bacteria[7], fungi[8] and plant extract. Green synthesis of nanoparticles is very cost effective, environment friendly and non toxic. In the present scenario, there is an urgent and continuous need of exploration and development of cheaper, effective new plant based nanoparticles with better bioactive potential and least side effects. The entire plant of Tridax procumbens is used by indigenous people in Guatemala for the treatment of protozoal infections (malaria, leishmaniasis, dysentery) and gastrointestinal disorders (colic/stomach pains, gastritis/enterocolitis)[9-11]. Local people known it as "Ghamara", in English popularly called 'coat buttons' and is dispensed for "Bhringraj" by some of the practitioners of Ayurveda. Tridax procumbens is a widely

occurring medicinal herbs used by Ethnomedicinal practionars. To the best of my knowledge, the use of Tridax procumbens leaf extract for the biosynthesis of iron oxide nanoparticles has been less reported. The extension of our previous work[12] we investigated the synthesis of Iron oxide nanoparticles with the bioreduction method using Tridax procumbens leaf extract.

MATERIAL AND METHODS

Reagents and Chemicals:

For the synthesis of iron oxide nanoparticles, Tridax procumbens leaf extract was used as reducing agent. Ferric chloride ($Fecl_3$) was used as precursor. Milli Q water was used throughout the experiment.

Preparation of Tridax procumbens Leaf Extract:

About 10-20 gm of fresh and healthy leaves of Tridax procumbens were collected, washed thoroughly with Milli Q water, cut into fine pieces and boiled with 100 ml Milli Q water in Erlenmeyer flask at 80 ^{0}c for 15-20 minutes. The extract was cooled at room temperature and filtered using Whatman No.42 filter paper and stored at 4^{0}c for further analysis.

Green synthesis of Iron oxide Nanoparticles:

In a typical experiment, 50 ml of 0.01M ferric chloride solution was mixed with 20 ml of the Tridax procumbens leaf extract at a temperature of about 50-60^{0}c [13]. After the addition of leaf extract to the salt solution, the colour changed from faint yellow to brownish yellow and finally blackish green indicating the formation of iron oxide nanoparticles. The reaction mixture was centrifuged at 10,000 rpm for 15 minutes. The supernatant was discarded and the pellets were repeatedly washed with Milli Q water and dried for the evaporation of aqueous phase in hot air oven.

Characterization of Iron oxide Nanoparticles:

The blackish green colored solid characterized for the bioreduction of Fe^{2+} ions using UV-Visible spectroscopy, Morphology of iron oxide nanoparticles using Scanning electron microscopy (SEM), X-ray diffraction spectroscopy (XRD) and Elemental analysis was performed by Electron Diffraction X-ray analysis (EDX).

RESULTS AND DISCUSSIONS

The addition of ferric chloride solution to the plant extract containing carbohydrates as a major component which have aldehyde group may cause the partial reduction of Fe^{3+} to form Fe_3O_4. The possible reduction mechanism giving to Fe_3O_4 only from the single iron precursor, $Fecl_3$ is proposed in the following equations.

$Fe^{3+} + 3H_2O \rightarrow Fe(OH)^3 + 3H^+$ ……(1)

$Fe(OH)^3 + R\text{-}CHO \rightarrow Fe_3O_4 + R\text{-}COOH$ ……..(2)

UV-Visible Analysis of Iron Oxide Nanoparticles:

UV-Visible spectroscopy is most widely used technique to investigate the optical properties of the particles. The colour changes from faint yellow to blackish green indicated the formation of iron oxide nanoparticles (Fig.1). UV-Visible spectroscopy was done in the range of 200-800 nm. Absorption spectra

of iron oxide nanoparticles formed in the reaction media has absorbance peak 450 nm (Fig.2). The broadening of peak indicated that the particles are polydispersed.

Figure 1: Visual observations of A - Leaf extract, B - Ferric chloride, C - Iron oxide Nanoparticles

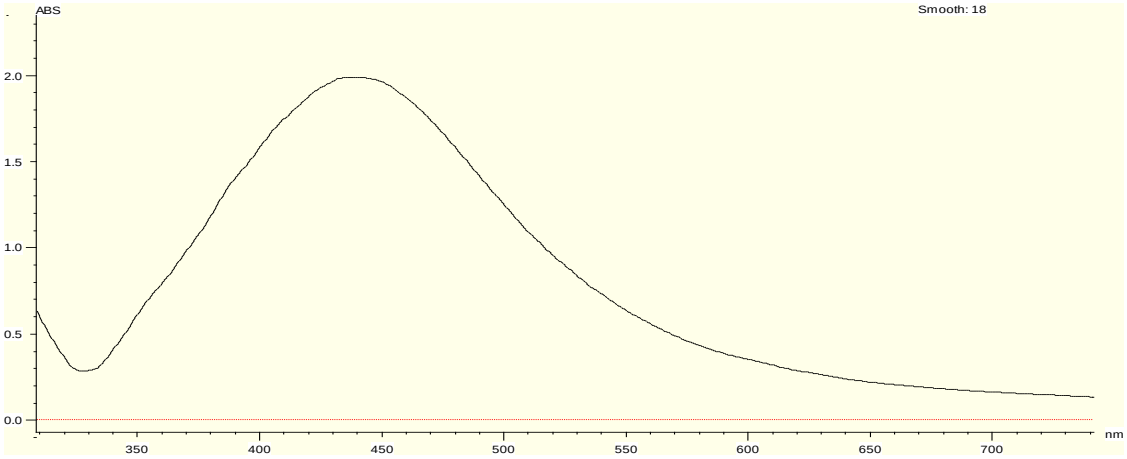

Figure 2: UV-Visible spectrum of Fe_3O_4 nanoparticles synthesized using Tridax procumbens leaf extract

SEM Analysis of Synthesized Iron Oxide Nanoparticles:

The powdered sample was analyzed for the structure and morphology of the synthesized iron oxide nanoparticles using SEM (Fig.3). SEM images revealed that the synthesized iron oxide nanoparticles were aggregated.

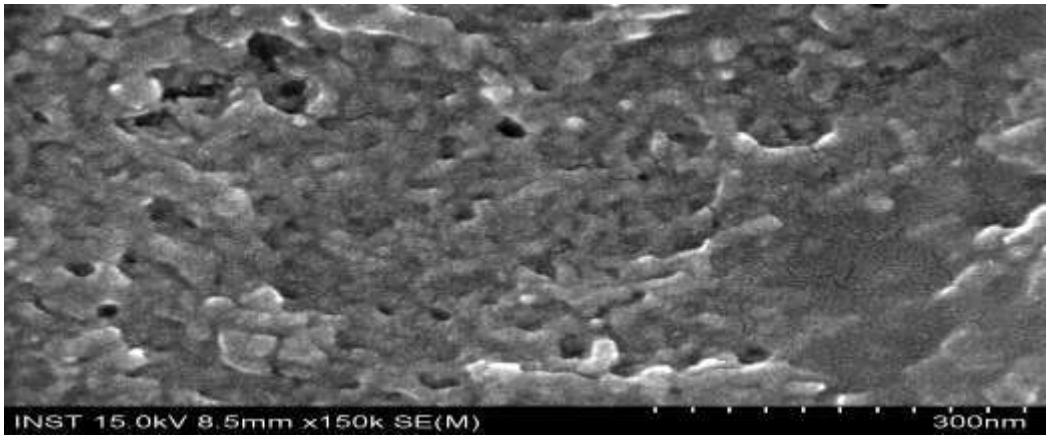

Figure 3: SEM micrograph of Fe_3O_4 nanoparticles synthesized using Tridax procumbens leaf extract

XRD Analysis of Synthesized Iron Oxide Nanoparticles:

The X-ray diffraction patterns obtained for the Fe_3O_4 nanoparticles synthesized using Tridax procumbens leaf extract is shown in (Fig.4). The XRD spectrum contains two peaks that are clearly distinguishable. All of them can be perfectly indexed to crystalline. The peaks with 2θ values of 28º, 32.4º Fe_3O_4 resp. The crystallite sizes can be estimated using Scherrer's formula $D=k\lambda/\beta\cos\theta$ where the constant K is taken to be 0.94, d is the wavelength of X-ray and β and θ are the half width of the peak and Bragg angle resp. Using the equation , the crystallite sizes found to be in the range of 4-5 nm.

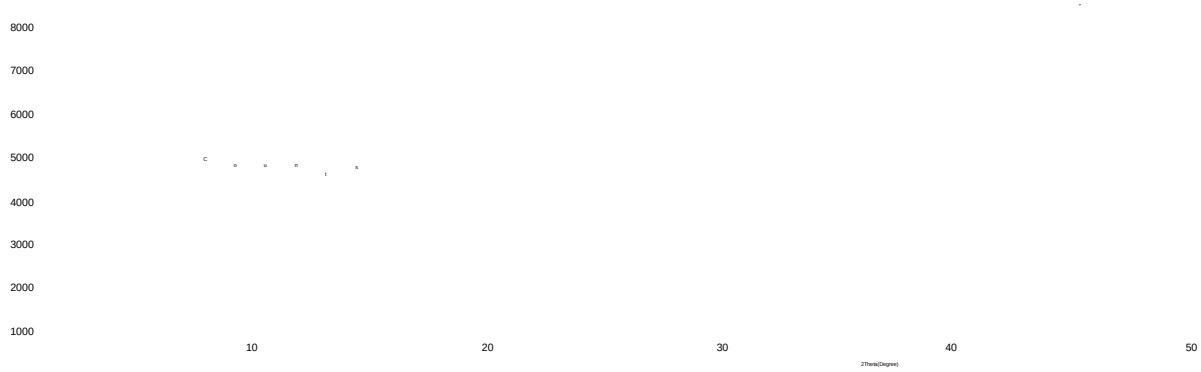

Figure 4: XRD pattern of Fe_3O_4 nanoparticles synthesized using Tridax procumbens leaf extract

EDX Analysis of Synthesized Iron Oxide Nanoparticles:

EDX analysis gives qualitative as well as quantitative status of element that may be involved in the formation of nanoparticles. Fig.5. Shows elemental profile of synthesized nanoparticles using Tridax procumbens leaf extract.

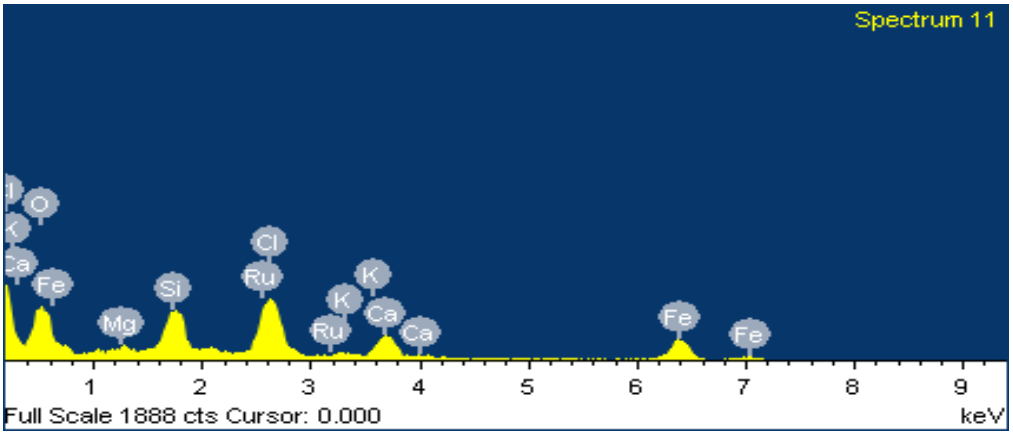

Figure 5: EDX pattern of Fe_3O_4 nanoparticles synthesized using Tridax procumbens leaf extract

CONCLUSIONS

The rapid biological synthesis of Iron oxide nanoparticles using leaf extract of Tridax procumbens provides an environment friendly simple and efficient route. SEM study revealed that the synthesized nanoparticles were in the form of irregular shape in aggregated form. This Fenps may be used in effluent treatment and in environmental remediation. In addition, this simple, low-cost and greener method for development of nanoparticles will give a positive message that nanoparticles synthesized thoroughly greener routes are much safer for human use.

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Synthesis and Characterization of MgO Nanoparticles by Using Sol-Gel Method

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Abstract

Nanaparticles of mgo is formed by successive sol-gel method. Nanaparticles are obtained by dissolving solid $mgso_4$ aqueous medium with 0.1M solution of acetic acid. The crystals of mgo were obtained by addition of 1 M naoh. The precipitate is dried at 60^0 C temperature for 12 hours to get the final growth of mgo nanoparticles. The structural morphology, optical property of particles were studied by X-ray diffraction (XRD), Scanning electron microscop (SEM), UV spectrophotometer and furrier transformer infra-red spectroscopy (FTIR). The study of surface morphology reveals that mgo nanoparticles shows nanorods, niddle and spindles like shapes. The obtained nanoparticles of mgo shows optical band gap of 5.17 ev.

Keywords: MgO nanoparticles, Characterization: SEM, XRD, UV and FTIR.

Introduction

Nanoscience is the study of phenomena on a nanometre scale. Atoms are a few tenths of a nanometre in diameter and molecules are typically a few nanometres in size. The smallest structures humans have made have dimensions of a few nanometres and the smallest structures we will ever make will have the dimensions of a few nanometres. This is because as soon as a few atoms are placed next to each other, the resulting structure is a few nanometres in size [1]. The smallest transistors, memory elements, light sources, motors, sensors, lasers, and pumps are all just a few nanometres in size. Nanoscience is the study of phenomena and manipulation of materials at atomic, molecular and macromolecular scales, where properties differ significantly from those at a larger scale. Besides the technological relevance of nanoscience, there is an enormous hype associated with it. Fantastic claims have been made about faster computers, cheap production of goods, and medical breakthroughs. Nanotechnology is expected to appear in products such as tennis rackets, self-cleaning cars, paint, food, cosmetics, and thermal underwear. The European Union is has identified nanotechnology as an important research area [2]. The goal of this study is to introduce the concepts of nanoscience so that the issues can be understood and a constructive contribution to the debates can be made. Nanoscience is a science that describes manipulation of chemical and biological architectures with dimensions in the range from 1 to 100 nanometers. Nanoscience is about developing new chemical and biological nanostructures, uncovering and understanding their characteristics, and ultimately about learning how to organize and join these new nanostructures into larger and more complex functional architectures [3]. It is integrated with nanotechnology because both of them are almost same in use. Nanoscience building blocks ranges from 100 to millions of atoms in a single block.There are different methods are discovered for synthesis

for nonmaterial's viz: (1) Physical method such as high Energy Ball Milling, Melt Mixing, Physical Vapor Deposition With Consolidation, Ionized Cluster Beam Deposition, Laser Vaporization, Laser Pyrolysis, Sputter Deposition:-DC & RF Sputtering, Chemical Vapour Deposition, Electric arc Deposition. (2) Chemical methods such as Colloids And Colloids in Solution, Langmuir-Blodgett (L-B) Methods, Micro emulsions, Sol-Gel Methods, Hydrothermal Methods. (3) Biological method as Synthesis using microorganisms, Synthesis using plant extracts, Synthesis using DNA [4-5].

In the present study, a simple procedure is described for the synthesis of mgo nanoparticles via sol-gel method. Nanomaterials have attracted interest for their novel optical properties, which differ remarkably from bulk materials. The reduction in the particle size in the case of semiconductors results in the increase in the band gap which results in the shift of the light absorption towards in the high energy region. The aim of the present work is to study the microstructure and optical band gap of the synthesized nanoparticle.

Experimental Procedure (MgO):

Weight accurately 2.46 gm $MgSo_4$ on butter paper using balance. Transfer this substance to a beaker & add 100 ml distilled water to it and dissolve the substance completely to get 0.1M $MgSo_4$ solution. Stir the solution with magnetic niddle for 5 minutes. By using measuring cylinder take 0.6 ml acetic acid in a test tube. Transfer this into 100 ml distill water to get 0.1M solution of acetic acid .Stir the solution with magnetic niddle for 5 min. Weight accurately 8 gm NaOH substance on butter paper using balance & transfer into other beaker & add 200 ml distill water & proceed as above. Take out 100 ml $MgSO_4$ + 100 ml acetic acid in a beaker to get homogenous solution with continuous stirring. Fill burette with 1 M NaOH solution & add from burette NaOH solution drop by drop till the colorless solution changes white. This shows that precipitated is formed. This precipitated obtained was washed several time with distill water & filter this solution by filter paper. Collect the precipitated in Petri dish. Dry the precipitated kept at 60^0 for 12 hours to get the final product of MgO nanoparticles. The resultant product further used for characterization [6-7].

Results and Discussions:

Structural characterization (XRD):

The peak of this graph (XRD of MgO powder) is obtained at:
$2\theta = 37.16^0$ therefore, $\theta = 18.58^0$ and intensity = 4841a.u Since $d = (n\lambda)/2\sin\theta$ &n = 1, $\lambda = 1.54A^0$, we get; $d = (1*1.54)/2*0.3186) = 2.4168A^o$ *and grain size* = $D = K\lambda/\beta \cos\theta$ Where β = full width half maxima $(\theta_1-\theta_2) = 0.0.006639$ rad, k = constant = 0.9 for spherical particle, $\lambda = 1.54A^o$, θ = Corresponding angles for peaks, $\cos\theta = 0.9438$
$D = 0.9*1.54/0.0.006639rad *0.9438 = 221.197A^0 = 22.1197nm.$

The peak of this graph (XRD of MgO powder) is obtained at: $2\theta = 49.99^0$. Therefore, $\theta = 24.99^0$ and Intensity = 2891a.u, Since $d = (n\lambda)/2\sin\theta$ &n=1, $\lambda = 1.54A^0$, we get; $d = (1*1.54)/2*0.4224) = 1.8229A^o$ *and grain size* = $D = K\lambda/\beta \cos\theta$
Where β = full width half maxima $(\theta_1-\theta_2) = 0.01328/868$ rad, k = Constant = 0.9 for spherical Particle, $\lambda = 1.54A^o$, θ = Corresponding angles for peaks, $\cos\theta = 0.9063$
$D = 0.9*1.54/0.01328/868 *0.9063 = 115.0825A^0 = 11.50825nm.$
The peak of this graph (XRD of MgO powder) is obtained at: $2\theta = 57.85^0$. Therefore, $\theta = 28.925^0$

and Intensity = 3273a.u, Since d = (n λ)/2sinθ&n = 1, λ =1.54A^0 , we get; d = (1*1.54)/2*0.48366) =1.5922A^o and grain size = D = Kλ/β cosθ
Where β = full width half maxima (θ_1-θ_2) = 0.013438rad, k = Constant = 0.9 for spherical particle, λ=1.54A^o, θ = Corresponding angles for peaks, cosθ = 0.8752
D = 0.9*1.54/0.013438*0.8752 = 221.197A^0 = 11.7845nm.

The greatest peak of this graph (XRD of MgO powder) is obtained at:2θ = 61.33^0 therefore, θ=30.665^0 and intensity = 1640a.u, Since d = (n λ)/2sinθ&n = 1, λ =1.54A^0 , we get; d = (1*1.54)/2*0.5100) = 1.5098A^o *and grain size* = D = Kλ/β cosθ
Where β = full width half maxima (θ_1-θ_2) = 8.9606*10-^{3} rad, k = Constant = 0.9 for spherical particle, λ =1.54A^o, θ = Corresponding angles for peaks, cosθ = 0.8601, D = 0.9*1.54/8.9606*10-3*0.8601 = 179.8347A^0 = 17.98347nm.

XRD pattern of MgO nanoparticles and characteristics properties are shown in Fig. 1 and Table 1**.**

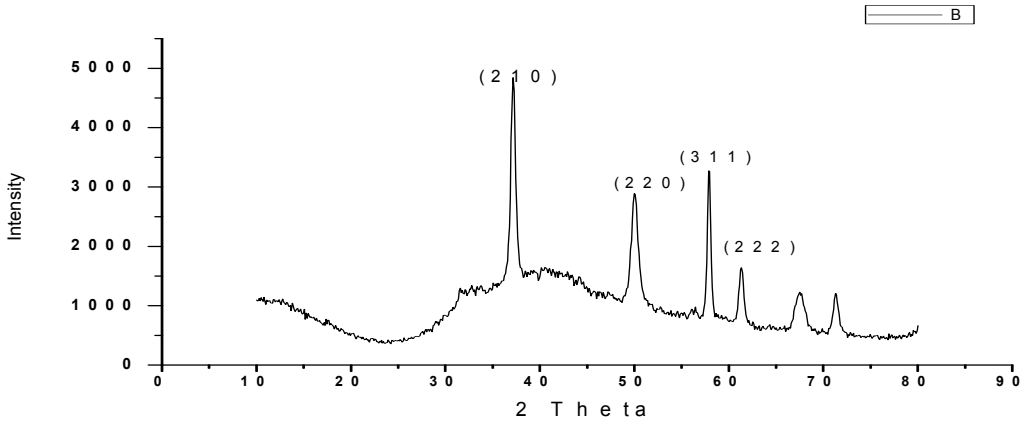

Fig. 1. XRD pattern of MgO nanoparticles

Table1. Characteristics of Mgo Nanoparticles

2θ (degree)	θ (degree)	sinθ	d=λ/2sinθ	I(intensity)	I/I$_0$*100%	hkl	D nm
37.16	18.58	0.3186	2.4168	4841	100	(210)	22.1197
49.99	24.99	0.4224	1.8229	2891	59.71	(220)	11.5082
57.85	28.925	0.48366	1.5922	3273	67.60	(311)	11.7845
61.33	30.665	0.5100	1.5098	1640	33.87	(222)	17.9834

Optical Characterization:

UV absorption Spectra of MgO particles are shown in fig. 2.The UV-Visible spectra were taken from MgO powder and according to the graph slope is at λ=240 nm and by the following formula we get band gap energy: E=hc/λ, since c=3*10^8 m/s, h=6.625*10^{-34}J.S & 1eV=1.6*10^{-19}J, Therefore E=3*10^8*6.625*10^{-34}/240nm or E = 5.17eV [8]

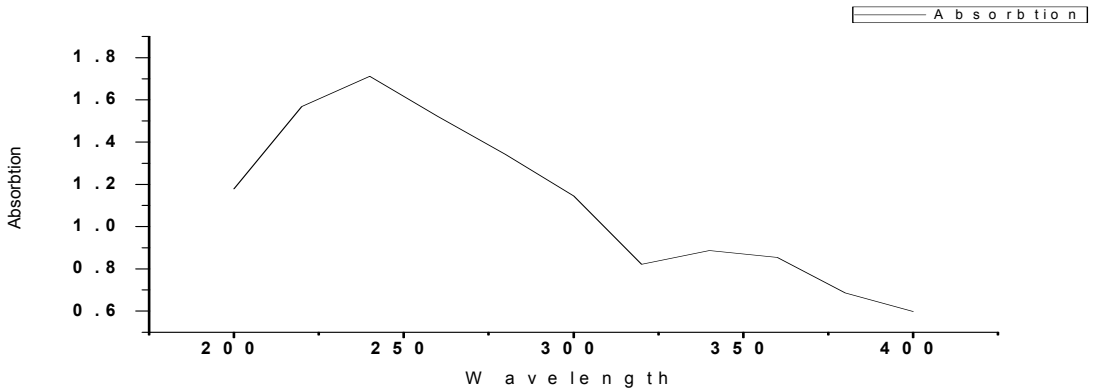

Fig. 2. UV absorption pattern of MgO nanaparticles

FTIR analysis:

FTIR Spectra of MgO particles are shown in fig. 3. Peaks at 3664 cm^{-1}, 3448cm^{-1} corresponding to the O-H stretching mode of hydroxyl groups were present on the surface due to moisture. Peak at 1672 cm^{-1} was attributed to the bending vibration of water molecule. The major peaks at 449 cm^{-1}, 511cm^{-1}, 671cm^{-1} which confirmed the presence of Mg-O vibration [9].

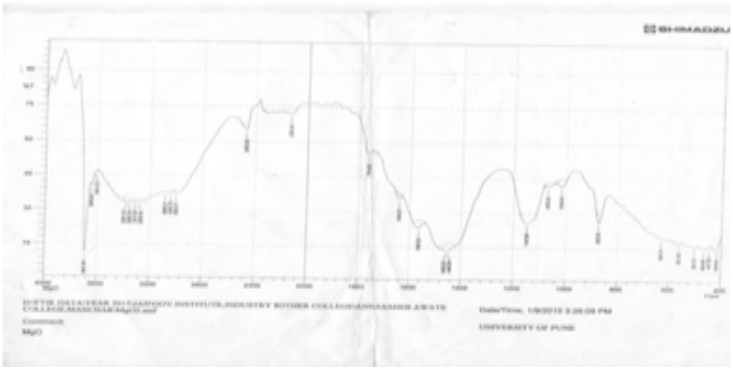

Fig. 3. FTIR spectrum of MgO nanaparticles

Scanning Electron Micrograph:

The surface morphology of prepared MgO nanoparticles was revealed through the SEM image shown in Fig, 4. It shows homogeneous distribution of spherical particles of the prepared MgO nanoparticles [10].

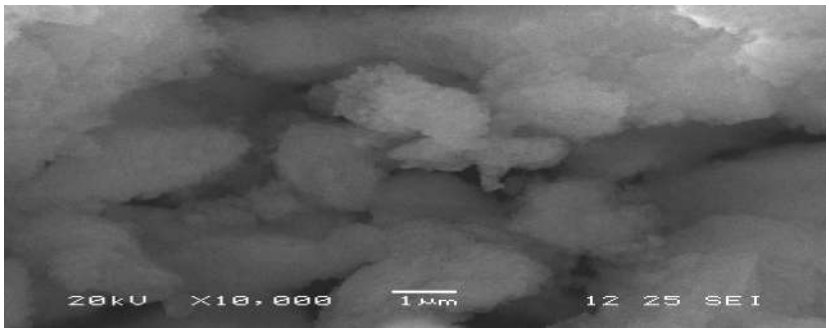

Fig. 4. SEM image of MgO nanoparticles

Conclusion*:*

Nanomaterials are important because of their extremely useful properties. They are exceptionally strong, hard and ductile at high temperatures. They resist wear, erosion and corrosion and are chemically very active.In must cases, nanomaterials out perform their conventional counterparts because of their superior chemical, physical and mechanical properties and outstanding formability. It is grain size and the order of 10^{-9} **m** (1nm). Some of the benefits like getting unique materials such as aerogels, zeolites, ordered porous solids by organic-inorganic hybridization are unique to sol-gel process. It is also possible to synthesize nanoparticles , nanorods, nanotubes etc. using sol-gel technique. The idea behind sol-gel synthesis is to "dissolve" the compound in a liquid in order to bring it back as a solid in a controlled manner. Multi component compounds may be prepared with a controlled stoichiometry bymixing sols of different compounds. The sol-gel method prevents the problems with co-precipitation.

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Impact of nutri-psycho counseling on self-esteem of obese school going children

Dr. Anushree R Khaire and Dr. RMK amble

Abstract
Impact of nutri-psycho counseling on self-esteem of obese school going children was assessed Western Maharashtra i. e. Pune, Nashik and Ahmednagar districts. For this study, 180 obese school going children were selected, from which 90 boys and 90 were girls and 60 from each selected district in 6- 16 age group. The self-esteem of selected children was assessed by using 'Battle's Self Inventory for Children' by Prof. Anand Kumar. It was found that, the self-esteem in relation with general, social, academic and parental was found increased after NP counseling.

Keywords: Snail, bovine, porcine, physicochemical properties, mucin, mucoadhesives

Introduction

Obesity is a global nutrition concern confined not only in adults but also in children and adolescents. With changing life-style and growing urbanization, there has been a rapid increase in health problems related to over nutrition such as overweight and obesity in developing countries worldwide [1]. Childhood obesity is a condition where excess body fat negatively affects a child's health or wellbeing [2]. The prevalence rate of overweight and obesity in India are 12.8 and 10.3 per cent respectively and about 30 per cent of obesity begins in childhood [3]. Negative outcomes from being overweight during childhood include being at higher risk number of chronic and acute conditions as well as negative social and psychological outcomes [4, 5]. They may eat more often when they are feeling sad, stresses or bored and they are more likely to do so, if this pattern was demonstrated to them through their parents. The link between obesity and emotions is tight, yet frequently undefined. The study states that the issues of rejections, fear, anger, depression, stress, loneliness, other emotional disturbance and its ties to overeating. The feeling of distress reached a point at which eating becomes a suitable and temporary relief from their pain. Eating and its impartation seemed to provide the troubled person with a distraction, a reward, gratification, comfort or a sense of being loved [6]. Several authors mention that psychological problems such as negative self-esteem, withdrawal from interaction with peers, depression, anxiety and feeding of chronic rejections are characteristics of obese children [7, 8]. Overweight individuals have a socially disvalued identity. Children who are overweight become aware and others negative views on obesity, which in turn, diminishes their self-esteem. Furthermore, those who are obese may expect others to judge them based on their weight, which in turn may affect their own behavior in ways that produce negative social interactions [9]. Children who are obese not only experience lowered self-esteem as a result of peer taunting, they also show significantly elevated levels of loneliness, sadness and nervousness. Because approved from peers is particularly important within the adolescent years, such negative experiences can be detrimental to the development of self-esteem [10]. The study conducted by Pesic (2006) [11] recognized that obesity amongst children can be traumatic as it is may cause social stigma and lead to withdrawal in socializing with peers, obese children may develop a poor self-image and be of the opinion that they are not good enough. [11] As society views obesity as something negative, obese children may stop interacting with children of their age and tend to shy away from peers. Obese children prefer to stay at home rather than spending time with their friends. This may already be an early sign of depression. Against this background, the present study was undertaken to assess the impact of nutri-psycho counseling on obese school going children.

Materials and methods

An exploratory research has been conducted in three districts such as Pune, Ahmednagar and Nasik of Western Maharashtra. Total 600 (obese) children among obese children having age between 7 to 12 years including male and female were selected by (purposive) simple random sampling method. About 200 obese children were randomly selected from each district. Out of 600 obese children 224 were male and 376 were female. From this samples, only 60 children from each district were taken from study, in which 30 male and 30 females were there. The obese children were selected by calculating BMI through school information of height and weight of children with prior permission of principal. The self-esteem of obese children was assessed by 'Battle's Self Esteem Inventory for Children (SEIC) recommended by Dr. Anand Kumar. This inventory contains 50 items and following four sub-scales-General, Social, Academic and Parental self-esteem. The individual checks each item either 'yes' or 'no'. the self-esteem score is done as per given in manual. There are 20 items on General SE, 10 items on Social SE, 10 items on Academic SE and 10 items on Parental SE. The collected data were pooled, tabulated and analysed statistically.

Results and discussion

The self-esteem of obese children was assessed by 'Battle's Self Inventory for Children' by Prof. Anand Kumar. The impact of nutri-psycho counseling was assessed on children's self-esteem. Their rating assessment after nutritional and psychological counseling was compared with their ratings before NP counseling.

Table 1: Impact of 'NP' counseling on Self-esteem of selected school going obese boys:

Areas of Self-esteem	Level	Boys(90)				'Z' Values
		Before		After		
		Frequency	%	Frequency	%	
General	High	12	13.3	15	16.7	(2.71)*
	Intermediate	29	32.2	41	45.6	(3.42)**
	Low	32	35.6	22	24.4	-(3.29)**
	Very low	17	48.9	12	13.3	-(3.78)**
Social	High	09	10.0	13	14.4	(2.60)*
	Intermediate	24	26.7	38	42.2	(3.81)**
	Low	27	30.0	21	23.3	-(3.53)**
	Very low	30	33.3	18	20.0	-(3.72)**
Academic	High	11	12.2	13	14.4	$(1.21)^{NS}$
	Intermediate	42	46.7	44	48.9	$(1.18)^{NS}$
	Low	22	24.4	28	31.1	-(2.49)*
	Very low	15	16.7	05	5.6	-(2.81)*
Parental	High	05	5.6	09	10.0	(2.63)*
	Intermediate	47	52.6	53	58.9	(2.55)*
	Low	28	31.1	26	28.9	-(2.51)*
	Very low	10	11.1	02	2.2	-(2.79)*

*Significant at 5% level;**Significant at 1%level; NS non-significant

The self-esteem of obese boys is classified in general, social, academic and parental self-esteem. Regarding general self-esteem it is observed that there is significant increase in high and intermediate per cent level i.e. from 13.3 to 16.7 and from 32.2 to 45.6 respectively. It is also observed that there is significant decrease in low and very low level i.e. from 35.6 to 24.4 and from 48.9 to13.3.

It is also seen regarding social self-esteem that high from 10.0 to 14.4 percent and intermediate from 26.7 to 42.2 per cent level were increased significantly. Whereas regarding low and very low level there is significant decrease i.e from 30.0 to 23.3 and from 33.3 to 20.0 due to impact of NP counseling.

The academic self-esteem of selected obese school going boys observed difference in before and after NP counseling. But the difference is non-significant. Whereas negative significant difference was found at low and very low level i.e. from 24.4 to 31.1 per cent and from 16.7 to 5.7 respectively.

The parental self-esteem of obese boys significantly improved at high (from5.6 to 10.0%) and intermediate level (from 52.2 to 58.9%) after NP counseling. The low and very low level were also significantly decreased i.e. from 31.1 to 28.9 and11.1 to 2.2 per cent respectively.

Table 2: Average Statistical analysis of self-esteem of selected obese boys

Parameter	Mean Before	Mean After	Z cal	'p' value	Level of significance	Result	Conclusion
General	1.589	1.78	1.99	0.0466	0.05	Reject H0	Significant
Social	1.46	1.8	3.65	0.0003	0.05	Reject H0	Significant
Academic	1.711	1.811	1.07	0.285	0.05	Reject H0	Significant
Parental	1.511	1.74	2.54	0.0111	0.05	Reject H0	Significant

Moreover, the table 6.7.2 reveals the average statistical analysis of self-esteem of selected school going obese boys. It is found from observations that there is significant difference in mean averages for general, social, academic and parental self-esteem of obese boys.

Table 3: Impact of 'NP' counseling on Self-esteem of selected school going obese girls:

Areas of Self-esteem	Level	Girls(90)				'Z' Values
		Before		After		
		Frequency	%	Frequency	%	
General	High	17	18.9	19	21.1	$(1.09)^{NS}$
	Intermediate	34	37.8	43	47.8	(2.61)*
	Low	24	26.7	17	18.9	-(3.70)**
	Very low	15	16.7	11	12.2	-(2.52)*
Social	High	14	15.6	19	21.1	(2.63)*
	Intermediate	38	42.2	47	52.2	(2.74)*
	Low	13	14.4	11	12.2	-(2.47)*
	Very low	25	27.8	13	14.4	-(3.26)**
Acade-Mic	High	07	7.8	09	10.0	(2.55)*
	Intermediate	52	57.8	56	62.2	(2.48)*
	Low	29	32.2	24	26.7	-(3.22)**
	Very low	02	2.2	01	1.1	-(2.19)*
Paren-Tal	High	11	12.2	13	14.4	(2.35)*
	Intermediate	33	36.7	43	47.8	(2.39)*
	Low	37	41.1	32	35.6	-(2.44)*
	Very low	09	10.0	02	2.2	-(2.71)*

*Significant at 5% level;**Significant at 1%level;NS non-significant

It gives clear idea that the general self-esteem of obese girls in intermediate level i.e. from 37.8 to 47.8. Whereas, there is increase in high level from 18.9 to 21.1, but this difference is non-significant. It is also observed that there is significant decrease in low and very low level i.e. from 26.7 to 18.9 and from 16.7 to12.2 respectively.

Regarding with social self-esteem, high and intermediate level of these girls were increased significantly from 15.6 to 21.1 per cent and from 42.2 to 52.2 per cent respectively. Whereas, regarding low and very low level there is significantly improved from 14.4 to 12.2 and from 27.8 to 14.4 respectively after NP counseling.

The academic self-esteem of selected obese school going girls observed significant difference in before and after NP counseling for high and intermediate level i.e from 7.8 to 10.0 and from 57.8 to 62.2. Whereas negative significant difference was found at low and very low level i.e. from 32.2 to 26.7 per cent and from 2.2 to 1.1 respectively.

The parental self-esteem of obese girls significantly improved at high (from 12.2 to 14.4%) and intermediate level (36.7 to 47.8%) after NP counseling. The low and very low levels were also significantly decreased i.e. from 41.1 to 35.6 and10.0 to 2.2 per cent respectively.

Table 4: Average Statistical analysis of self-esteem of selected obese girls

Parameter	Mean		Z cal	'p' value	Level of significance	Result	Conclusion
	Before	After					
General	1.589	1.78	1.99	0.0466	0.05	Reject H0	Significant
Social	1.46	1.8	3.65	0.0003	0.05	Reject H0	Significant
Academic	1.711	1.811	1.07	0.285	0.05	Reject H0	Significant
Parental	1.511	1.74	2.54	0.0111	0.05	Reject H0	Significant

The table 6.7.2 reveals the average statistical analysis of self-esteem of selected school going obese girls. It is found from observations that there is significant difference in mean averages for general, social, academic and parental self-esteem of obese girls.

Conclusion

On the whole it can be concluded that, the self-esteem in relation with general, social, academic and parental was found increased after NP counseling among these selected obese children. This impact was noticed more significant in girls than boys. Academic self-esteem was noted improved in only obese girls at more significant level than the boys.

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3.2.1 ***Number of papers published per teacher in the Journals notified on UGC website during the last five years***

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Persistence of Organic Pollutants in Ground Water Around Kurkumbh Industrial Area (Daund) from Pune District, (MS) INDIA

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ABSTRACT

The global distribution of persistence of organic pollutants (POPs) has become one of the main environmental problems in the last decade. The environmental exposure to persistent of organic pollutants (POPs) become emerging risk factor for contribution of the knowledge of atmospheric transport and persistent organic pollutants (POPs) in remote area. Such persistent of organic pollutants (POPs) which includes chlorinated pesticides were determined in water sample collected around Kurkumbh industrial area during Pre-monsoon and post monsoon 2014. Concentration of total presticides ranges from 0.02 to 0.07 ng/L and 6.39 to 149.4 ng/L. The rate of percolation of pesticides and polycyclic aromatic hydrocarbons (PAHs) were high at site second as compare to site first from study area because of high slope of area. The organic pesticides like Hexachlorocyclohexane (HCH) as a-HCH, b-HCH, y-HCH, Heptachlor, Dieldrin, Aldrin Total pesticides (TP), Total cyclodiene (TC), Heptachloroepoxide (HCP) Dichloridiphenyl Trichloro ethane (DDT) and organic pollutants like Naphthalene, Phenathane, Pyrene, Toulene were studied. The concentration of organic pesticides and (PAHs) were bellow the detection limit in the study area.
Keywords: Chlorinated pesticides, (PAHs) and organic pollutant water around Kurkumbh industrial area.

I. INTRODUCTION

Persistance is the ability of substance to remain without change in the environment for a long period of time. It is the potential of this substance to travels hundreds to thousands kilometers away from its original sources. It causes damage or death to living organism. Some of them may cause cancer immunological and reproduction defects. They also disturb the nervous and respiratory system, affects the level of liver enzymes[1]. The POPs are bioaccumulation in living organism by capture it either directly from the environment and are indirectly from their food supply. The PCBs, DDT, PAHS may be responsible for occurrence of the breast cancer. Kurkumbh is considered as semi closed water body affected mainly from loading unloadind operation[2]. POPs have a wide range of industrial anthrpogenic and agriculture applications. They include pesticides such as DDT (dichlorodiphency / trichloroethane) and lindane (Y-HCH) in addition to petroleum hydrocarbons which are organic chemicals composed of fused benzene rings formed during incomplete combustion of coal, oil, petrol and wood. The soil is polluted by these substances primarily as use of pesticides application in agriculture. Another soil pollution sources may be also the over irrigation. Some pesticide is soluble in water which causes pollution of soil as well as ground water. Number of industrial sources such as power stations heating station as well as household furnaces transport and use of agricultural spray[3]. Evaporation of water or soil surfaces causes air pollution. Hence POPs concentration in atmosphere is increases gradually which are harmful to human being and any other living organism. To overcome these analytical problems, pesticides should be pre-concentrated as large possible to enable detection by the instruments[4].

POPs are synthetic organic compounds which are widely spread on land and in aquatic environment. There are commonly considered the most persistent anthropogenic organic compounds introduced in to the environment. Some of these are highly toxic and have a wide range of chronic effects including endocrine description mutagenicity and carcinogenicity. Furthermore POPs are chemically stable and therefore not easily degraded in the environment or in organism. They are lipophilic and

accumulate in the food chain[5]. Organo-chlorine pesticides are synthetic compounds that are chemically stable and hydrophobic. They include Dichlorodiphenyl Trichloro ethane (DDT). The Pesticides used in agriculture as an insecticide. This pesticide such as BHC (Hexachlorocyclohexane), chlordane and aldrin are other chlorinated pesticides use in agricultural. It is generally agreed that, the pollution around Kurkumbh industrial area has reached a critical level[6]. River runoff (Bhima) has the direct effect of reducing the salinity of the water. Untreated domestic waste water with agricultural and industrial wastes is still release through a number of drainages along the coastal area of study. The orgonochlorines pesticides actas never poisons and are highly toxic to fish because of their chemical structure and their persistence. The health hazard posed by these compounds has been studied extensively by several authors. The Kurkumbh are big industrial area which discharge industrial waste water in ground as well as on the surface (Fig. 5). The Bhima River is longest river nearby the area. Peoples are used river water for irrigation. The over irrigation used of insecticides, pesticides, fertilizers polluted the ground water[7-8]. There were various organic pollutants are percolated in ground water which causes harmful effects on living organism[9].

The organic pollutants cause harmful effects on human being, plant and living organism. The building blocks of living organisms are organic compounds which contain carbons and hydrogen[10]. However human have learnt to manufacture organic compounds that are extremely difficult to breakdown and as a result have become widely dispersed throughout the environment. These chemicals re-termed persistent organic pollutants (POPs) and are extremely resistant to nature break down processes and therefore are stable and long-lived. Most do not occurred in nature built are created through artificial process[11].

Once released (POPs) in to the environment many persist few years even decodes therefore even if production of all (POPs) ceased today. They would contain to pollute the environment for many years to come. Many POPs are also highly toxic and built up in the fatty tissues of animals and humans. In order to understand more clearly the behavior of these pollutants on a global scale and to prepare the future environmental policies; a baseline study is aimed to determine the occurrence of POPs in water of around Kurkumbh industrial area[12].

II. Material and Methods

Ten ground water samples were collected 5 km away from (site 1) Kurkumbh industrial area during (May, 2014). However another ten water samples are collected 10 km away from (site 2), during January 2014 (Fig. 2, 3a3b, 4a and 4b). According to slope and grading pattern (Fig. 1, 6a and 6b). The studied areas were represented by four sector, western sector, southern sector and northern sector. Water samples were extracted in the field and stored at 4^0c and transported to the laboratory for PAHs analysis using well established techniques[13]. The result measured in water samples using UV, Spectrophotometer (Sequoia-Tummer model 450) at 360 mm recitation and 415 mm emission. A calibration wave was determined by analyzing five separate concentration (0.5, 1, 2, 1 and 6 mg/L) of chrysene using h-hexane as the solvent. Clamp up and fractionation was performed prior to gas chromatograph / flame ionization detector and electron capture detector (GC/FID/ECD)[14].

The 1st ml of the extracted volume was passed through the silica column prepared by slurry packing 20 ml (10 gm) of silica followed by 10 ml (10 ml) of alumina and finally 1 gm of anhydrous sodium sulphate. Elution was performed using 40 ml of hexane/dichloromethane (90:10) followed by 20 ml of hexane/dichloromethane (50:50) which combined contain PAHs. Finally eluted samples were concentrated under a gentle stream of purified nitrogen to about 0.2 ml prior to be injected into GC/FID for pesticides analysis[15]. All samples were analyzed by a Hewlett Packard 5890 series II GC gas chromatography equipped with a flame ionization detector (FID) and electron capture detector. For hydrocarbon analysis the instrument was operated in split less mode (3ml split less injection) with the injection Dieldrin, DDT, to control the analytical reliability and assure recovery efficiency and accuracy of the results. Four analysis were conducted on organo-chlorine compounds[16].

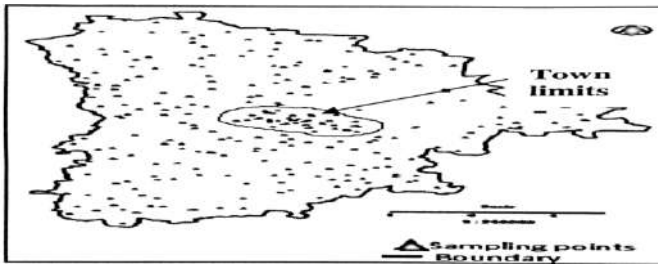

Figure 1. Location map of the study area.

Figure 2. Agricultural field and irrigation type around study area.

Figure 3(a). Source of irrigation around study area.

Figure 3(b). Source of irrigation around study area.

Figure 4(a). Dug well for around study area.

Figure 4(b). Dug well for around study area.

Figure 5. Chemical industry around study area.

Figure 6(a). First sampling site around study area.

Figure 6(b). Second sampling site around study area.

III. Result and discussion

Table (1 and 2) shows the residual concentration of organochlorine compounds determined in water samples collected from study areas. The data of Table (1 and 2) indicates that PP-DDT [2, 2, bis (P-Chloropheny)-1, 1, 1 trichlorothane] is the most dominant orgonochlorine compound during summer reason.The maximum concentration was 147.4 ng/L recorded DDT is generally used against a wide variety of agricultural and forest pests and pests including, vectors such as mosquito and test –test fly in the environment. DDT can be degraded by solar radiation or metabolized in organism Heptachlor is the common name for 1.4, 5, 6, 7, 8, 8- heptachloro 3a, 4, 7, 7a tetrahydro -4, 7-methane – 1H – indane. It is generally use as insecticides and also occurs technically as chlorodane. In the environment, degraded or metabolized and is more commonly found as its epoxide compared with a mean concentration of 0.151ng/L for all locations during summer from study area second[17].

Aldrin is an alicyclic chlorinated hydrocarbon and is rapidly converted to the epoxide form. Dieldrin. The presence of an average of 0.097 ng/L of aldrin with mean clue of 0.071 ng/L of dieldrin. Recorded at site second during summer season, part maintained at 29^0C and the detector maintained at 3^0C samples were analyzed on a fused silica capillary column HP-1 100% dimethyl polysiolane (30 m. length 0.32 mm i.d., 0.17 mm film thickness). The oven temperature was programmed from 60-29^0C changing at a rate of 3^0C min and maintained at 29^0C for 25 min. The carrier gas was nitrogen flowing at 1.2 ml /min. However HP-5 capillary column film thickness with Ni63 – electron capture detector (ECD) was used for pesticides analysis. The oven temperature was programmed from 9^0C – 14^0Cat rate of 5^0C / min maintained at 14^0C for 1 min then from 14^0C – 25^0C at rate of 3^0C /min maintained at 25^0C for 1 min then from 25^0C – 35^0C at rate of 2^0C /min and maintained at 30^0C for 1min the carrier gas was nitrogen flowing at 1.5 ml/min [18-19]. A stock solution containing the following PAHs was used for quantification of hydrocarbons naphthalene phenathrene, pyrene, Touluene by dilution to create a series of calibration standards of PAHs at 0.1, 0.25, 0.5, 0.75, 1.0, 2.0, 5.0 and 10 ng ml/L. The detection limit was approximately 0.01 ng /L for each PAH for analytical reliability and recovery efficiency of the results, six analyses were conducted on PAH reference material[20].

Orgonochlorine pesticides were quantified from individually resolved peak areas with corresponding peak areas of the external standards. They includes a, B and u. Hexachlorocyclohexanes, Heptachlor, Aldrin, heptachloroe epoxide It is declare that there is a renewal of Aldrin in water[21]. HCH (hexachlorocyclohexane) is a fully chlorinated alicyclic compound .The most common ismers are, a, B and u HCH they u isomer known as Lindane is one normally used as an agricultural pesticides. HCH is a responsibly stable compounds and only under alkaline condition decomposes to yield trichloro-benzane. It is considered as one of the less persistence organochlorine pesticides. A maximum of 0.25 ng/L of HCH was declared at the location second[22].

The data of tables I&II declared also that pesticides concentration were higher in study area second (10 km away) than study area first (10 km away). Total HCHs were the major pollutant followed by total DDTs, total cyclodines (TC) with an average calue of 0.063, 0.022 and 0.014ng/ L respectively in study area first[23].The average concentration of Nephthalene is 0.072 ng/L in side second than that of side first 0.298 ng/L. The order of concentration of phenanthrene pyrene and toluene from study area second is high than concentration of phenanthrene, pyrene and toluene from study area first because atmospheric fallorct (rain water) is the major source of pollution. Agricultural runoff river and discharge of industrial waste[24]. Form above observation it is that POPs construction recorded is more at site

second than site first n the study area. The residual polynuclear aromatic hydrocarbons Nephthalane, Phenathrene, pyrene and toluene were investigated in water of study area.

Table 1. Description sampling locations during May 2014

Sampling station	Sampling locations	Water Source	Soil Type	Crop
T1	10 Km. South from Industrial area Tal. Daund, Dist. Pune	Dug well	Black cotton	Sugar cane
T2	07 Km. West of Aalegaon Sugar factoryTal. Daund, Dist. Pune	Lift Irrigation from Bhima river	Black cotton	Paddy
T3	20 Km. West from Bank of Bhima river near Siddhatek.	Lift Irrigation from Bhima river	Alluvial	Cowpea
T4	05 Km. North from Industrial area Shindewadi Tal. Daund, Dist. Pune	Lift Irrigation from Bhima river	Black cotton	Pumpkin
T5	10Km. North from Industrial area jiregaon, Tal. Daund, Dist. Pune	Dug well	Black cotton	Ground nut
T6	15 Km. West from Industrial area, Malad, Tal. Daund, Dist. Pune	Dug well	Black cotton	Fenugreek
T7	02 Km. South from Industrial area, Pune Solapur highway	Lift Irrigation from Canal	Black cotton	Paddy

Table 2. Description sampling locations during January 2014

Sampling station	Sampling locations	Water Source	Soil Type	Crop
T1	10 Km. North from Industrial area Tal. Daund, Dist. Pune	Dug well	Black cotton	Sugar cane
T2	07 Km. East of Aalegaon Sugar factoryTal. Daund, Dist. Pune	Lift Irrigation from Bhima river	Black cotton	Sugar cane
T3	20 Km. East from Bank of Bhima river near Siddhatek.	Lift Irrigation from Bhima river	Alluvial	Sugar cane
T4	05 Km. South from Industrial area Shindewadi Tal. Daund, Dist. Pune	Dug well	Black cotton	Spinach
T5	10Km. South from Industrial area jiregaon, Tal. Daund, Dist. Pune	Dug well	Dark grey	Tomato
T6	15 Km. East from Industrial area, Malad, Tal. Daund, Dist. Pune	Dug well	Black cotton	Vegetables
T7	02 Km. North from Industrial area, Pune Solapur highway	Lift Irrigation from Canal	Black cotton	Sugar cane

Table 3. Concentration of (POPs) in ground water around Kurkumbh industrial area in May, 2014.

Organic pollutants	S1	S2	S3	S4	S5	S6	S7
Alpha-HCH	0.031	0.0012	0.0031	0.0099	0.0017	0.0011	0.0023
Beta-HCH	0.0068	0.0022	0.0068	0.0032	0.0019	0.0021	0.0012
Gama-HCH	0.0166	0.0013	0.0017	0.0011	0.0039	0.0012	0.0011
Naphthalene	0.0544	0.0048	0.0116	0.0139	0.0075	0.0044	0.0046
Heptachlor	0.0027	ND	0.0027	0.0063	0.0097	ND	0.0018
Aldrin	0.0024	0.022	0.0024	ND	0.0018	ND	0.0014
HCP	0.0003	0.0003	0.0028	ND	0.0027	ND	ND
Dieldrin	0.0003	ND	0.0026	ND	0.0035	0.0009	0.0229
TC	0.0057	0.0223	0.0105	0.0063	0.0177	0.0009	0.0061
Phenathrene	0.0013	0.0002	0.0013	ND	0.0084	0.0018	0.0079
Pyrene	0.0052	0.0083	0.0052	ND	0.0055	0.003	ND
PP-DDT	0.0019	ND	0.0019	0.0022	0.0025	0.0085	ND
Toulene	0.0083	0.0085	0.0083	0.0022	0.0164	0.0127	0.0099
Tp	0.0684	0.0156	0.0304	0.0224	0.0415	0.018	0.0207

TP: Total pesticides, **TC:** Total cyclodines, **HCP:** Heptachlorepoxide, **ND:** Not detected

Table 4. Concentration of (POPs) in ground water around Kurkumbh industrial area January 2014.

Organic pollutants	S1	S2	S3	S4	S5	S6	S7
Alpha-HCH	0.17	0.097	0.02	0.35	0.24	0.09	0.27
Beta-HCH	0.04	0.19	0.02	0.04	0.03	.001	0.02
Gama-HCH	0.01	0.25	0.01	0.0	0.02	0.01	0.01
Naphthalene	0.023	0.023	0.023	46	029	0.11	0.29
Heptachlor	0.13	0.44	0.08	0.2	0.07	0.03	0.12
Aldrin	0.07	0.32	0.04	0.16	0.05	0.04	0.05
HCP	0.17	0.49	0.04	0.22	0.05	0.06	0.04
Dieldrin	0.04	0.23	0.03	0.11	0.03	0.03	0.02
TC	0.42	0.42	0.2	0.69	0.2	0.15	0.23
Phenathrene	0.09	0.71	0.07	0.31	0.06	0.05	0.07
Pyrene	0.16	0.64	0.14	0.31	0.08	0.04	0.16
PP-DDT	69.79	147.4	58.83	14.97	54.5	6.0	78.99
Toulene	70.0	148.7	59.0	15.59	54.64	6.13	79.22
Tp	70.69	149.4	59.46	16.75	55.17	6.39	79.73

TP: Total pesticides, **TC:** Total cyclodines, **HCP:** Heptachlorepoxide, **ND:** Not detected

IV. Conclusion

The present study declared that the concentration of POPs from side second is more than concentrations of POPs from side first. Since rate of persistence of organic pollutants is high from higher slope area to lower slope area. The total average concentration of some POPs, a-HCH, B-HCH, u-HCS Nepthalane, Aldrin, Dieldrin TC, phenathrene pyrene HCP is bellow the admissible environment level but the POPs, P.P-DDT, toluene and total pesticides were above the permissible limit. The maximum levels of toxic substances, recommended for the protection of aquatic biota has been published. The environmental quality objectives set by European community is 10ng/l. of P-P DDT and for HCH isomers at 20ng/L. for Heptachlor. 10-100ng/L. Thus land based activities mainly agricultural and industrial wastes are the major sources of POPs pollution around study area.

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Synthesis and Characterization of Silver Nanoparticles using Azadirachta indica (Neem) leaf extract

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Abstract: *The synthesis of stable silver nanoparticles by the bioreduction method was investigated. Aqueous extract of Azadirachta indica (Neem) plant was used as reducing and stabilizing agent respectively. On treating silver nitrate solution with Azadirachta indica (Neem) leaf extract rapid reduction of silver ions was observed leading to the formation of stable silver nanoparticles in solution. The characteristics of silver nanoparticles were studied using UV-Vis spectroscopy, X-ray diffraction analysis (XRD), Scanning electron microscopy (SEM) and Energy dispersive spectroscopy (EDX). The UV-Vis spectra gave surface Plasmon resonance for synthesized silver nanoparticles at 450 nm.*

Keywords: *Azadirachta indica (Neem) leaf extract, Biosynthesis, Silver nanoparticles.*

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I. INTRODUCTION

Nanotechnology is emerging as a rapidly growing field with its application in Science and Technology for the purpose of manufacturing new materials at the nanoscale level[1]. In recent years, noble metal nanoparticles have been the subject of focused research due to their unique, optical, electronics, mechanical, magnetic and chemical properties that are significantly different from those of bulk materials[2]. The synthesis of noble nanoparticles for electronics and environmental and biotechnology applications is an area of continued research. Preparation of silver nanoparticles has attracted particularly considerable attention due to their diverse properties and uses, like magnetic and optical polarizability[3], electrical conductivity[4], catalysis[3], antimicrobial and antibacterial activities[5-6], DNA sequencing[7], and surface enhanced Raman scattering (SERS)[8].

Various techniques of synthesizing silver nanoparticles, such as chemical reduction of silver ions in aqueous solutions with or without stabilizing agents[9], thermal decomposition in organic solvents[10], chemical reduction and photo reduction in reverse micelles[11] and radiation chemical reduction[12-14] have been reported in the literature. Most of these methods are extremely expensive and also involve the use of toxic, hazardous chemicals which may poses potential environmental and biological risks, thus there is a growing need for green synthesis that includes clean, non toxic and environment friendly methods of nanoparticles synthesis[15] with sustainable commercial viability. Green synthesis makes use of environmental friendly, non-toxic and safe materials[16] like bacteria, fungi, enzymes, plants or plant extracts have been suggested as possible eco-friendly alternatives to chemical and physical methods. Sometimes the synthesis of nanoparticles using plants or parts of plants can prove advantageous over other biological processes by eliminating the elaborate processes of maintaining microbial cultures[17]. Azadirachta indica, commonly known as Neem belongs to Meliaceae family, and is well known in India and its neighboring countries for more than 200 years as one of the most versatile medicinal plant having a wide spectrum of biological activity. Every part of the tree has been used as a traditional medicine for household remedy against various human ailments from antiquity[18-20].

It has been reported that silver nanoparticles are non-toxic to humans and most effective against bacteria, virus and other eukaryotic micro-organisms at low concentrations and without any side effects[21]. The most important application of silver and silver nanoparticles is as tropical ointments to prevent infection against burns and open wounds[22]. The extension of our previous work[23] we investigated the synthesis of stable silver nanoparticles with the bioreduction method using Azadirachta indica (Neem) leaf extract which acted as reducing agent and its characterization.

II. EXPERIMENTAL

2.1 Preparation of Azadirachta indica leaf extract:

Fresh leaves of Azadirachta indica (Neem) were collected from A.C.S. College campus, Satral, MS, India, and 5 g of the healthy leaves washed thoroughly with double distilled water, cut in to fine pieces and boiled with 50 mL double distilled water in 250 mL Erlenmeyer flask for 25 min. The extract was cooled to room temperature and filtered through Whatman filter paper no.42. The filtrate was stored at 4 ^{o} C for further experiments.

2.2 Synthesis of Silver Nanoparticles:

In a typical reaction procedure, 10 mL of Azadirachta indica (Neem) leaf extract was added to 50 mL of 1 mmol L^{-1} aqueous silver nitrate solution, with stirring magnetically at room temperature. The reddish color of the reaction mixture of silver nitrate solution and Azadirachta indica (Neem) leaf extract at 0 min of reaction time changed very fast at room temperature and after 5 min to reddish- brown suspended mixture, this indicated the biosynthesis of silver nanoparticles.

2.3 Characterization of Silver Nanoparticles:

The bioreduction of Ag^{+} in solutions was monitored by measuring a UV-Vis spectrum at room temperature operated at a resolution of 1nm between 300-700 nm range. The leaf extract was used as reference blank. The biosilver nanoparticles solution thus obtained were purified by repeated centrifugation at 5000 rpm for 20 min followed by redisperation of the pellet into 10 mL of deionized water and freeze-dried. The dried mixture was collected for determination of silver nanoparticles by a BRUKER D8 advance X-ray diffractometer. Scanning electron microscopy (SEM) analysis of synthesized silver nanoparticles was done using a Hitachi S-3000 N. Japan. The elemental composition of the synthesized silver nanoparticles was analyzed by Energy dispersive X-ray microanalysis spectroscopy.

III. RESULTS AND DISSCUSSIONS

It is well known that silver nanoparticles exhibit a reddish brown color in aqueous solution due to excitation of surface Plasmon vibrations in silver nanoparticles[24]. Reduction of silver ions to silver nanoparticles could be followed by a color change and UV-Vis spectrum. The photographs of sample solutions containing silver nitrate and silver nitrate in presence of optimized amount of Azadirachta indica leaf extract solutions after the completion of the reaction [Fig.1]. The appearance of a reddish brown color confirms the formation of silver nanoparticles.

Figure 1: Solution of silver nitrate 1mmol L^{-1} before (left) and after (right) addition of Azadirachta indica leaf extracts solution

The production of silver nanoparticles by reduction of silver ions due to the addition of Azadirachta indica leaf extract was followed by UV-Vis spectroscopy. The absorption spectrum of the synthesized nanoparticles was observed in the range of 450 nm; this observation indicates that there is no aggregation in UV-Vis absorption spectrum [Fig.2].

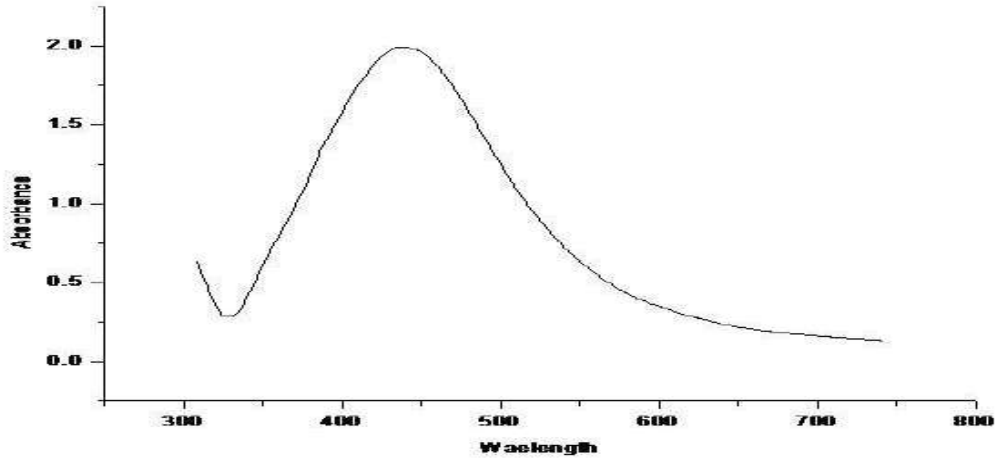

Figure 2: UV-Vis absorption spectrum of obtained silver nanoparticles

Analysis through X-ray diffraction was carried out to confirm the crystalline nature of the silver nanoparticles. The dry powders of the silver nanoparticles were used for XRD analysis. The diffracted intensities were recorded from 20^o to 100^o at 2θ angles. A comparison of our XRD spectrum with the standard confirmed that the silver nanoparticles formed were in the form of nanocrystals, as different diffraction lines were observed at 2θ angle 28.5, 32, 38.5, 46 respectively [Fig.3].

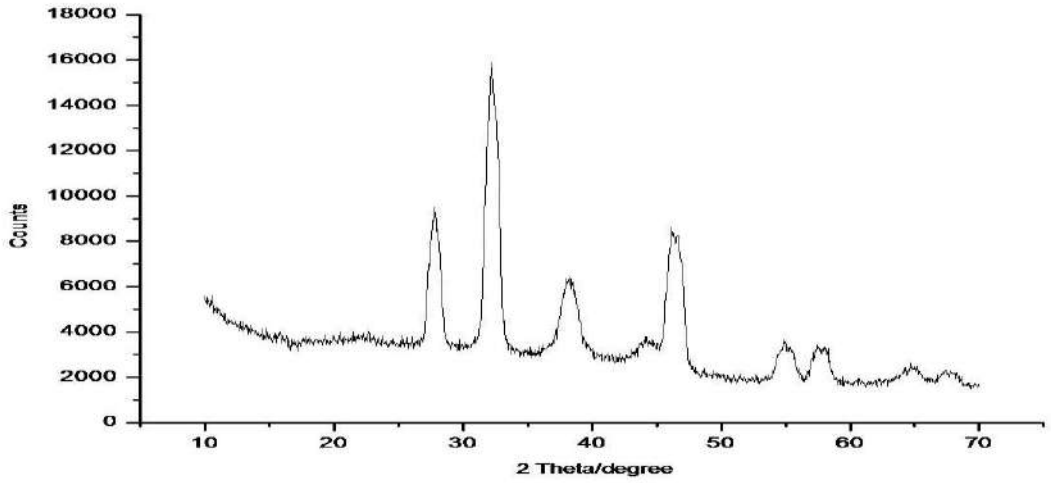

Figure 3: X-ray diffraction pattern of prepared silver nanoparticles

The average particle size of the silver nanoparticles synthesized by present green method can be calculated by using Debye-Scherrer's equation. $D = K\lambda / \beta \cos \theta$. Where D is the crystal size, k is the Scherrer's constant with the value 0.94, λ is the wavelength of the X-ray, β is the full width at half maximum and θ is the Bragg angle. Calculations using Scherrer's equation showed that the average particle size was in the range of 6 to 8 nm. To gain further insight into the features of the silver nanoparticles, analysis of the sample was performed using SEM [Fig.4].

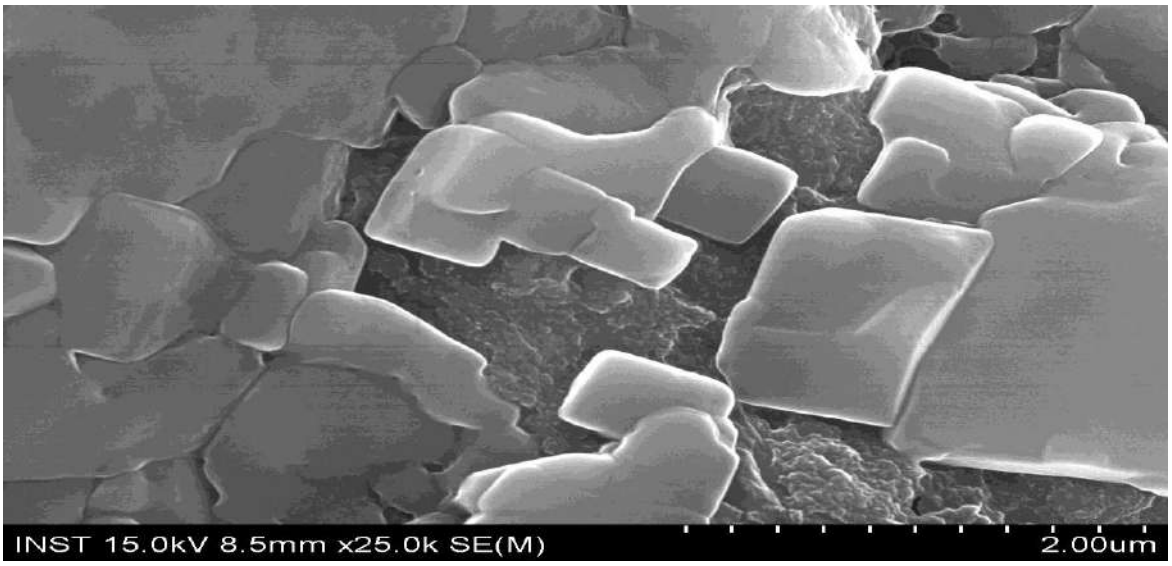

Figure 4: SEM image of silver nanoparticles prepared using Azadirachta indica (Neem) leaf extract

Scanning electron microscopy provided the morphology and size details of the silver nanoparticles. It was identified that shapes of silver nanoparticles appeared like irregular rod shapes with rough surface. All the nanoparticles were well separated and no agglomeration was noticed. The elemental analysis of the silver nanoparticles was studied using Energy-dispersive microanalysis (EDX) [Fig.5]. The analysis revealed highest proportion of silver in the nanoparticles followed by carbon, silicon, oxygen.

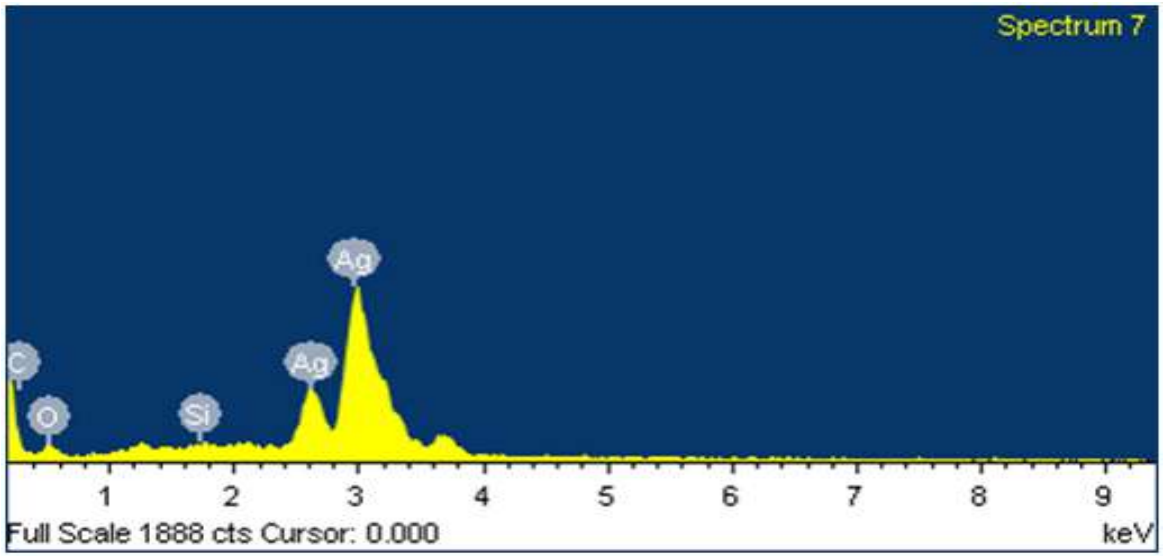

Figure 5: Energy-dispersive spectroscopy spectrum of prepared silver nanoparticles

IV. CONCLUSION

In this study, a simple approach was attempted to obtain a green eco-friendly way for the synthesis of silver nanoparticles. The primary confirmation for the silver nanoparticles was color changes and UV-Vis absorption spectra peak at 450 nm. The result showed that Neem leaf extract plays an important role in the reduction and stabilization of silver to silver nanoparticles. This green method has advantages like ease with which the process can be scaled up and economic viability.

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SOLVENT EXTRACTION, SPECTROPHOTOMETRIC DETERMINATION OF SELENIUM (IV) AT MICROGRAM LEVEL USING O-METHYLPHENYL THIOUREA AS A SENSITIVE REAGENT: ANALYSIS OF PHARMACEUTICALS, SYNTHETIC MIXTURES AND REAL SAMPLES

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ABSTRACT

A simple and rapid method has been developed for solvent extraction and spectrophotometric determination of selenium (IV) using o-methylphenyl thiourea (OMPT) as a sensitive reagent. The basis of proposed method is formation of selenium (IV)-OMPT complex. Selenium (IV) was extracted with 0.015 mol L^{-1} OMPT in chloroform from aqueous solution in 3.6 mol L^{-1} hydrochloric acid. The absorbance of complex was measured at 335 nm. Beer's law was obeyed up to 800.0 µg mL^{-1} for selenium (IV). The molar absorptivity and Sandell's sensitivity of the complex were 4.066×10^2 L mol^{-1} cm^{-1} and 0.1942 µg cm^{-2} respectively. The Stiochiometry of selenium (IV)-OMPT complex was 1:2 established from slope ratio method, mole ratio method and job's continuous variation method. The stability of selenium (IV)-OMPT complex was >48 h. The proposed method is free from interferences from foreign ions and suitable masking agents were used wherever necessary to enhance selectivity of method. The

proposed method was successfully applied for separation and determination of selenium (IV) from pharmaceuticals, synthetic mixtures and real samples. Precision of method was checked by finding relative standard deviation for 10 determinations was 0.44%.

KEYWORDS: Solvent extraction, Analysis, Pharmaceuticals and Vegetable, Selenium (IV).

INTRODUCTION

The selenium (IV) content in earth crust is 5.0 ppm, 0.2 ppb in sea water and 1 nanogram per cubic meter of air. Selenium (IV) is the essential micronutrient to different biological systems. There are numerous applications of selenium with its use in various fields and different sectors viz: pharmaceuticals, poultry, pesticide, fungicide formulations, rubber production and in anti dandruff shampoos. Selenium (IV) also exhibits enhanced electrical properties. It is resistance to the electrical flow and is proportional to amount of light shining. By considering its properties, it is used in devices sensitive to intensity of light viz: electric eyes, photocells, photoelectric cells, light meters, solar cells and photocopiers. The problems of selenium (IV) fractionation in soils, rich in organic matter have been focused.[1] Selenium (IV) performs different cellular functions and one of the important function is protection of cell membranes from oxidative damage. After long time exposer of elemental selenium and selenium oxides may result into different disorders viz: irritation of respiratory tract, bronchitis, breathing problems, coughing and stomach pains. The body content of selenium after exceeding the optimum levels starts affecting the nervous system. Selenium (IV) has been found to exhibit anticancer properties. Increasing evidence suggests that selenium plays an important role in normal growth and reproduction in animals and humans.[2] Several analytical methods are reported to determine the selenium (IV) in large variety of samples. These methods include gas chromatography-electron capture detection (GC-ECD)[3], atomic absorption spectroscopy (AAS)[4-7], atomic fluorescence spectroscopy (AFS)[8], inductively coupled plasma optical emission spectrometry (ICP-OES)[9], hydride generation system and atomic fluorescence spectrometer (HG-AFS)[10], hydride generation atomic fluorescence spectrometer (HG-AFS)[11], stripping voltammetry[12] and integrated coupled plasma mass spectroscopy.[13] From the literature survey, it is clear that, different instrumental techniques are available for the determination of selenium (IV) in variety of samples. But the detailed study of these advanced instrumental techniques has drawbacks associated with these methods like, high cost of investment, large scale electricity consumption during continuous

analysis, necessity of regular maintenance of these instruments and tedious analysis methodology.

In comparison with different instrumental techniques spectrophotometric technique has certain advantages. The analytes can be determined at micro level for the analysis of samples. This type of analysis has good sensitivity. It has comparatively simple instrumentation with easy handling set up. Also the initial expenditure for the instrumentation is minimum. The additional merit for the use of UV-visible spectrophotometer is that it can be used for the analysis in both ultraviolet and visible region along with high precision of results. Quantitative separation allied with spectrophotometric determination of selenium(IV) has been reported, based on various techniques like solvent extraction[14,15] micro extraction[16], cloud point extraction[17-19], flotation[20] and solid phase extraction.[21,22] Spectrophotometric determination of selenium (IV) has been studied recently by catalytic kinetic determination[23-30] and flow injection kinetic determination.[31] Also a huge literature is available for direct spectrophotometric determination of selenium (IV) using various reagents.[32-42] Extractive spectrophotometric determination of selenium (IV) has been reported using a sensitive reagent allied with direct extraction-spectrophotometric determination at quantitative level using selective solvent.[43-45]

The reported methods were sensitive with some merits but they are also associated with serious drawbacks viz: narrow beer's range, need of temperature controlled oxidation condition for catalytic and catalytic kinetic determination, laborious procedure, interferences from foreign ions, need of heating for complex formation, long time equilibration for quantitative extraction, less stability of the complex and rarely available reagent. Thus the detailed survey of literature explains that there is a wide range for the work on development of a sensitive methodology for the quantitative recovery of selenium (IV) with minimum drawbacks.

In present investigation, the solvent extraction and ultraviolet-spectrophotometric determination of selenium (IV) is studied at microgram level. The extraction reagent used in the present work is o-Methylphenyl thiourea (OMPT). It forms 1:2 (selenium (IV): OMPT) complex in 3.6 mol/L hydrochloric acid media. In earlier study OMPT has been studied in our laboratory for selective extraction spectrophotometric determination of platinum group metals.[46-51] Proposed method has merits compared to reported spectrophotometric

determination methods for selenium. Comparison of developed method with reported methods for spectrophotometric determination of selenium is given in Table 1.

Table 1. Comparison of present method with other spectrophotometric determination methods for selenium (IV)

Reagents	λ_{max} (nm)	Condition	Beer's Law validity range,	Solvent	Molar Absorptivity, (L $mol^{-1}cm^{-1}$)	M : L	Remark	Ref
Methylene Blue	668	2.5 ml conditioner, 0.5 ml Na_2S solution & 1.0 ml methylene blue	2.5 to 30 ppb	Distilled Water	NM	NM	Less Sensitive method 91.84% recovery percentage for water sample. More number of chemicals required in the recommended method. Zn^{2+} and Fe^{3+} interferes the determination. Developed method is not applied for real samples. Shaking time 10 min.	[23]
2,4-Dinitrophenyl hydrazine hydrochloride +_N-(1-naphthyl) ethylenediamine dihydrochloride	520	5 ml concentrated HCl &10 min standing	0.03 to 3.5 µg mL^{-1}	Distilled Water	3.10×10^4	NM	Standing time 10 min, higher acidic condition, 5 ml concentrated HCl	[33]
4-Aminoresorcinol hydrochloride	495	4 ml of concentrate H_2SO_4 and 10 min standing	0.07 to 2.5 µg mL^{-1}	Distilled Water	2.85×10^4	NM	Standing time 10 min, higher acidic condition, 4 ml of concentrate H_2SO_4 used for the determination	[33]
1,3,3-Trimethyl-2-[3-(1,3,3-trimethyl-1,3-	556	Sodium iodide media	0.01 to 3.84 mg dm^{-3}	toluene	2.4×10^5	NM	Lengthy procedure, standing time 5 min in dark for iodine liberation, iodine extraction by	[34]

dihydroindol-2ylidene)propenyl]-3H-indolium chloride							organic phase and ion associated species formation after 30 sec shaking	
Azure B	644	1.0 ml, 2 % KI & 1.0 ml, 2 mol/L HCl	2.0-10.0 µg ml^{-1}	Distilled Water	0.9473×10^5	NM	Narrow Beer's range, Only few diverse ions studied, Stoichiometry not determined, In recommended method time for yellow color development not mentioned	[36]
Starch and iodine	570	Iodide media	2 to 12 µg ml^{-1}	Distilled Water	1.40×10^4	NM	Narrow Beer's range, Less selective method	[39]
Leuco malachite green	615	pH 4.2 to 4.9, acetic acid buffer	0.04–0.4 µg ml^{-1}	Distilled Water	1.67×10^5	NM	Heating essential for color development	[40]
Thionin	600	Potassium iodide media	0.1 to 0.5 µg ml^{-1}	Distilled Water	7.33×10^4	NM	Standing needed for liberation of iodine. No Real sample analyzed	[41]
J ACID	520	pH 4.5, acetate buffer	0.03-0.3 µg mL^{-1}	Butanol	1.85×10^1	1:2	More number of chemicals required for the determination as per recommended method	[44]
o-Methylphenyl thiourea (OMPT)	335	HCl 3.6 mol L^{-1}	up to 100 µg mL^{-1}	Chloroform	4.066×10^2	1 : 2	Simple and precise, 5.0 min equilibration time, No heating required, large beer's range, low reagent concentration, complex stability > 48 h, applicable for analysis of real samples	PM

MATERIALS AND METHODS

Apparatus and reagents

A double beam UV-visible spectrophotometer (Systronics make model AU-2701) with matched 10 mm quartz cells was used for absorbance measurements. Contech make electronic balance model CA-123 was used for weighing purpose. Calibrated glassware were used and cleaned by soaking in dilute nitric acid followed by washing with soap water and rinsed two times with distilled water.

O-Methylphenyl thiourea (OMPT) was synthesized as per method reported by Frank and Smith.[52] A 0.015 mol L^{-1} solution was prepared by dissolving 0.125 g OMPT in 20 mL chloroform and diluted with chloroform in a 50 mL calibrated volumetric flask.

Metal solutions

A standard stock solution of selenium(IV) was prepared after dissolving analytical reagent grade 3.513 g of selenium dioxide in concentrated hydrochloric acid and distilled water and was made up to mark in a 250 mL volumetric flask with distilled water. This stock solution was standardized using standard method.[53] The working standard solution, 500 µg mL^{-1}, was prepared from standard stock solution.

Standard solutions of different metal ions used for interference study were prepared after dissolving exactly weighed quantities of their respective salts in distilled water or dilute hydrochloric acid. Standard solutions of anions were prepared after dissolving their respective alkaline metal salts in distilled water. Different synthetic mixtures were prepared by combining their definite compositions.

Recommended procedure

In a 25 mL volumetric flask a aliquot of solution containing 500 µg selenium(IV) and hydrochloric acid was added to make the solution 3.6 mol L^{-1} in hydrochloric acid after dilution with water. This mixture was equilibrated with 10 ml, 0.015 mol L^{-1} OMPT in chloroform for 5 min. After equilibration and separation of two phases the chloroform layer containing selenium (IV)-OMPT was transferred to a dry beaker and traces of water was removed by using 1.0 g anhydrous sodium sulphate. This solution was transferred to a 10 mL volumetric flask and made up to mark with chloroform. The selenium (IV)-OMPT complex was measured at λ_{max} 335 nm against reagent blank.

RESULTS AND DISCUSSION

Absorption spectra

Selenium (IV)-OMPT complex shows absorbance in the range of 310 nm to 450 nm. The wavelength of maximum absorbance (λ_{max}) is 335 nm. The reagent blank shows no absorption at the wavelength 335 nm (Fig.1). Physico-chemical characteristics of the selenium (IV)-OMPT complex are reported in Table 2.

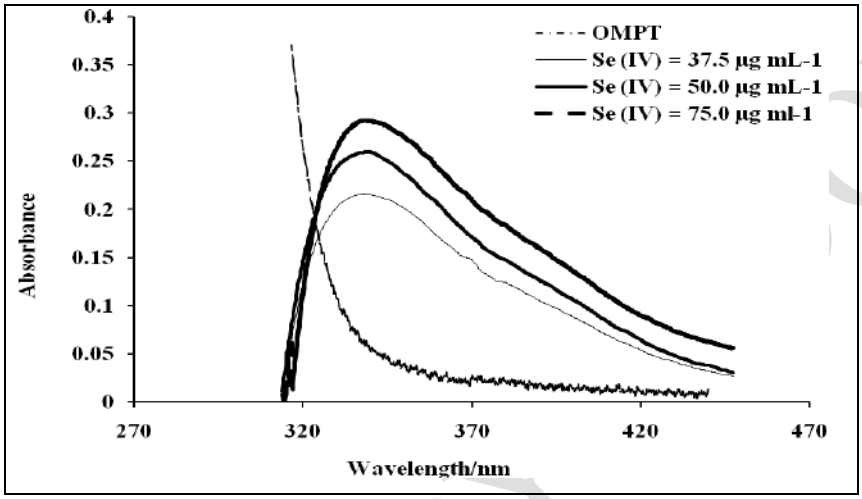

Fig. 1 Absorption spectra of selenium(iv)-OMPT complex

Selenium(IV): 37.5,50.0,75.0µg mL^{-1}; OMPT:0.015 mol L^{-1} ;HCl:3.6 mol L^{-1}

Table 2. Spectral and physico-chemical characteristics of selenium (IV) - OMPT complex study

Se(IV) = 500 µg, hydrochloric acid concentration = 3.6 mol/L,

OMPT = 0.015 mol/L, equilibration time = 5.0 min, λ_{max} = 335 nm.

Characteristics	Parameters
Concentration hydrochloric acid	3.6 mol/L
Concentration of reagent	0.015 mol/L
Equilibration time	5.0 min
Solvent for Extraction	chloroform
Wavelength of maximum absorption (λ_{max})	335 nm
Molar absorptivity	4.066×10^2 $Lmol^{-1}$ cm^{-1}
Sandell's sensitivity	0.1942 µg cm^{-2}
Conc. range as per Beer's law	up to 800.0 µg mL^{-1}
Ringbom's optimum range	26.0 to 70.0 µg mL^{-1}
Limit of detection	0.20 µg mL^{-1}
Relative standard deviation (R.S.D.)	0.44 %
Stoichiometry (se (IV):OMPT)	1:2
Stability of complex	> 48 h
Correlation coefficient	0.94

Effect of acid concentration

Selenium (IV)-OMPT complex formation takes place in hydrochloric acid media and it depends upon the hydrochloric acid concentration. The hydrochloric acid concentration was varied from 1.0 to 5.0 mol L^{-1} it shows complete complexation and maximum extraction at the concentration range 3.2 to 4.2 mol L^{-1} hydrochloric acid. The role of hydrochloric acid is distribution of metal in between organic and aqueous phase for maximum extraction and complexation. (Fig. 2).

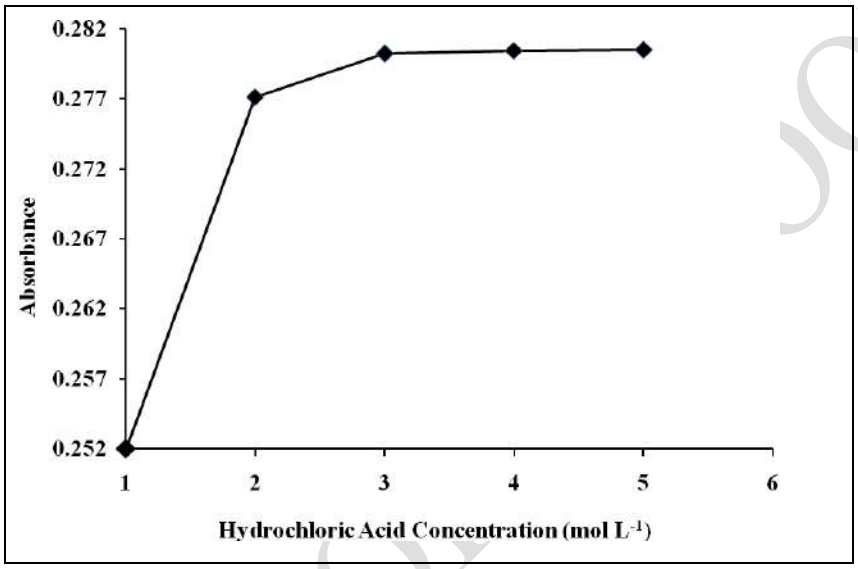

Fig. 2 Hydrochloric acid concentration for quantitative extraction

Selenium (IV): 500 µg mL^{-1}; OMPT:0.015 mol L^{-1},λ_{max}: 335 nm.

Effect of reagent concentration

Different molar concentrations of OMPT in chloroform in the range of 0.002 - 0.026 mol L^{-1} was used to a extract selenium (IV), 500 µg, and absorbance measurement was performed as per recommended procedure. A 0.015 mol L^{-1} reagent was sufficient for complete complex formation. All metal ions take part in complexation at 0.015 mol L^{-1} reagent concentration, therefore no metal ions remains further complexation so no adverse effect on excess of reagent. (Fig. 3).

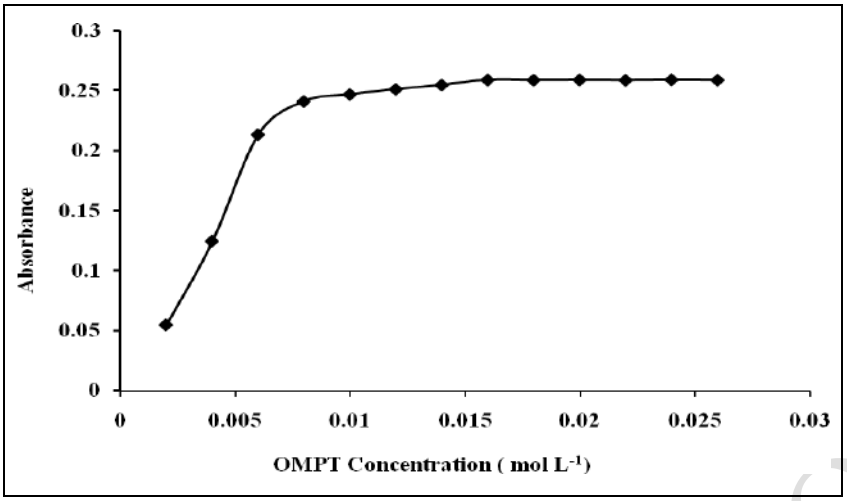

Fig. 3 Effect of reagent concentration

Selenium(IV): 500µg mL^{-1}; HCl:3.6 mol L^{-1},λ_{max}: 335 nm.

Effect of equilibration time

The study of change in absorbance with variation in equilibration time was carried out over 1.0 min to 30.0 min. It has been observed that extraction was completed in 5.0 min and there was no any adverse effect of prolonged equilibration on extraction of selenium (IV)-OMPT complex up to 30 min. Hence 5 min. equilibration time was fixed for further study.

The stability of complex was studied with the absorbance value measurement at regular time intervals of 1.0 h each at room temperature. The selenium (IV)-OMPT complex was stable for more than 48 h.

Analytical figures of merit

The selenium (IV)-OMPT complex obeys Beer's law over the concentration range up to 800.0 µg mL^{-1} (Fig. 4). Ringbom's plot has the range of linearity in the absorbance and concentration 26.0 to70.0 µg mL^{-1} with a slope value of 0.749 (Fig.5). The molar absorptivity and Sandell's sensitivity of the complex are 4.06 × 10^2 $Lmol^{-1}$ cm^{-1} and 0.1942 µg cm^{-2} respectively. The correlation coefficient values of selenium (IV)-OMPT complex with an independent variable as concentration in 0.9380 µg mL^{-1} and dependent variable as absorbance was 0.94. For selenium(IV)-OMPT complex, the graph of log $D_{[Se(IV)]}$ against log $C_{(OMPT)}$ at 2.6 mol L^{-1} and 3.6 mol L^{-1} hydrochloric acid concentration (Fig. 6), gave the slope values as 1.72 and 1.66 respectively. The composition of complex was also confirmed as 1:2 by mole ratio method (Fig. 7) and Job's continuous variation method (Fig. 8). Hence the probable composition of extracted species was calculated to be 1:2 selenium (IV)-OMPT.

Selenium(IV) was extracted from aqueous phase at 3.6 M hydrochloric acid with 10 mL of 0.15 M OMPT in chloroform. It was found that the extraction of selenium (IV) was quantitative, when aqueous to organic phase volume ratio was 1:1 to 2.5:1. This may simply be due to the unavailability of the reagent for metal extraction, so a crowding effect occurs at low phase ratio. Hence, the aqueous to organic volume ratio recommended in the procedures is 2.5:1.

To access reproducibility of the results and the accuracy of the method, absorbance measurements of ten identical solutions containing 500 µg selenium (IV) was carried out as per recommended method, average of these ten determinations and the relative standard deviation was determined. The relative standard deviation was 0.44%. The results indicate that the developed method was accurate and precise.

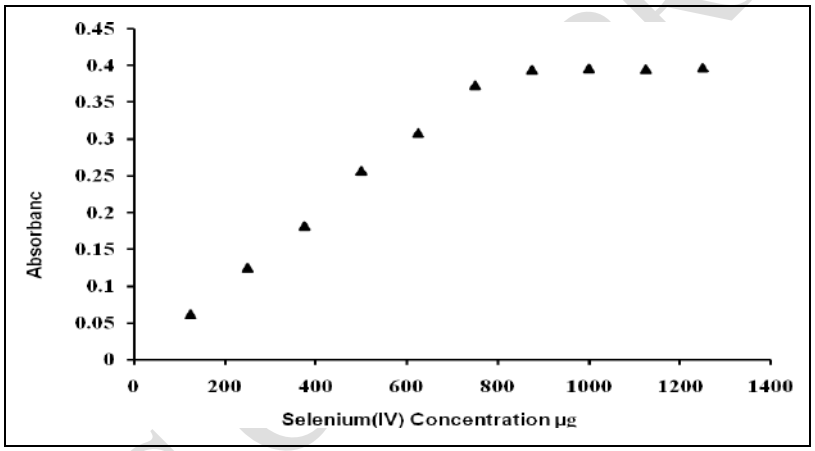

Fig. 4 Beer's law range for selenium(IV)-OMPT complex

OMPT: 0.015 mol L^{-1}, HCl:3.6 mol L^{-1}, λ_{max}: 335 nm.

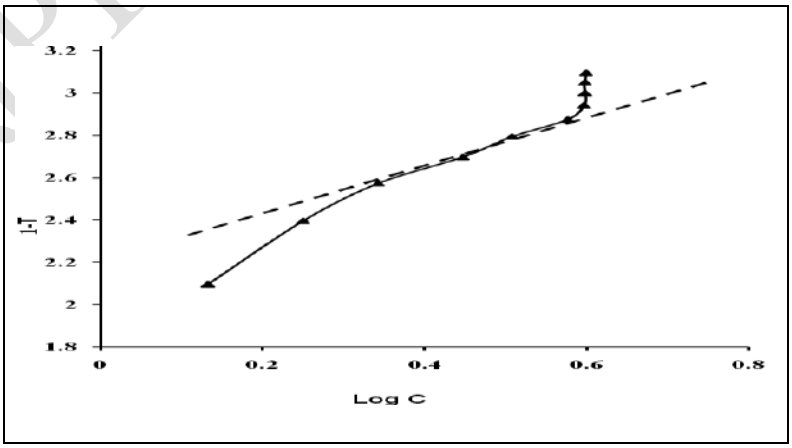

Fig. 5 Ringbom's plot for selenium(IV)-OMPT complex

OMPT: 0.015 mol L^{-1}, HCl:3.6 mol L^{-1}, λ_{max}: 335 nm.

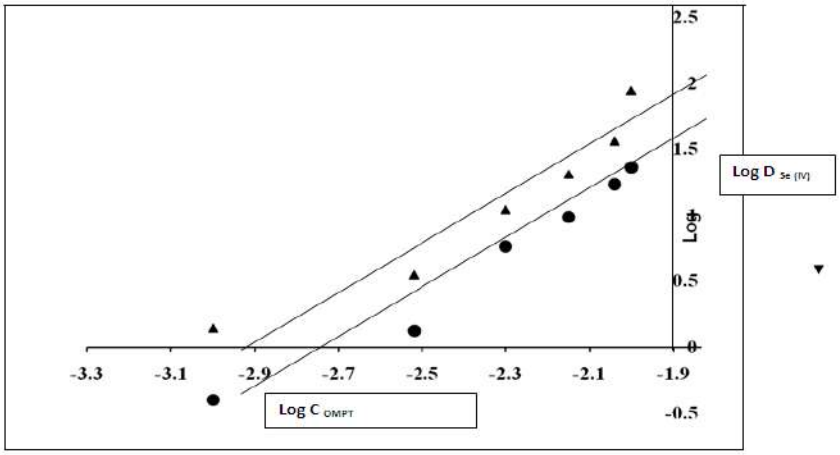

Fig. 6 Plot of log C $_{(OMPT)}$ vs. log D $_{[Se(IV)]}$

Selenium(IV): 500µg mL^{-1} OMPT: variable conc. mol L^{-1}, HCl: 2.6 mol L^{-1} and 3.6 mol L^{-1} , λ_{max}: 335 nm.

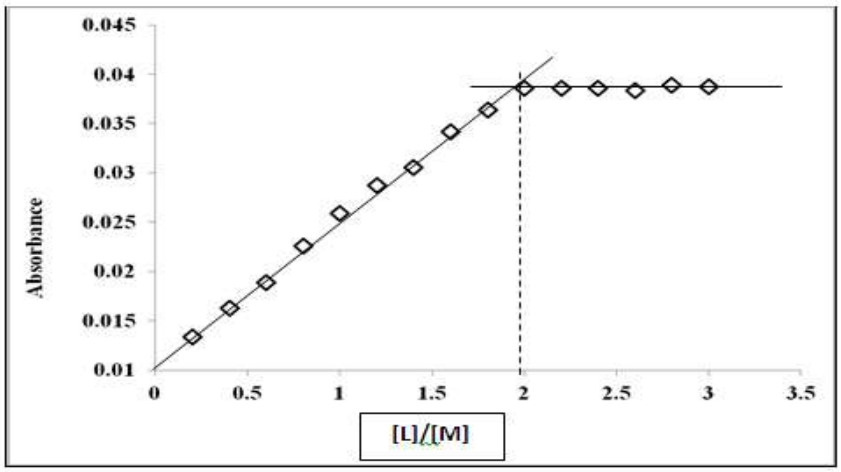

Fig. 7 Mole ratio method for selenium(IV)-OMPT complex

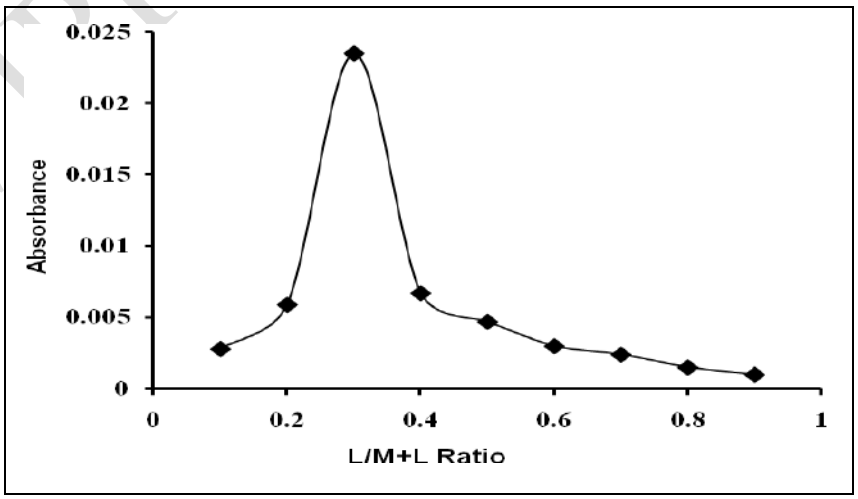

Fig. 8 Job's variation method for selenium (IV)-OMPT complex

Interference study

By testing different foreign ions the selectivity of method was checked. The tolerance limit was fixed for the ions which do not cause deviation more than ± 2% in the absorbance value for selenium (IV)-OMPT complex. The suitable masking agents are used to remove interference due to cations. Maximum limit of cations added was 50 mg and the maximum limit of anions added was 100 mg. Determination of selenium (IV) was precise and highly selective with the tolerance limit in the range of milligrams in presence of many added cations and anions. The interference due to Fe(III),Al(III), La(III), Ti(III), Mo(VI), In (III), Ce(IV) and Ba(II) was removed by masking with EDTA (Table 3).

Table 3. Interfering ions study

Se(IV) = 500 µg, hydrochloric acid concentration = 3.6 mol/L,OMPT = 0.015 mol/L, equilibration time = 5.0 min, λ_{max} = 335 nm.

Foreign Ions	Added as	Tolerance limit (mg)[a]	Foreign Ions	Added as	Tolerance limit (mg)[a]
Mn(II)	$MnCl_2.6H_2O$	1.0	In(III)[b]	$InCl_3.4H_2O$	0.50
Cd(II)	$CdCl_2.2H_2O$	10.0	Rh(III)	$RhCl_3$	0.40
Fe(III)[b]	$(NH_4)Fe(SO_4)_2.12H_2O$	0.025	Ru(III)	$RuCl_3.6H_2O$	0.16
Hg(II)	$HgCl_2$	50.0	Ir(III)	$IrCl_3$	0.63
Bi(III)	$BiCl_3$	15.0	Os(IV)	OsO_4	1.8
Ni(II)	$NiCl_2.6H_2O$	0.5	Ce(IV)[b]	$Ce(SO_4)_2.4H_2O$	0.10
Cu(II)	$CuSO_4.5H_2O$	1.0	Pb(II)	$PbCl_2$	0.05
Al(III)[b]	$AlCl_3.6H_2O$	1.0	V(V)	V_2O_5	5.0
Cr(III)	$CrCl_3$	0.5	Co(II)	$CoCl_2.6H_2O$	1.0
Zn(II)	$ZnSO_4.7H_2O$	1.0	Ba(II)[b]	$BaCl_2.6H_2O$	2.5
La(III)[b]	$LaCl_3.7\ H_2O$	0.45	Ca(II)	$CaCl_2.2H_2O$	50.0
Li(I)	LiCl	50.0	Sr(III)	$SrCl_3.6H_2O$	10.0
Ti(III)[b]	$(Ti_2SO_4)_3$	0.15	Tl(III)	Tl_2O_3	1.0
Mg(II)	$MgCl_2.6H_2O$	0.5	Fluoride	NaF	100
Sn(II)	$SnCl_2.2H_2O$	1.0	Sulphate	K_2SO_4	11.4
Ga(III)	$GaCl_3$	0.25	Malonate	$CH_2(COONa)_2$	75.0
Au(III)	$HAuClO_4.H_2O$	2.20	E.D.T.A.	Na_2EDTA	100
Mo(VI)[b]	$(NH_4)_5MO_7.2H_2O$	0.25	Tartarate	$(CHOH.H_2O)$	100
As(III)	As_2O_3	1.0	Citrate	$(C_6H_8O_7.H_2O)$	50.0
Zr(IV)	$ZroCl_28H_2O$	12.5	Succinate	$(CH_3COONa)_2.6H_2O$	50.0
Sb(III)	Sb_2O_3	2.5	Phosphate	(Na_3PO_4)	25.0
Be(II)	$BeSO_4.4H_2O$	5.0	Acetate	$CH_3COONa.3H_2O$	100.0

a=average of six determinations(n =6), b=masked with 100 mg E.D.T.A.

APPLICATIONS

Separation and determination of selenium (IV) from Pharmaceutical samples

The proposed method was applied for the separation and determination of selenium (IV) from pharmaceutical samples. The pharmaceutical samples (5 to 10 tablets or capsules) were dissolved in water and the content was evaporated to moist dryness. Organic matter present was destroyed after treatment with 5 mL, 60% perchloric acid, the content was cooled and water was added. Mixture containing selenium (IV) in solution was evaporated to moist dryness. The residue was cooled and the content was made up to required volume with water. Aliquot of the diluted solution containing selenium (IV) was analyzed as per recommended method. Precise results were obtained and the data of analysis for different pharmaceutical samples is reported in Table 4.

Table 4. Analysis of pharmaceutical samples: Se (IV) = 100 µg, 60 µg, 33 µg; HCl = 3.6 mol/L, OMPT = 0.015 mol/L, equilibration time = 5.0 min, λ_{max} = 335 nm.

Sample	Composition	Certified value of Se(IV) in µg	Amount of Se(IV)[a] found in µg	Recovery %	R.S.D. %
Menopace ISO	10 mg - Nicotinamide, 75 mg - Vit-C, 20 mg - Vit-E, 5 mg - Iron, 225 µg - Iodine, 100 µg - Selenium	100	99.87	99.87	0.36
Cardio-Vit-plus	3 mg - Pyridoxine hydrochloride, 100 mg - Nicotinamide, 15 µg - Cyanocobalmin, 5 mg - Folic acid, 1.250 µg - Chromium picolinate, 100 µg - Selenium, 61.8 mg - Zinc sulphate monohydrate	60.0	58.60	97.66	0.05
Betared	100 mg - Vit-C, 25 IU - Vit-E, 1.5 mg - manganese, 10.33 mg - Beta carotene, 75 µg - Selenium	60.0	59.0	98.33	0.05
Casera	IU - Vit-A 2500, 100 mg - Vit-C, 25 IU - Alphatocophenyl acetate, 6 mg - Beta carotene, 55 µg - Selenium, 7.5 mg - Zinc, 25 µg - Molybdenum	33.0	32.64	98.91	0.10

a=average of six determinations (n =6)

Separation and determination of selenium (IV) from vegetable samples

Selenium (IV) content in the environmental sample (cabbage) was determined as per recommended method. A 5.0 g cabbage sample was processed like cutting, chopping and crushing. Water was added to this crushed sample and the content was mixed properly. The mixture was heated to moist dryness. The organic matter was decomposed after addition of nitric acid followed by heating up to moist dryness. After cooling, the residue was dissolved in water and the content was diluted to 50 ml in a volumetric flask. A 3.0 mL aliquot of this sample was analyzed using recommended method for the separation and determination of selenium (IV). The number of repetitions (n) was 6. Results are reported in Table 5.

Table 5. Analysis of environmental sample (cabbage): Se (IV) = 7.165 µg, hydrochloric acid conc. = 3.6 mol/L, OMPT = 0.015 mol/L, equilibration time = 5.0 min, λ_{max} = 335 nm.

Cabbage sample	Selenium(IV) content in µg	Recovery [a] (%)	RSD (%)
5.0 gm	7.165	99.87	0.23

a=average of six determinations (n =6)

Separation and determination of selenium (IV) from binary synthetic mixtures

Binary synthetic mixtures were analyzed by reported method for separation and determination of selenium(IV) content in presence of different associated metal ions viz: Ni(II), V(V), Mg(III), Ca(II), Co(II) and Mn(II) (Table 6). The number of repetitions (n) was 6. After applying the recommended method, selenium (IV) was separated from added associated metal ions (left behind in aqueous phase). The selenium (IV)-OMPT complex extracted in chloroform was measured at 335 nm. After quantitative separation of selenium(IV) the aqueous phase containing added associated metal ions was evaporated to moist dryness, followed by addition of 3.0 mL concentrated hydrochloric acid and again evaporated to moist dryness. The residue containing added associated metal ions was cooled, dissolved in water and the metal ions were determined by reported methods spectrophotometrically[54] Table 6.

Table 6. Separation of selenium (IV) from binary synthetic mixtures: Se(IV) = 500 µg, hydrochloric acid concentration = 3.6 mol/L, OMPT = 0.015 mol/L, equilibration time = 5.0 min, λ_{max} = 335 nm.

Metal ions	Amount taken (µg)	Recovery [a] (%)	RSD (%)
Se(IV)	500	99.6	0.40
Ni(II)	100	99.5	0.50
Se(IV)	500	99.5	0.33
V(V)	125	99.5	0.91
Se(IV)	500	99.5	0.59
Mg(III)	50	99.6	0.60

a=average of six determinations (n =6)

Separation and determination of selenium (IV) from ternary synthetic mixtures

To a 10 mL volumetric flask containing 500 µg selenium (IV), other associated metal ions were added in varying proportions giving ternary mixtures. Hydrochloric acid was added to this ternary synthetic mixtures and the content was diluted up to mark giving the mixture at 3.6 mol/L hydrochloric acid. Selenium (IV) was extracted from mixture as selenium (IV)-OMPT complex and measured at 335 nm. From absorbance measurement selenium (IV) content was determined. Results reported in Table 7. Ternary mixture analysis was performed with the number of repetitions six times (n=6).

Table 7. Separation of selenium (IV) from ternary synthetic mixtures: Se (IV) = 500 µg, hydrochloric acid concentration = 3.6 mol/L, OMPT = 0.015 mol/L, equilibration time = 5.0 min, λ_{max} = 335 nm.

Composition (µg)	Recovery [a] (%)	RSD (%)
Se(IV) 500; Ca(II) 50; Ni(II)50	99.6	0.48
Se(IV) 500; Co(II)50; Ni(VI)25	99.6	0.25
Se(IV) 500; Ca(VI) 25; Co(II)25	96.8	0.41

a=average of six determinations(n =6)

CONCLUSION

o-Methylphenyl thiourea (OMPT) is a potent analytical reagent for separation and spectrophotometric determination of selenium (IV). Proposed method has following merits:

(i) OMPT is sensitive and selective reagent for selenium (IV)

(ii) The selenium (IV)-OMPT complex is highly stable with no change in absorbance value for more than 48 h.

(iii) The developed method has wide Beer's range up to 800.0 µg mL^{-1} and it has lower limit of detection (0.20 µg mL^{-1}).

(iv) The direct determination of selenium (IV) is possible with no need of either highly controlled conditions or no need of heating.

(v) Quantitative separation is achieved with a simple apparatus separatory funnel.

(vi) The clear phase separation allied with direct spectrophotometric determination is possible.

(vii) The points expressing sensitivity of method are like relative standard deviation (0.44%), Sandell's sensitivity (0.1942 µg cm^{-2}) and correlation coefficient (0.94).

(viii) Method permits various applications viz: analysis of binary, ternary mixture, analysis of pharmaceutical and vegetable samples.

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Solvent Extraction, Spectrophotometric Determination of Antimony(III) from Real Samples and Synthetic Mixtures Using *O*-Methylphenyl Thiourea as a Sensitive Reagent

Shashikant R. Kuchekar, Shivaji D. Pulate, Vishwas B. Gaikwad

Abstract:-A simple and selective method is developed for solvent extraction, spectrophotometric determination of antimony(III) using *O*-MethylphenylThiourea (OMPT) as a sensitive chromogenic chelating agent. The basis of proposed method is formation of antimony(III)-OMPT complex, was extracted with 0.0025 M OMPT in chloroform from aqueous solution of antimony(III) in 1.0 M perchloric acid. The absorbance of this complex was measured at 297 nm against reagent blank. Beer's law was obeyed up to 15µg mL^{-1} of antimony(III). The Molar absorptivity and Sandell's sensitivity of the antimony(III)-OMPT complex in chloroform are 1.66730×10^3 L mol^{-1} cm^{-1} and 0.0730282 µg cm^{-2} respectively. The Stiochiometry of antimony(III)-OMPT complex was established from slope ratio method, mole ratio method and Job's continuous variation method was 1:2. The complex was stable for more than 48 h. The interfering effect of various foreign ions was studied and suitable masking agents are used wherever necessary to enhance selectivity of the method. The proposed method is successfully applied for determination of antimony(III) from real sample and synthetic mixtures. Repetition of the method was checked by finding relative standard deviation (R.S.D.) for 10 determinations which was 0.42%.

Keywords - Antimony (III), *O*-MethylphenylThiourea, Spectrophotometry.

Introduction

The abundance of antimony in the earth's crust is 0.20 ppm. Antimony is used in lead alloy, storage battery, grids, rubber, matches, ceramics, paints and textile industries[1]. It is well known that the toxicity and physiological behavior of antimony depends on its oxidation state.

Antimony is a potentially important element for plants; it not shows identified essential function in animals. The trivalent antimonials are more toxic than the pentavalentantimonials, they are used for 283 therapy. In other metal such as lead and zinc mixed antimony frequently to form mixtures of metals called alloys. In lead storage batteries, solder, ammunition and pewter these alloy are used [2]. Antimony possibly originates in the environment as a result of various anthropogenic behaviors. Antimony and its compounds shows industrially significant role in manufacturing of alloys, paper, plastics, paints, textiles, glass, clay products and rubber. Highly pure antimony has been worn in the construction of the semiconductor compound, indium antimonide also in the formulation of bismuth telluride type compound used for thermoelectric applications.

In the production of glass and ceramics as well as fire retardants antimony containing compounds is used. Street traffic is also an important source as it is used in brake linings and tyre vulcanization that require antimony containing additives. Antimony is harm on human being health seriously; micro quantity of antimony will inspire respiratory zone, mucous membrane of alimentary canal and skin, still lead to pulmonary edema. Antimony have conventional relatively little concentration since it is unnecessary for life and because it's content in most matrices is very low[3]. Elementalantimony is more toxic than its salts, in addition to commonly trivalent antimony compounds are ten times higher toxic than pentavalent antimony species , it might cause lung cancer[4]. The highly toxic gas stibine is capable of causing mutually serious injury to the central nervous system and hemolysis. Inductively coupled plasma mass spectrophotometer and atomic absorption spectrometry [5]-[6], plasma emission spectroscopy [7], Neutron activation analysis[8]and chromatography techniques [9]-[10] are used in the antimony speciation. These techniques are comparatively expensive, not adequately selective and simply adapted to routine analyses. It requires costly maintenance and skilled hands for process. Due to simplicity, spectrophotometry technique is most widespread method of analysis and also used in determination of antimony. The separation and determination of antimony(III) is of analytical importance. For the extraction of antimony(III) high molecular weight amines (HMWA) are used. The bromo complex of antimony(III) was extracted with 3% trioctylamine in isobutyl methyl ketone (MIBK) and determined by the AAS method. Dyes are used for spectrophotometric determination of antimony through malachite green [11]. Antimony is determined spectrophotometrically with vanallylfluorone in presence of poly vinyl alcohol in acidic media. Tin, thorium, bismuth and thiosulphate interfere seriously. By extraction of reduced molybdoantimonyl phosphoric acid with butyl acetate antimony can be determined colorimetrically [12]. Different micellar media had different effect on adsorption spectra of complexes of bromopyrogallol with antimony (III and V). A method for quantitative separation of antimony (III) by absorption on polyether based polyurethane foam and its spectrophotometric determination has been described. The

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H-point standard addition method [13] was applied to kinetics data for simultaneous determination of antimony(IV and III) and also selectively determines antimony(V) in the presence of antimony(III). Quantitative extraction of antimony(III) was observed in 0.1–1.0 mol L^{-1} sulfuric acid and 0.1–2.0 mol L^{-1} hydrochloric acid with 8.5-10, 2 mol L^{-1}cyanex 302 in toluene [14]. This method was successfully applied to a real sample. An appraisal of the extractants used for the recovery of antimony from copper electrolyte has been presented. The extractants used for this process were TBP, an ester of phosphoric acid, mono-(2-ethylhexyl)) phosphoric acid, D_2EHPA acid and mono-(iso-octadecyl) phosphoric acid, DS-5834, esters of alkylphosphnic acids, trialkylphosphine oxide, Cyanex 923 and 301, hydroxamic acids, LIX 1104, alcohols (2-ethylhexanol and others), hydrophobic diols and alkyl polyphenols[15].2-Ethylhexyl-phosphonic acid mono-2-ethylhexyl ester was used as an extractant for antimony(III) from 0.1 M hydrochloric acid media [16]. A new selective and sensitive on-site spectrophotometric method for determination of antimony at trace level in water, soil and dust sample of central India has been established. It is based on the color reaction of antimony(III) with ions in presence of a cationic surfactant cetylpyridinium chloride (CPC) in acidic media, and subsequent extraction of complexes with N-phenyl benzimidoyalthiourea (PBTIU) [17] in to chloroform to give a yellow colored complex. N-n-octylaniline could also be used for the extraction separation of antimony(III) from chloride media. This method is rapid and provides separation of antimony(III) from tellurium(IV), selenium(IV), lead(II), bis-muth(IV), tin(IV), germanium(IV), copper(II), gold(III), iron(III) and zinc [18] .

In our laboratory we have developed extraction and spectrophotometric determination of rhodium(III) [19], ruthenium(III) [20], iridium(III) [21], palladium(II) [22] and osmium(IV) [23] using *o*-methylphenylthiourea (OMPT). In the extension of our work we have developed extraction spectrophotometric determination methods for cerium(IV) [24] palladium(II) [25], osmium(IV) and ruthenium(III) [26] with *o*-methoxyphenyl thiourea (OMePT). Current study reports the analytical applications of *o*-methylphenylthiourea (OMPT) for spectrophotometric determination of antimony(III).

Experimental

Instrumentation

Absorptionmeasurements were made with a Systronics make digital spectrophotometer model AU-2701 using 1 cm quartz cells. Contech make electronic balance model CA-123 was used for weighing. Glassware's were cleaned by soaking in acidified solution of potassium dichromate followed by washing with soap water and rinsed two times with distilled water.

Reagents

A stock solution of antimony(III) was prepared by dissolving 0.468gm of antimony trichloride in concentrated hydrochloric acid and diluted up to mark in 250 mL standard volumetric flask with water and was standardized by reported method [27].

O-Methylphenylthiourea (OMPT) was synthesized as per method reported by frank and smith [28]. A 0.0025 mol L^{-1} solution was prepared by dissolving 0.042 g OMPT in 50 mL chloroform and diluted up to mark with chloroform in a 100 mL calibrated volumetric flask.

Foreign ion (cations) solutions required for interference ions study were prepared by dissolving weighed quantities of their salts in water or dilute hydrochloric acid and were made up to mark in a calibrated volumetric flask. Solutions of anions were prepared after dissolving their respective alkaline metal salts in distilled water and were made up to mark in a calibrated volumetric flask. Synthetic mixtures containing antimony(III) and other commonly associated metal ions were prepared by combining definite compositions. Distilled water was used through the work wherever required.

Recommended procedure

Aaliquot of solution containing 15 µg of antimony(III) and perchloric acid was transferred in a 25 mL calibrated volumetric flask and diluted up to mark with water giving the solution 1.0 M in perchloric acid. This solution was equilibrated with 10 ml, 0.025 M OMPT in chloroform for 10 min. The two phases were allowed to separate and the chloroform layer was dried over 1.0 g anhydrous sodium sulphate, transferred in to 10 mL calibrated volumetric flask and made up to mark with chloroform. The absorbance of antimony(III)-OMPT complex was measured at 297 nm against reagent blank prepared in similar manner.

Absorption Spectra

The absorption spectra of antimony (III)-OMPT complex shows a maximum absorbance at 297 nm and the reagent blank have no absorbance at the maximum absorbance wavelength of antimony(III)-OMPT complex (Fig. 1).

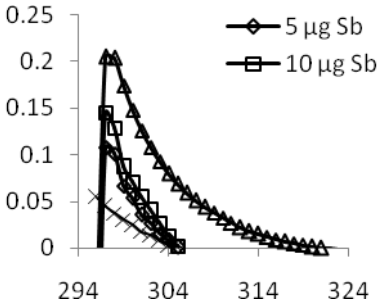

Fig .1- Absorption spectra of antimony (III)-OMPT complex

Spectral characteristics

Antimony(III) forms 1:2 (antimony(III)):OMPT) complex, 1.0 mol L^{-1} perchloric acid media, further extracted into chloroform. This complex shows maximum absorption at 297 nm and was stable for more than 48 h. The optimum conditions for the extraction of antimony(III) were established after studying the perchloric acid concentration, OMPT concentration, extraction solvent, equilibration time and interference of various foreign ions. The spectral and physico-chemical characteristic along with the precision data is reported in Table I.

Effect of Perchloric acid concentration

Quantitative Extraction of antimony(III)-OMPT complex occurs from Perchloric acid media when the reagent is present in chloroform and this extraction depends upon the perchloric acid concentration. The complex formation was studied from 0.46 to 1.30 M perchloric acid concentration, shows maximum absorbance in the range of 1.0 to 1.12 M (Fig. 2).Hence all subsequent studies were performed at 1.0M perchloric acid concentration.

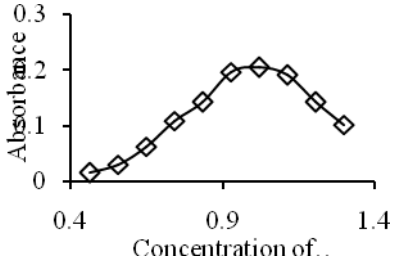

Fig. 2. Effect of concentration of Perchloric acid

Effect of OMPT concentration

Concentration of OMPT in chloroform was varied from 0.0010 M to 0.0040 M and the absorbance measurements were performed as per recommended procedure. The absorbance value increases up to 0.0025 M, OMPT in chloroform. Thus the reagent concentration of 0.0025M was sufficient for maximum absorbance (Fig. 3).

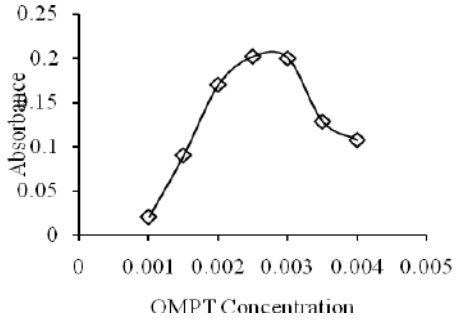

Fig. 3- Effect of OMPT on complex formation

Results and Discussion

Beer's law and sensitivity

Beer's law was obeyed over the concentration range up to 15 µg ml^{-1}as shown in (fig. 4). Ringbom's plot was sigmoid shape with a linear segment at intermediate absorbance values of 7.5 to 15 µg ml^{-1} and with a slope value of 0.3758 (Fig. 5). The sensitivity of method as defined by sandell was 0.073 µg cm^{-2} and the molar absorptivity was 1.66730×10^3 L $mol^{-1}cm^{-1}$. The correlation coefficient values of antimony(III)-OMPT complex with an independent variable as concentration in µg ml^{-1} and dependent variable as absorbance was found to be 0.97. The relative standard deviation calculated from 10 determinations of a solution containing 15 µg antimony(III) was 0.42%.

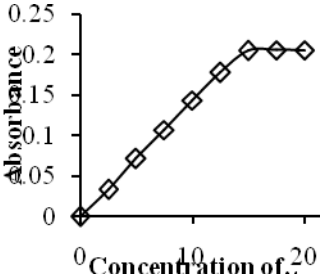

Fig. 4- Study of Beer's law validity

TABLE 1.SPECTRAL AND PHYSICO-CHEMICAL CHARACTERISTICS OF ANTIMONY(III) - OMPT COMPLEX

Characteristics	Parameters
Acid concentration	1.0 mol L^{-1}
Reagent concentration	0.0025 mol L^{-1}
Equilibration time	10.0 min
Extraction solvent	chloroform
λ_{max}	297 nm
Molar absorptivity	1.66730×10^3 L mol^{-1} cm^{-1}
Sandell's sensitivity	0.0730282 µg cm^{-2}
Beer's law range	up to 15 µg ml^{-1}
Ringbom's optimum range	7.5 to 15 µg ml^{-1}
Limit of detection	0.30 µg mL^{-1}
Relative standard deviation	0.42%
Stiochiometry	1:2 (antimony(III):OMPT)
Stability of complex	> 48 h
Correlation coefficient	0.97

TABLE 2. INFLUENCE OF FOREIGN IONS ON THE EXTRACTION OF THE ANTIMONY(III)-OMPT COMPLEX

Foreign Ions	Added as	Tolerance limit mg
Mn(II) [a]	$MnCl_2.6H_2O$	1.0
Cd(II) [a]	$CdCl_2.2H_2O$	0.05
Fe(III) [a]	$(NH_4)Fe(SO_4)_2.12H_2O$	0.05
Hg(II)	$HgCl_2$	0.25
Bi(III)[a]	$BiCl_3$	0.02
Ni(II)	$NiCl_2.6H_2O$	1.00
Cu(II)	$CuSO_4.5H_2O$	0.10
Al(III) [a]	$AlCl_3.6H_2O$	0.10
Cr(III) [b]	$CrCl_3$	0.01
Zn(II)	$ZnSO_4.7H_2O$	0.01
La(III)	$LaCl_3.7\ H_2O$	0.75
Li(I)	LiCl	0.50
Ti(III)	$(Ti_2SO_4)_3$	0.50
Mg(II)	$MgCl_2.6H_2O$	0.025
Sn(II)	$SnCl_2.2H_2O$	0.10
Ga(III)	$GaCl_3$	0.10
Au(III) [a]	$HAuClO_4.H_2O$	0.005
Mo(VI)	$(NH_4)_5MO_7.2H_2O$	1.00
W(VI)	$Na_2WO_42H_2O$	0.50
Zr(IV)	$ZrOCl_28H_2O$	0.05
U (VI)[b]	$Uo_2(CH_3COO)_2$	0.025
In(III)	$InCl_3.4H_2O$	0.05
Rh(III)	$RhCl_3$	0.03
Ru(III)	$RuCl_3.6H_2O$	0.03
Ir(III)	$IrCl_3$	0.25
Os(IV)	OsO_4	0.3
Ce(IV)	$Ce(SO_4)_2.4H_2O$	0.10
Pb(II)[b]	$PbCl_2$	0.05
V(V)	V_2O_5	0.25
Co(II)[a]	$CoCl_2.6H_2O$	1.00
Ba(II)[b]	$BaCl_2.6H_2O$	0.25
Ca(II)	$CaCl_2.2H_2O$	1.00
Sr(III)	$SrCl_3.6H_2O$	0.10
Tl(III)	Tl_2O_3	0.04
Se(IV)	SeO_2	0.10
Pt(IV)	$H_2PtCl_6.H_2O$	0.03
Fluoride	NaF	100
Sulphate	K_2SO_4	100
Malonate	$CH_2(COONa)_2$	100
E.D.T.A.	Na_2EDTA	100
Tartarate	$(CHOH.\ H_2O)$	100
Citrate	$(C_6H_8O_7.H_2O)$	100
Succinate	$(CH_3COONa)_2.6H_2O$	1.00
Acetate	$(CH_3COONa).3H_2O$	25.0

a-Masked with EDTA, b-Masked with Tartarate

Effect of foreign ions

The selectivity of proposed method was checked for

the determination of antimony(III)(15 µg) in presence of high concentration of various foreign ions . The tolerance limit was fixed for the ions which do not cause deviation more than ±2% in the absorbance of the antimony(III)-OMPT complex ,the determination proves the investigated method is highly selective (Table II).

Effect of equilibration time and stability of complex

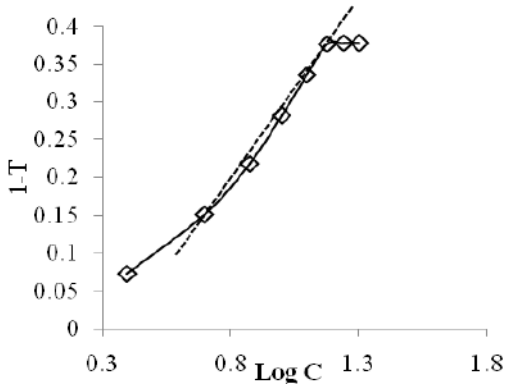

Fig. 5- Ringbom's plot for Sb(III)-OMPT

Equilibration time plays an important role in quantitative extraction. The absorbance values increases with equilibration time from 1.0 min to 10.0 min and above 10.0 min absorbance value was constant in the range studied 10.0 to 15.0 min. Hence, optimum equilibration time of 10.0 min was fixed for quantitative extraction of antimony(III). The stability of antimony(III)-OMPT complex was studied at room temperature by measuring the absorption at regular time intervals of 1.0 h each, shows the absorbance value of complex was stable for more than 48 h.

Stoichiometry of the complex

The composition of antimony(III):OMPT complex as ascertained using slope ratio method in which the graph of log $D_{[sb]}$against log $C_{(OMPT)}$ at 0. 5 and 1.0 M perchloric acid concentration was plotted(Fig. 6). The plots were linear havingslope values as 1.93 and 2.0 respectively. Hence the probable composition of extracted species was calculated to be 1:2 (antimony(III):OMPT). The composition of complex was also confirmed by mole ratio method (Fig.7).and job's continuous variation method (Fig.8). OMPT act as a multidentate ligand, sulphur from thio group (-C = S) and nitrogen from amine group ($-NH_2$) coordinate with antimony(III) to form a 1:2 (antimony(III):OMPT) complex.

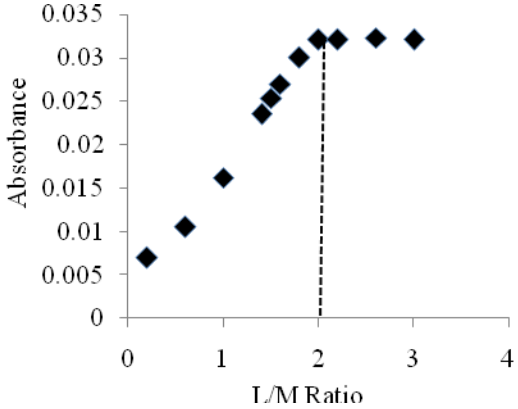

Fig. 7-Plot for Mole ratio method

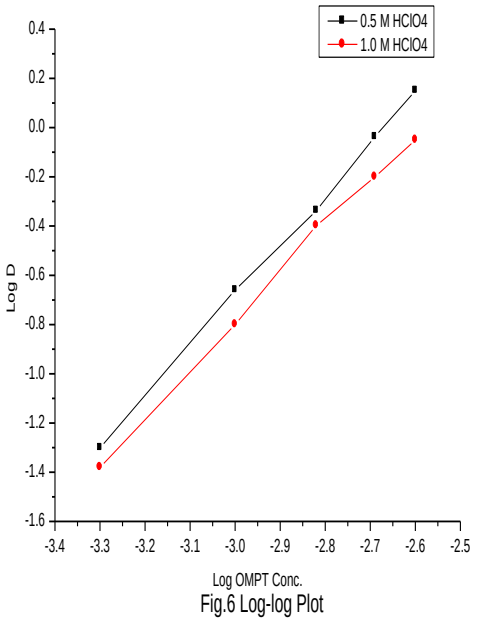

Fig.6 Log-log Plot

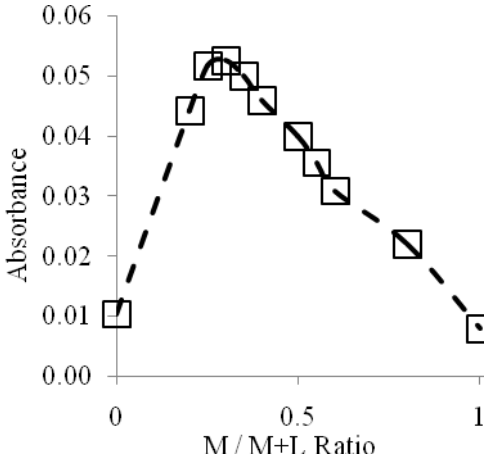

Fig. 8. Plot for Job's continuous variation method

TABLE 3.SEPARATION OF ANTIMONY (III) FROM BINARY SYNTHETIC MIXTURES

Metal ions	Amount taken (µg)	Recovery [a] (%)	RSD (%)	Chromogenic Ligand
Sb(III)	15	98.7	0.39	OMPT
Ni(II)	100	99.3	0.44	DMG
Sb(III)	15	95.4	0.09	OMPT
V(V)	125	99.4	0.36	Tugastate
Sb(III)	15	98.3	0.30	OMPT
Mg(II)	20	99.5	0.43	Titan yellow
Sb(III)	15	94.4	0.08	OMPT
Mo(VI)	20	99.7	0.06	Thiocynate
Sb(III)	15	99.1	0.10	OMPT
W(V)	40	99.4	0.36	Thiocynate

Applications

Separation and determination of antimony(III) from binary synthetic mixtures

The proposed method was applied for separation and

determination of antimony(III) from associated metal ions Viz : Ni(II), V(V), Mg(II), Mo(VI), W(V). Antimony(III)-OMPT complex formation was carried out in presence of these associated metal ions in aqueous phase as per recommended procedure. Further this complex was quantitatively separated from associated metal ions after extraction. After quantitative extraction of antimony(III) the aqueous phase was evaporated to moist dryness followed by 3.0 mL concentrated hydrochloric acid. The residue obtained was cooled, dissolved in water and the added metal ions were determined by reported methods[29].

Separation of antimony(III) from ternary synthetic mixtures

Ternary synthetic mixtures with varying compositions of associated metal ions and fixed antimony(III) (15 µg) were transferred in to 25 mL calibrated volumetric flask followed by addition of OMPT, perchloric acid and distilled water. antimony(III) was separated quantitatively using recommended method and the results were in good agreement with the amount of antimony(III) present.

TABLE 4. SEPARATION OF ANTIMONY(III) FROM TERNARY SYNTHETIC MIXTURES

Composition (µg)	Recovery [a] (%)	RSD (%)
Sb(III) 15; V(V) 125; Mn(II) 10	99.6	0.13
Sb(III) 15; Tl(III) 20; Zn(II) 10	99.7	0.27
Sb(III) 15; Sn(II) 25; Ca(II) 25	99.7	0.08
Sb(III) 15; W(VI) 50; Mo(VI)50	97.9	0.33
Sb(III) 15; Cu(II) 20 ; Ni(II) 20	93.9	0.15

[a]Recovery of antimony(III) for six determinations

Analysis of Real sample:

A known weight (1 gm) of ELSOLD (BLEIWERK GOSLAR)alloy was dissolved in a mixture of 9 ml of conc. H_2SO_4 and 50ml of distilled water. After initial reaction was finished, the solution was heated with 5 ml portion of Conc. HNO_3 untilled white fumes observedboil to dissolve the soluble matter and finally filter to remove metastanic acid. The filtratewas diluted to an appropriate volume. An amount of antimony(III) presentaliquot of thissolution was analyzed by recommended method (Table V).

TABLE 5. DETERMINATION OF ANTIMONY (III) FROM ALLOY SAMPLE

Weight of alloy sample mg	antimony present mg	antimony content as per recommended method mg	% antimony
1000	0.544	0.5415	99.54

Conclusion

Synthetic Applications

The validity of the method was verified by applying the proposed method for extraction of antimony(III) from synthetic mixtures corresponding to alloys. The compositions were prepared in laboratory for Antimony-Calcium Alloy, Antimony-Copper Alloy, Antimony-Zinc Alloy, Antimony-Manganese Alloy and Antimony-Magnesium Alloy (Table VI). The antimony(III) was separated and determined as per recommended method. The results obtained were in good agreement with the amount of antimony (III) added

TABLE 6.DETERMINATION OF ANTIMONY (III) FROM SYNTHETIC ALLOY SAMPLE

Sr. No.	Compositon of Alloy	Amount taken	Amount found	RSD %	Recovery %
1	Antimony-Calcium Alloy (Sb 92 % + Ca 8 %)	15 µg	14.89 µg	0.27	99.26
2	Antimony-Copper Alloy (Sb 77 % + Cu 23 %)	15 µg	14.77 µg	0.20	98.50
3	Antimony-Zinc Alloy (Sb 80 % + Zn 20 %)	15 µg	14.82 µg	0.28	98.83
4	Antimony-Manganese Alloy (Sb 90.5 % + Mn 9.5 %)	15 µg	14.98 µg	0.07	99.91
5	Antimony-Magnesium Alloy (Sb 86 % + Mg 14 %)	15 µg	14.72 µg	0.31	98.17

0-Methylphenyl thiourea (OMPT)newly proposed reagent has been proved to be a potent analytical reagent for solvent extraction, spectrophotometric determination of antimony(III). Considering the literature survey a large number of methods are reported for extraction and spectrophotometric determination of antimony(III). A numerous variety of organic reagents are available, but comparatively proposed reagent *o*-methylphenyl thiourea and the recommended method has higher sensitivity, easy determination, less expensive, less tedious procedure at trace level and no interferences from associated metal ions. Thus considering the comparison with reported extraction spectrophotometric determination methods for antimony(III) the proposed method is with positive merits.

Salient features of the proposed method:

1. Proposed method is simple, precise and sensitive with enhanced selectivity using suitable masking agents.
2. It permits, highly stable complex formation (>48h), wide Beer's range (up to 15µg ml^{-1}), lower limit of detection at microgram level (0.30 µg mL^{-1}), direct determination without heating and without interferences from associated metal ions.
3. No sophisticated instrument required and quantitative separation achieved using a simple equipment seperatory funnel.
4. A clear phase separation and single stage extraction with direct spectrophotometric determinationis possible.
5. Method is reproducible with relative standard deviation0.42%, Sandell's sensitivity0.0730282 µg cm^{-2}, and correlation coefficient 0.97.
6. Method permits enhanced applicability with

analysis of binary and ternary synthetic mixtures, analysis of real samples.

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ORIGINAL RESEARCH PAPER

Home Science

KEY WORDS: Knowledge, Nutrition, Mother, Preschool children

KNOWLEDGE ON NUTRITION AMONG SELECTED MOTHERS OF PRESCHOOL CHILDREN

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ABSTRACT

Background: Nutrition of Pre-School child is of paramount importance, because the foundation for life time health, strength and intellectual vitality is laid during this period. Nearly half of all deaths in children under 5 are attributable to undernutrition. India is one among the many countries where child malnutrition is severe. A mother is the principle provider of the primary care that her child needs during the first five years of life. Hence knowledge of mothers has an important role in the maintenance of nutritional status of the children.

Objective:- The aim of this study was to ascertain the level of knowledge of mothers towards nutrition of preschool going children.

Materials & methods: The base line study was carried out in Pravaranagar region, of Ahmednagar District of Maharashtra State with a sample size of 504. A pretested structured questionnaire was used to collect data.

Result:-In this present study the majority of the respondents (75.20%) were between the ages of 18 and 30 years. majority of respondent were Hindu (88.49%). Most of the respondents (mothers) were literate and educated up to secondary and higher secondary school level (57.94%), followed by 45.24 % up to under graduate (UG) and post graduate(PG) level. Most of the respondents (mothers) i.e 61.11 % obtained poor scores about various aspects of nutrition knowledge and 38.89 % of the respondents belonged to the fair and the good scores. This study finding revealed that the mothers need to be counseled about nutritional knowledge of preschool child

Conclusion: This study finding revealed that there is need to counsel the mothers about nutritional knowledge of preschool child and efforts should be enhance to increase the awareness of nutrition.

INTRODUCTION

Health is a fundamental human right and health is central to the concept of quality of life (Sundar Lal, 2007). Nutrition of Pre-School child is of paramount importance, because the foundation for life time health, strength and intellectual vitality is laid during this period. Child of today is a citizen of tomorrow and has valuable hand in nation building. Inadequate nutrition among the children leads to develop improper development of their body and mind, resulting into lower level of efficiency (Nazrin Ahmed 2012). It is well documented that the growth and nutritional status of preschool children are useful and sensitive indicators for judging health of a community or a nation (Sachdev HPS 1995, Bishnoi P et al 2004).Early childhood is a period of rapid growth and that nutritional insults during this period result into under or over nutrition (Sen PK 1994, Deonis M, et al 1993).Hence improving nutritional status of children becomes extremely important.

As per UNICEF (2017) nearly half of all deaths in children under 5 are attributable to undernutrition. This translates into the unnecessary loss of about 3 million young lives a year. 22.9 per cent, or just under one in four children under age 5 worldwide had stunted growth.

India is one among the many countries where child malnutrition is severe. As per NFHS 4 (2015-16), in India 38.4% of children under age five years are stunted (too short for their age) which indicates that, near about half of the country's children are chronically malnourished.

As per NFHS 4 (2015-16), in Maharashtra, 34.4% of children under age five are stunted, or too short for their age, which indicates that they have been undernourished for some time. 25.6 % are wasted, or too thin for their height, which may result from inadequate recent food intake or a recent illness. 36% are underweight, which takes into account both chronic and acute undernutrition.

The problem of malnutrition has caught the attention of policy makers and researchers for several decades. Various studies and surveys have been conducted to find out the root causes of child malnutrition. All these studies including the three National Family Health Surveys (NFHS) reveal that malnutrition is not the result of a single cause; the problem is multifaceted, the causes acting singly or in combination with other complex factors like poverty, purchasing power, health care, ignorance on nutrition and health education, female illiteracy, social convention etc (Children in India 2012). As per the NFHS 4 data (2015-16), Mother's education has a direct impact on the nutritional status of the children.

A mother is the principle provider of the primary care that her child needs during the first five years of life. Nutritional awareness of mothers plays an important role in the health of children aged 0-5 years. The type of care she provides depends to a large extent on her knowledge and understanding of some aspects of basic nutrition and health care (Kiranpreet Kaur et al 2015).Nutrition education plays a significant role in bringing a permanent and favourable solution to the problem of malnutrition among school children (Sati and Dahiya, 2012; and Ramchandran, 2013).

Considering above background, which highlighted the importance of mother's knowledge regarding preschool children. This study was conducted as a base line study to assess the mother's knowledge on nutrition of preschool children.

1. OBJECTIVESOF THE STUDY

1) To assess the socio-economic profile of the mothers.
2) To ascertain the level of knowledge of mothers towards nutrition of preschool children.

2. MATERIAL AND METHODS

3.1.1 TARGET POPULATION

The target population was mothers of preschool children aged 3-5 years.

2.1.2 STUDY POPULATION

The study population was mother of preschool children aged 3-5 years living in pravaranagar region of Ahmednagar District, Maharashtra State, India.

3.1.3 INCLUSION CRITERIA

- Mothers of preschool children aged 3-5 years belongs to pravaranagar region of Ahmednagar District.
- Mothers who agreed to participate in the study.

3.1.4 EXCLUSION CRITERIA

- Mothers who had no children aged below 3 years.
- Mothers, who were unavailable, were excluded from the study.

3.1.5 SAMPLE SELECTION

The study was carried out in Pravaranagar region, which are situated in Rahata, Shrirampur, Rahuri and Sangamner Talukas of Ahmednagar District of Maharashtra State. The List and names of the preschool children (3-5 years of age) and their mothers had been collected from the various preschools, private and anganwadi schools of selected villages.

Based on the assumption that as per NFHS-3 (2005-06) the Children under 5 years who are underweight (weight-for-age) in Ahmednagar District was 31%, with a desired 95% confidence interval and a standard error margin of 5% the sample size for the study was calculated. The minimum sample size needed for the study was 335.39. But to increase the validity and for analysis convenience, a sample of 504 mothers of preschool children (3-5 years of age) were selected for the base line study.

3.1.6 METHOD OF DATA COLLECTION

A structured questionnaire was developed, pre-tested and finalized based on the results of the pre-test. The validated questionnaire was distributed to all the mothers, at the beginning of the study and explained about the questions included. The socioeconomic information of the 504 selected respondents i.e Age, sex, caste, religion, education, monthly income of the family and type of family etc, knowledge of mothers about nutrition was collected for the base line study.

3. RESEARCH AND DISCUSSION

According to Rao, (2000) Socio-economic and demographic factors play an important role in the pattern of consumption of food and nutrients. Sunita Kejriwal and Santoshi Halder(2017) suggested that SES and nutritional awareness of mother are significantly associated and effect child cognitive development. Hence, it is very essential to evaluate the socio-economic status of family of mothers and their preschool children.

The information on the profile of the mothers in terms of age, religion, education, occupation, monthly family income, type of family, type of house, source of water and sanitation facilities etc. were analyzed. The results are presented in the Table no.1.

Table no.1 showed socio-demographic characteristics. The age of the respondent (mothers) found that 35.12% of the respondents were in the age group of 18-25 years, 40.08 % of the respondents were in the age group of 25-30 years, 18.25 % of the respondents were in the age group of 30-35 years and the rest 6.55 % were above the age group of 35 years. The above table data showed that the majority of the respondents (75.20%) were between the ages of 18 and 30 years.

In Indian Society religion and caste has a very strong hold. Every religion has a different food preparations and eating beliefs directly affected on health and nutritional status of their family. Table also pertaining to religion the of the respondent (mothers) shows that majority of respondent were Hindu (88.49%), followed by 7.14% of were Muslim and 3.57 % of were Christian. Only 0.60% and 0.20 % of respondents belong to Buddhist and other religion respectively. As per the Census 2011 out of total population of Ahmadnagar district, 90.4 % population belongs to Hindu religion, followed by 7.06 % Muslim, 0.5 % Christian and 0.75% Buddhist religion.

A proper educational background of the family is very essential for better development of their children (Moestue 2008). Especially Mothers' education level even within the same social class is a key determinant of their children's health. A high level of maternal education could lower childhood malnutrition through other pathways such as increased awareness of healthy behaviour, sanitation practices and a more equitable sharing of household resources in favour of the children (Vella V et al 1992 and Smith LC 2000).

As stated by researcher, importance of mother's education the present study finding showed that most of the respondents (mothers) were literate and educated up to secondary and higher secondary school level (57.94%), followed by 45.24 % up to under graduate (UG) and post graduate(PG) level. Only11.11 % was found up to primary school level. Table also indicates that most of the respondents (75.20%) were housewives and remaining were working as teacher (6.75%), farmer (6.15%), farm worker (6.15%), self employed (4.76%), social worker (1.59%) and used to spend 6 hours outside their homes in their job for six days in a week.

Nutritional status is also influenced by factors such as household income, the skills and capacity of care givers especially mother, use of limited resources for better care of children, as well as local availability of health-care services (WFIM 2013).The present study finding showed that most of the respondents (40.28%) household income per month ranged between Rs.5000-10000 and followed by 24.21% ranged between Rs.10000-20000, whereas 27.38% respondents were having more than Rs.20,000 per month. Only 8.13 % of respondent's household income were having less than Rs.5000 per month.

The sources of information regarding nutrition and hygiene information were asked and multiple answers were given. The results distribution shows that Television was on the top (84.92 %), followed by anganwadi worker/health worker/ social worker (60.11 %) and the radio (33.13 %) occupied the third place. Friends and family member (29.96 percent) were mentioned in the fourth place, News paper (28.57 %) were mentioned in the fourth order. Only 4.76 % received from magazines and 3.76 % from internet and social media. The Television and anganwadi worker/health worker/ social worker played an important role in the dissemination of information regarding health and nutrition.

This study was conducted as a base line study to assess the mothers knowledge on nutrition of preschool going children. From the Table no .2 it has been revealed that most of the respondents (mothers) i.e 61.11 % obtained poor scores about various aspects of nutrition knowledge and 38.89 % of the respondents belonged to the fair and the good scores taken together. The table also indicates that as the educational level of the mothers decreased the knowledge scores were also went low. A high proportion of the respondents whose were illiterate or had studied only up to primary and secondary school had 'poor' knowledge on nutrition. As the education level of the mothers raised the proportion of the respondents with 'fair' and 'good' knowledge on nutrition also increased. However 40.82 % Post graduate (PG) level of education of the respondents (mothers) had obtained poor knowledge scores. The similar finding with this result was found in a study done by Gupta Mahesh et al (1991) which reported that there was no significant association between mothers' KAP and educational level. This is also supported by a study on relationship between the mothers' nutrition knowledge and literacy done by Parul Christian et al found that the great majority of both literate and illiterate mothers had scores in the poor range (1-3 points).

Conclusion:

It has been revealed that most of the respondents (mothers) i.e 61.11 % obtained poor scores about various aspects of nutrition knowledge; Overall knowledge regarding nutrition among study subjects was not satisfactory. Hence this study finding revealed that the mothers need to be counseled about nutritional knowledge of preschool children and efforts should be enhance to increase the awareness of nutrition.

Table. 1 The Socio-demographic characteristics of the respondents (n=504)

Variables	n	%
Age Years		
18-25	**177**	**35.12**
25-30	**202**	**40.08**
30-35	**92**	**18.25**
Above 35	**33**	**6.55**

Religion		
Hindu	**446**	**88.49**
Muslim	**36**	**7.14**
Christian	**18**	**3.57**
Buddhist	**3**	**0.60**
Others	**1**	**0.20**
Education level		
Illiterate (unable to read and write)	**5**	**0.99**
Primary School	**56**	**11.11**
Secondary School	**166**	**32.94**
Higher Secondary School	**126**	**25.00**
Under graduate (UG)	**102**	**20.24**
Post graduate(PG)	**49**	**9.72**
Occupation Status		
House wife	**379**	**75.20**
Teacher	**34**	**6.75**
Social worker	**8**	**1.59**
Health worker	**3**	**0.59**
Self employed	**24**	**4.76**
Farmer	**31**	**6.15**
Farm worker	**25**	**4.96**
Household income per month in Rupees		
< Rs.5000	**41**	**8.13**
Rs.5001-10000	**203**	**40.28**
Rs.10001-20000	**122**	**24.21**
Above Rs.20000	**138**	**27.38**
Source Receiving Nutrition and Hygiene Information		
Radio	**167**	**33.13**
Television	**428**	**84.92**
Newspaper	**144**	**28.57**
Magazine	**24**	**4.76**
Friends/Family members	**151**	**29.96**
Anganwadi /Health worker/Social worker	**303**	**60.11**
Other (Internet media, social media etc)	**19**	**3.76**

n=number %= percentage

Table no. 2 Distribution of Respondents (Mothers) by Nutritional Knowledge Scores

Respondents (Mothers) educational level	**Respondents (Mothers) n=504**	**Respondents(Mothers) knowledge on Nutrition n=504**					
		Good (>38)		**Fair (>19 to 38)**		**Poor (<19)**	
	n	**n**	**%**	**n**	**%**	**n**	**%**
Illiterate (unable to read and write)	5	-	-	-	-	5	100
Primary School	56	-	-	7	12.5	49	87.5
Secondary School	166	-	-	30	21.67	136	78.31
Higher Secondary School	126			64	50.79	62	49.21
Under graduate (UG)	102	30	29.41	36	35.29	36	35.30
Post graduate(PG)	49	19	38.77	10	20.41	20	40.82
Total	**504**	**49**	**9.72**	**147**	**29.17**	**308**	**61.11**

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3.2.1 ***Number of papers published per teacher in the Journals notified on UGC website during the last five years***

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Solvent Extraction and Spectrophotometric Determination of Cerium(IV) by Using *o*-Methoxy Phenylthiourea as an Analytical Reagent

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A solvent extraction spectrophotometric determination method was developed for cerium(IV) using *o*-methoxy phenylthiourea (OMePT) as a selective reagent. A ternary complex was formed after liquid-liquid extraction from 0.05 mol L^{-1} potassium iodide aqueous media using 2.0×10^{-4} mol L^{-1} OMePT in chloroform and is measured spectrophotometrically at 318 nm. The validity of Beer's law was in the concentration range up to 22.5 μg mL^{-1}, with molar absorptivity and Sandell's sensitivity values of 3.38×10^{3} L mol^{-1} cm^{-1} and 0.041 μg cm^{-2} respectively. The stoichiometry of the cerium(IV)-OMePT-iodide complex was determined by the slope ratio method and verified by the mole ratio method. The complex was stable for more than 48 h. The method is free from interferences from large number of cations and anions. The developed method was successfully employed for the determination of cerium(IV) from binary synthetic mixtures, ternary synthetic mixtures, soil, tap water and sea water samples.

1. Introduction

Thorium required for atomic energy programmes in India is extracted from ores which contain cerium like monazite ore. The presence of cerium(IV) in the environment is dangerous. Cerium has a number of applications, including magnetic catalysis, polishing powder, ceramic technology [1] and is also used in nuclear reactors, in alloys with nickel and chromium, microwave devices, lasers, masers, and television sets [2,3]. Cerium(IV) differs significantly from other lanthanides due to its oxidizing ability in acidic solutions. This property of cerium(IV) stands in the way of determination by organic reagents.

Solvent extraction processes represent a significant technique in rare earth elements extraction and separation, as well as in industrial separation processes [4,5]. A Chinese patent [6] describes the process for extraction and separation of cerium(IV) from rare earth elements (REE III) in sulphuric acid solutions. The recovery of cerium(IV) and thorium(IV) from rare earths (RE III) with Cyanex 923 in sulphate solutions has been reported [7] and then developed into a practical process for Panxi bastnaesite liquors leached with sulphuric acid [8]. The study of the applications of rare earth elements in agriculture and biological fields has made significant progress in recent years [9]. Cerium reacts with many organic reagents. However some of the reagents recommended suffer through limitations such as slow or incomplete extraction of metal and lack of sensitivity [10]. The comparison of the present method with reported methods [11-16] for spectrophotometric determination of cerium(IV) is reported in Table 1. A literature survey reveals that the

Table 1. Comparison of present method with other extraction spectrophotometric determination methods of cerium(IV).

Reagents	λ_{max} (nm)	Condition	Beer's Law validity range, (µg mL^{-1})	Solvent	Molar Absorptivity, (L $mol^{-1}cm^{-1}$)	Remark	Ref
Malchite green - iodide	605	1.0 M HCl	0.6 – 4.6 µg per 25 mL	Aqueous	1.36×10^{5}	Low Beer's Law range	[11]
Variamine Blue - iodide	560	1 mL of 2 M HCl	2 - 10	Aqueous	1.65×10^{4}	Low Beer's Law range	[12]
2,4_Dihydroxy Benzophenone Benzoic Hydrazone	400	pH 10.0	0.7 – 7.0	Aqueous	2.0×10^{4}	Very low Beer's Law range, Low tolerance limit for ions	[13]
O-phenylenediamine	470	1 M H_2SO_4	7 to 500 ppm	Aqueous	2.4×10^{3}	10 min standing time is required for complete reaction	[14]
Leuco Disulphine Blue	635	pH 1.3 to 3 in H_2SO_4 medium,	0.5 – 5.5	Aqueous	1.75×10^{4}	25 min heating in water bath (90°)	[15]
N-phenylbenzo-18-crown-6 hydroxamic acid (PBCHA)	450	pH 8.5 to 9.5	0.2 to 25	dichloromethane	6.5×10^{3}	Multiple extraction is required	[16]
o-Methoxy phenylthiourea (OMePT)	318	0.05 M KI	2.5 to 22.5	Chloroform	3.38×10^{3}	Simple and precise, instant complex formation at room temperature, large Beer's Law range, low reagent concentration (2.0×10^{-4}), single extraction.	PM

PM – Proposed Method

existing spectrophotometric determination method has a large number of drawbacks such as sensitivity, precision and a large number of interferences of foreign ions. Hence it is necessary to have a systematic study for extraction and spectrophotometric determination of cerium(IV). The proposed method is found to be more sensitive, selective and free from a large number of interferences.

In our laboratory we have developed extraction and spectrophotometric determination for rhodium(III) [17], ruthenium(III) [18], iridium(III) [19], palladium(II) [20] and osmium(IV) [21] using *o*-Methylphenyl thiourea (OMPT). In the extension of our work we have developed extraction spectrophotometric determination methods for palladium(II) [22], selenium(IV) [23], osmium(IV) and ruthenium(III) [24] with *o*-methoxy phenylthiourea (OMePT). The current study reports the analytical applications of *o*-Methoxy phenylthiourea (OMePT) for spectrophotometric determination of cerium(IV).

2. Experimental

2.1 Instrumentation

A double beam UV-visible spectrophotometer (Elico model SL-191) with matched 10 mm quartz cells was used for absorbance measurements. A Contech electronic balance 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 water and rinsed two times with water.

2.2 Reagents

A standard stock solution of cerium(IV) was prepared by dissolving 2.885 g ceric sulphate (John Baker Inc. Colorado, U.S.A.) in 0.1 mol L^{-1} sulphuric acid and diluted to 1000 mL in a calibrated flask with distilled water and standardization of the diluted solution was carried out by gravimetry as ceric oxide after oxalate precipitation and ignition [25]. A working standard solution of cerium(IV) 75 µg mL^{-1} was prepared by diluting the standard stock solution with distilled water. *o*-Methoxy phenylthiourea (OMePT) has been prepared using method reported by Frank and Smith [26]. The working reagent solution (2.0×10^{-4} mol L^{-1}) of OMePT was prepared in chloroform. Solutions to test the effects of interferences were prepared by dissolving specific quantities of respective salts in distilled water or in dilute hydrochloric acid solution and diluted suitably. Double distilled water was used throughout the work. All of the reagents used were of analytical reagent grade unless otherwise stated. Tap water was collected from Satral village, India. Sea water was collected from Kochi, Kerala, India.

2.3 Recommended procedure

A 1.0 mL solution of cerium(IV) (75 µg mL^{-1}), potassium iodide and water were transferred into a 25 mL volumetric flask in order to get a final concentration of potassium iodide as 0.05 mol L^{-1}. This solution was transferred into a 125 mL separatory funnel and shaken for 1 min with 10 mL 2.0×10^{-4} mol L^{-1} OMePT solution in chloroform. The two phases were

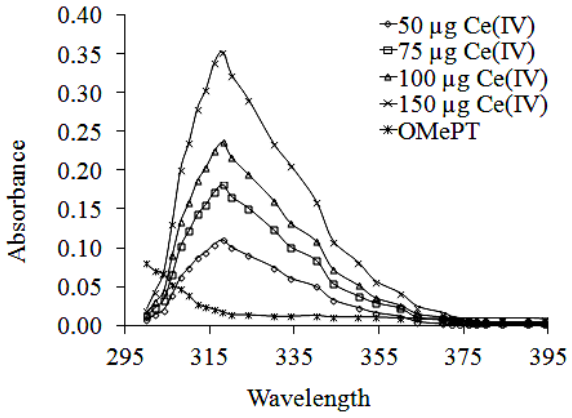

Figure 1. Absorption spectra of Ce(IV)-OMePT-iodide complex.

allowed to separate and the organic layer containing cerium(IV)- OMePT-iodide complex was dried over 1 g anhydrous sodium sulphate. The dilution ratio of chloroform was 2.5:1. The chloroform layer was transferred to a 10 mL volumetric flask and the final volume was made up to 10 mL with chloroform. The absorbance of the cerium ternary complex was measured at 318 nm against a similarly prepared blank without cerium(IV).

2.4 Absorption Spectra

The absorption spectrum of the cerium(IV)-OMePT-iodide complex against the reagent blank in chloroform shows a maximum absorbance at 318 nm, whereas the absorption spectrum of the reagent blank shows nothing. Thus further absorbance measurements of the complex were made at 318 nm against the reagent blank for further spectrophotometric determination of cerium(IV) (Figure 1).

2.5 Effect of potassium iodide concentration

The extraction of cerium(IV) with *o*-methoxy phenylthiourea in chloroform was carried out by the recommended method using 75 µg cerium(IV) and 10 mL of 2.0 × 10^{-4} mol L^{-1} OMePT in chloroform, with the potassium iodide aqueous solutions having concentrations varying from 0.1 to 3 mol L^{-1}. The absorbance value increases up to 0.05 mol L^{-1} potassium iodide concentration and a further increase in concentration has no adverse effect on the extraction of cerium(IV). Hence 0.05 mol L^{-1} potassium iodide was used for further study (Figure 2).

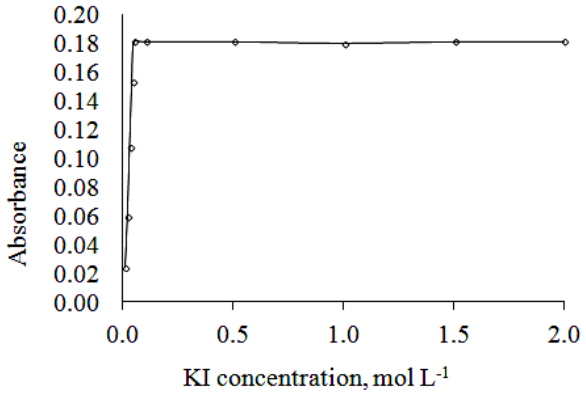

Figure 2. Effect of potassium iodide concentration on the Ce(IV)-OMePT-iodide complex.

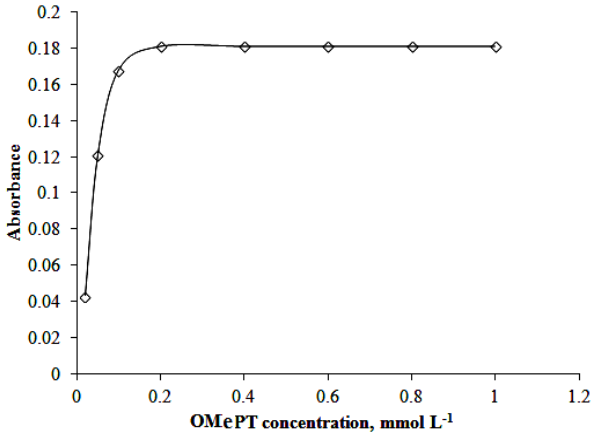

Figure 3. Effect of reagent concentration on the Ce(IV)-OMePT-iodide complex.

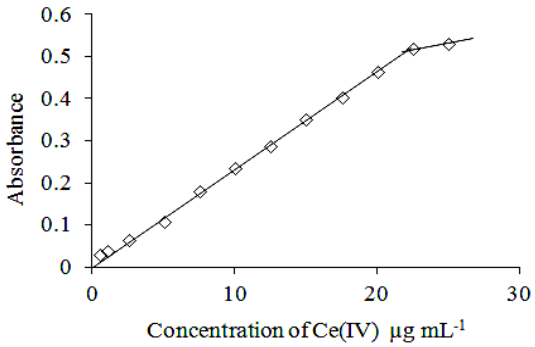

Figure 4. Applicability of Beer's law to Ce(IV)-OMePT-iodide complex.

2.6 Effect of OMePT concentration

The concentration of OMePT in chloroform was varied from 4×10^{-5} mol L^{-1} to 1×10^{-2} mol L^{-1} at 0.05 mol L^{-1} potassium iodide concentration. The extraction of cerium(IV) was quantitative and reproducible with 2.0×10^{-4} mol L^{-1} OMePT ensuring complete complex formation. With excess OMePT concentrations there is no adverse effect in the absorption measurements (Figure 3).

2.7 Choice of extraction solvent

Various extraction solvents viz. toluene, xylene, benzene, n-hexane, n-butanol, n-butyl acetate and chloroform were studied for the quantitative extraction of cerium(IV) with OMePT (Table 2). Amongst the extraction solvents studied, quantitative extraction with maximum absorbance values were obtained in chloroform. As it has a large distribution ratio and high stability under these conditions, chloroform was used as the solvent for further study.

Table 2. Effect of the solvent on the extraction of cerium(IV)-OMePT-iodide complex.

Solvent	Dielectric constant	Percentage extraction (%E)	Distribution Ratio (D)
Benzene	2.28	13.44	0.39
Toluene	2.38	15.59	0.46
Xylene	2.30	19.89	0.62
1,2-Dichloroethane	10.40	52.68	2.78
n-Butanol	17.10	70.42	5.95
n-Butyl acetate	5.00	68.27	5.38
Isoamly alcohol	14.70	76.87	8.31
Methyl isobutyl ketone	13.10	84.40	13.53
Chloroform	4.40	99.9	2500

2.8 Effect of equilibration time and stability of complex

The study of the change in absorbance with equilibration time was carried out over 15 s to 30 min. It has been observed that extraction was completed in 1 min and there was no any adverse effect of prolonged equilibration on the extraction of the complex up to 30 min. Hence 1 min equilibration time was fixed for further study. The absorbance of the complex remained stable and constant for more than 48 h (Table 3).

Table 3. Effect of equilibration time.

Shaking Time (s)	Recovery (%)
15	8.33
30	39.35
45	79.62
60	99.99
120	99.99
1800	99.99

2.9 Interference study

Various amounts of foreign ions were added to a fixed amount of cerium(IV) to establish the tolerance limit of these ions in the extraction spectrophotometric determination of cerium(IV). Table 4 lists the observed tolerance limits, defined as the highest concentration of the interfering ion causing an error of ± 2% in the absorbance values. Selectivity of the method was enhanced by the use of suitable masking agents. Selective extraction of palladium(II) (60 μg) was carried out from 1.0 mol L^{-1} hydrochloric acid medum with OMePT [22]. Cerium(IV) (75 μg) and palladium(II) (60 μg) was taken in a 25 mL volumetric flask and hydrochloric acid was added so that the concentration is 1.0 mol L^{-1} after dilution to 25 mL volume. This mixture was equilibrated with 10 mL of 1×10^{-4} mol L^{-1} OMePT in chloroform for 10 s, which quantitatively extracts palladium(II) while cerium(IV) remains in the aqueous phase. Then the aqueous phase was evaporated to moist dryness and the residue was dissolved in a small amount of dilute sulphuric acid. The cerium(IV) content was determined as per the recommended procedure. To remove

interference of osmium(IV) it is prior extracted with OMePT [24]. To the mixture of cerium(IV) and osmium(IV) solution, 2 mL of 0.009 mol L^{-1} OMePT in ethanol was added. This solution was made up to 0.8 mol L^{-1} with respect to hydrochloric acid, after dilution with water, it gives a pink coloured osmium(IV)-OMePT complex instantly at room temperature. This pink colored complex was extracted into 10 mL chloroform after a single extraction. Cerium(IV) remains in the aqueous phase. Then the aqueous phase was evaporated to moist dryness and the residue was dissolved in diluted hydrochloric acid. The cerium(IV) content was determined as per the recommended procedure. Platinum(IV) interferes in the determination of cerium(IV), it co-extracts with cerium(IV) during determination.

3. Results and Discussion

3.1 Analytical figures of merit

The cerium(IV)-OMePT-iodide complex obeys Beer's law over the concentration range up to 22.5 µg mL^{-1} (Figure 4). Above 22.5 µg mL^{-1} there may not be sufficient reagent for complete complexation. Ringbom's plot [27] has a linearity range for the absorbance and cerium(IV) concentration was 2.5 to 22.5 µg mL^{-1}. Due to the low concentration of the complex there is a lower limit of linearity. The slope value was 0.6884 (Figure 5). For the cerium(IV)-OMePT-iodide complex the ratio between the relative error in concentration and photometric error was 2.63, Sandell's sensitivity was 0.041 µg cm^{-2}, molar absorptivity was 3.38×10^3 L mol^{-1} cm^{-1}, and the correlation coefficient value was 0.99 which indicates a clear linearity between these variables.

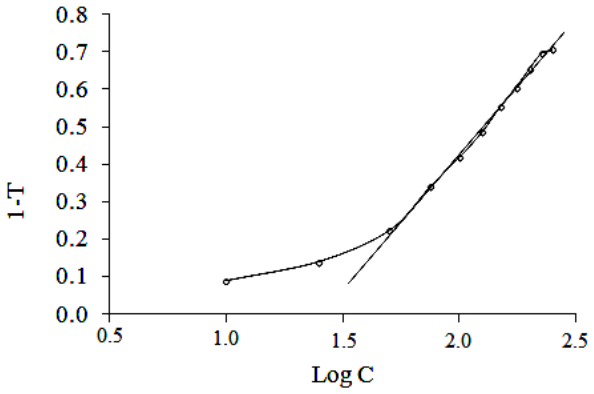

Figure 5. Ringbom's plot for Ce(IV)-OMePT-iodide complex T: Transmittance, C: Concentration mol L^{-1}.

The stoichiometry of the cerium(IV)-OMePT-iodide complex was determined by log-log plots [28]. Two plots were obtained as: 1) Log C (molar concentration) of OMePT in chloroform solvent versus Log D (distribution ratio) of cerium(IV) at a fixed KI concentration in the aqueous phase. 2) Log C (molar concentration) of KI versus log D (distribution ratio) of cerium(IV) at a fixed OMePT concentration of 2.0×10^{-4} mol L^{-1} in the chloroform solvent. The potassium iodide concentration was fixed at 0.05 mol L^{-1}. The amount of cerium(IV) taken was fixed at 75 µg and the OMePT concentration was varied from 2×10^{-3} to 9×10^{-2} mol L^{-1}. The recommended procedure was followed. As the concentration of OMePT increases the percentage extraction and hence, the distribution ratio (D) was obtained.

The log-log plot of cerium(IV) at fixed 0.05 mol L^{-1} KI concentration gives a slope of 1.34, confirming the cerium(IV):OMePT ratio as 1:1. Similarly another log-log plot was obtained for log C (molar concentration) of potassium iodide versus log D (distribution ratio) of cerium(IV) at a fixed reagent concentration of 2.0×10^{-4} mol L^{-1}. This gives a slope of 1.82 confirming a cerium(IV):iodide ratio of 1:2, hence the probable stoichiometry of the ternary complex (cerium(IV) : OMePT : iodide) is 1:1:2 (Figure 6).

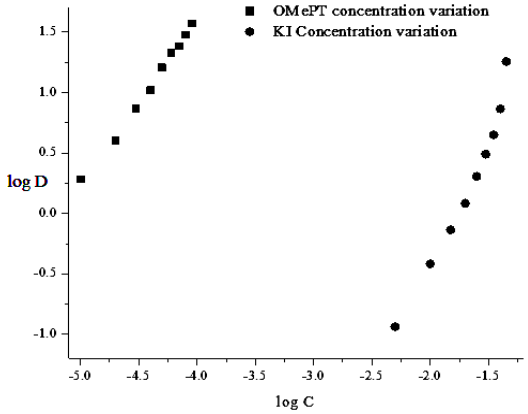

Figure 6. Plot of LogC(OmePT/KI) vs. $LogD_{(Ce(IV))}$ C: Concentration in mol L^{-1}.

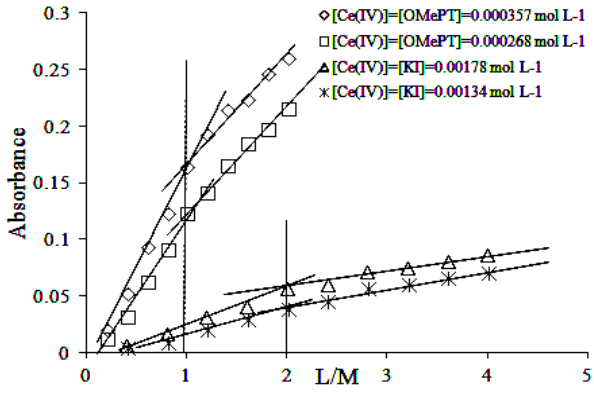

Figure 7. Mole ratio method for Ce(IV)-OMePT-iodide complex.

This composition of the complex was also verified by the mole ratio method (Figure 7). OMePT acts as a multidentate ligand with sulphur from the thio group (-C=S) and nitrogen from the amino group ($-NH_2$) coordinating with cerium to form a four membered chelate. Based on this investigation the recommended structure for the complex is given in Figure 8.

Table 4. Influence of foreign ions on the extraction of the cerium(IV)-OMePT-iodide complex.

Foreign Ions	Added as	Tolerance limit mg	Foreign Ions	Added as	Tolerance limit mg
Mn(II) [b]	$MnCl_2 \cdot 6H_2O$	4.00	Ba(II)	$BaCl_2 \cdot 6H_2O$	40.0
Cd(II)	$CdCl_2 \cdot 2H_2O$	5.00	Ca(II)	$CaCl_2 \cdot 2H_2O$	50.0
Fe(III) [b]	$(NH_4)Fe(SO_4)_2 \cdot 12H_2O$	1.30	Tl(III) [b]	Tl_2O_3	0.10
Hg(II)	$HgCl_2$	1.00	In(III) [c]	$InCl_3 \cdot 4H_2O$	1.00
Bi(III) [b]	$BiCl_3$	1.00	Rh(III)	$RhCl_3$	0.70
Ni(II) [b]	$NiCl_2 \cdot 6H_2O$	2.00	Sb(III) [c]	Sb_2O_3	1.50
Cu(II) [b]	$CuSO_4 \cdot 5H_2O$	1.00	Os(IV) [d]	OsO_4	0.20
Al(III) [b]	$AlCl_3 \cdot 6H_2O$	2.00	Ru(III)	$RuCl_3 \cdot 3H_2O$	0.70
La(III)	$LaCl_3 \cdot 7H_2O$	0.80	As (III) [c]	As_2O_3	0.05
Li(I)	LiCl	25.0	W(VI)	$Na_2WO_4 \cdot 2H_2O$	10.0
Mg(II) [b]	$MgCl_2 \cdot 6H_2O$	10.0	Se(IV) [b]	SeO_2	0.10
Sn(II)	$SnCl_2 \cdot 2H_2O$	19.0	Pd(II) [d]	$PdCl_2$	0.05
Ga(III) [c]	$GaCl_3$	5.00	Sr(III)	$SrCl_3 \cdot 6H_2O$	35.0
Au(III)	$HAuClO_4 \cdot H_2O$	0.90	Th(IV)	$Th(NO_3)_4 \cdot xH_2O$	0.80
Mo(VI)	$(NH_4)_6MO_7O_{24} \cdot 2H_2O$	2.50	Fluoride	NaF	100
V(V)	V_2O_5	15.0	Phosphate	Na_3PO_4	100
Cr(III) [b]	$CrCl_3$	1.00	Sulphate	K_2SO_4	100
Pb(II) [b]	$PbCl_2$	2.00	Succinate	$CH_3(COONa)_2 \cdot 6H_2O$	100
U(VI)	$UO_2(CH_3COO)_2 \cdot 2H_2O$	20.0	Citrate	$C_6H_8O_7 \cdot H_2O$	100
Co(II) [b]	$CoCl_2 \cdot 6H_2O$	2.50	Malonate	$CH_2(COONa)_2$	100
Zn(II)	$ZnSO_4 \cdot 7H_2O$	10.0	Tartrate	$(CHOH:COOH)_2$	100
Ti(IV)	$Ti_2(SO_4)_3$	2.50	Acetate	$CH_3COONa \cdot 3H_2O$	100
Be(II)	$BeSO_4 \cdot 4H_2O$	20.0	Oxalate	$Na_2C_2O_4 \cdot 2H_2O$	100
Ir(III)	$IrCl_3$	0.50	E.D.T.A	Na_2EDTA	100

[b]Masked with 100 mg EDTA; [c]Masked with 100 mg Tartarate; [d] prior extraction with OMePT

To test the accuracy and precision of the method, nine successive measurements on the sample solution were carried out. The small relative standard deviation, RSD (0.88%) indicates high precision and good accuracy. The detection limit for cerium(IV) is 0.16 µg mL^{-1} and it is determined as an amount corresponding to thrice the standard deviation blank value.

3.3 Applications

3.3.1 Separation and determination of cerium(IV) from binary synthetic mixtures

The proposed method permits separation and determination of cerium(IV) from associated metal ions containing Ni(II), Mn(II), Al(III), Fe(III), Mg(II) and Co(II). Each individual metal ion in solution was taken and a solution containing 100 mg of EDTA was added to mask these ions. 1 mL cerium(IV) solution (75 µg mL^{-1}) was added and, after extraction of cerium(IV) by the recommended method, the masked metal ions remaining in the aqueous phase were treated with 5.0 mL nitric acid and the mixture was boiled vigorously for 15 to 20 min with addition of water at intervals to maintain the volume. The mixture liberated violet vapours of iodine and after complete evolution of iodides in the form of iodine the raffinate was evaporated to moist dryness followed by treatment with HCl. The residue obtained was cooled, dissolved in water and again evaporated to moist dryness. The residue obtained was cooled, dissolved in water and then the added metal ions were determined by reported methods [29].

Table 5. Separation of cerium(IV) from binary synthetic mixtures.

Metal ion	Amount taken (µg)	Recovery[f] (%)	RSD (%)	Chromogenic ligand	Reference
Ce(IV)	75	99.35	0.70	OMePT	------
Ni(II) [a]	100	99.67	0.38	Dimethylglyoxime	[29]
Ce(IV)	75	99.54	0.44	OMePT	------
Co(II) [a]	300	99.55	0.49	Thiocynate	[29]
Ce(IV)	75	99.36	0.69	OMePT	------
Fe(III) [a]	75	98.54	1.25	1,10-Phenenthroline	[29]
Ce(IV)	75	98.99	0.83	OMePT	------
Mn(II) [a]	200	98.33	1.60	Potassium metaperiodate	[29]
Ce(IV)	75	99.35	0.70	OMePT	------
Mg(II) [a]	20	97.94	1.64	Titan yellow	[29]
Ce(IV)	75	99.08	0.76	OMePT	------
Al(III) [a]	50	98.97	1.58	8-Hydroxyquinoline	[29]
Ce(IV)	75	99.18	0.56	OMePT	------
Tl (III) [a]	10	99.6	1.01	Starch Iodide	[30]

[a] masked with 100 mg EDTA, [f] average of four determinations

To enhance the extraction of cerium(IV) in presence of thallium(III), the metal ion was masked with tartarate and the recommended procedure was followed for quantitative extraction of cerium(IV) in 10 mL

chloroform. The aqueous phase contained masked thallium(III). It was de-masked by treatment with 5.0 mL nitric acid and the mixture was boiled vigorously for 15 to 20 min with addition of water at intervals to maintain the volume. The mixture liberated violet vapours of iodine and after complete evolution of iodides in the form of iodine the raffinate was evaporated to moist dryness followed by treatment with HCl. The residue was cooled, dissolved in water and Tl(III) was determined spectrophotometrically as per the reported method [30] (Table 5).

3.3.2 Separation of cerium(IV) from ternary synthetic mixtures

An aliquot of solution containing 75 µg cerium(IV) was taken and a known amount of different compositions of associated metal ions were added followed by a suitable masking agent and cerium(IV) was separated and determined as per the recommended method (Table 6).

Table 6. Separation of cerium(IV) from ternary synthetic mixtures.

Composition (µg)	Recovery[f] (%)	RSD (%)
Ce(IV) 75; Ni(II) [a] 50; Mn(II) [a] 50	99.49	0.53
Ce(IV) 75; Co(II) [a] 20; W(VI) 20	99.35	1.09
Ce(IV) 75; Al(III) [a] 25; W(VI) 20	98.95	1.13
Ce(IV) 75; Pb(III) [a] 20; Bi(III) [a] 50	99.08	0.45
Ce(IV) 75; La(III) 50; Th(IV) 50	99.36	0.45

[a] masked with 100 mg EDTA, [f] average of four determinations

3.3.3 Determination of Cerium in soil Samples

Soil samples were collected from the fields of Satral village (India) with properly cleaned equipment. The samples were dried at 105°C until the weight reached a constant value. The samples were then ground in a blender and kept in clean polyethylene containers for analysis. Soil samples (1.0 g) were weighed accurately into a silica crucible and a known amount of cerium(IV) was added. The mass was then fused with 5 gm anhydrous sodium carbonate. The fused mass was dissolved in 25 mL distilled water and evaporated to dryness. To the residue about 20 mL distilled water was added and after stirring the solution was filtered through Whatman filter paper no. 42. The filtrate was neutralized with dilute ammonia and finally diluted to 25 mL in a volumetric flask. From an aliquot (5 mL) of solution, cerium(IV) was determined by the proposed method (Table 7).

Table 7. Determination of cerium(IV) from soil and tap water.

Sample	Ce (IV) added (µg)	Ce(IV) found (µg)	Recovery (%)	RSD*
Soil	25	24.48	97.91	2.44
	50	49.08	98.16	2.47
	75	74.17	98.89	1.47
Tap Water	25	24.75	99.00	0.87
	50	49.55	99.11	1.54
	75	74.45	99.27	1.26

* RSD calculated by 6 determinations

3.3.4 Determination of Cerium in Tap Water

Tap water (25 mL) was taken and a known amount of cerium(IV) was added. An aliquot of 5 mL was analyzed for added cerium(IV) by the proposed method. Recovery of cerium(IV) was close to 100% (Table 7).

3.3.5 Determination of Cerium in Sea Water

Sea water (200 mL) was placed in a 500 mL beaker and heated on a hot plate to moist dryness. Concentrated hydrochloric acid (5 mL) was added and again heated to moist dryness. The residue was dissolved in very dilute hydrochloric acid and finally diluted to 50 mL with distilled water. An aliquot (5 or 10 mL) of this solution was analyzed for determination of cerium(IV) as per the proposed method (Table 8).

Table 8. Determination of Ce(IV) from sea water.

pre-concentrated sample mL	Ce(IV) found µg mL^{-1}	RSD*
5	3.05	1.04
10	3.20	0.69

*RSD calculated by 4 determinations

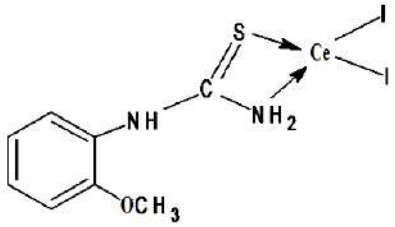

Figure 8. Probable structure of Ce(IV)-OMePT-iodide ternary complex.

4. Conclusion

o-Methoxy phenylthiourea (OMePT) has been proved to be a sensitive and selective spectrophotometric reagent for cerium(IV). The proposed method is simple, sensitive, selective, reproducible and rapid with low reagent concentration. Quantitative extraction was carried out in a single stage. The currently reported methods suffer from interferences from cations and anions and were less sensitive. The proposed methods are free from interferences from a large number of cations and anions. The cerium(IV)-OMePT-iodide complex was stable for more than 48 h. This confirms the applicability of the spectrophotometric method for various sample matrices. The proposed method was successfully applied for the determination of cerium(IV) from binary synthetic mixtures, a soil sample and a water sample.

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Rapid determination of tellurium(IV) by ultraviolet spectrophotometry using *o*-methylphenyl thiourea as a new chromogenic ligand

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O-Methylphenyl thiourea (OMPT) coordinates with tellurium(IV) as a 1:1 (tellurium(IV)-OMPT) complex in hydrochloric acid medium (7.0 mol L^{-1}). The novelty of the proposed method is the instant complex formation at room temperature with no need of heating or standing. Method is applicable over a wide Beer's range (up to 70 μg ml^{-1}). A low reagent concentration is required (2 ml, 0.018 mol L^{-1} in methanol). The complex exhibits maximum absorption at a wavelength of 280 nm. The molar absorptivity is 1.98×10^4 L mol^{-1} cm^{-1}, Sandell's sensitivity is 0.00641 μg of tellurium(IV) cm^{-2}. The proposed method was successfully applied for analysis of a real sample.

Keywords: Tellurium(IV); UV-spectrophotometry; Analysis, Real sample.

INTRODUCTION

Abundance of tellurium in the earth's crust is 0.001 ppm. Its compounds are used in metallurgy, mostly in making steel and non-ferrous alloys [1]. It is used as a semiconductor material. Tellurium and its compounds are widely used in thin films, rechargeable batteries and charge transfer systems. Compounds like hydrogen telluride are highly toxic in nature. Tellurium exposure results into garlic-like breath. Tellurium aerosol irritates the eyes and the respiratory track. Tellurium compounds may affect liver and central nervous system. It causes abdominal pain, constipation and vomiting. It is a potential toxic environmental pollutant [2]. Addition of tellurium to lead prevents corrosion [3]. Cadmium telluride photovoltaic modules have become the lowest-cost producer of solar electricity [4]. Trace abundance, application in metallurgy, solar and semiconductors, environmental toxicity and health hazards support the necessity and demand for the development of a simple, sensitive method for determination of tellurium and monitoring trace tellurium concentrations in various sample matrices.

Many analytical techniques have been studied and methods for determination of tellurium have been reported such as voltammetry [5], stripping voltammetry [6,7], inductively coupled plasma atomic emission spectroscopy (ICP-AES) [8,9], inductively coupled plasma mass spectrometry (ICP-MS) [10-12], atomic absorption spectrometry (AAS) [13,14] and hydride generation atomic fluorescence spectrometry [15]. These methods, based on different instrumental techniques, have positive merits like determination at trace level, low limit of detection, minimum interferences, analysis of various sample matrices and fast determination. However, practical application of these techniques has serious drawbacks and it requires sophisticated instrumentation. Spectrophotometric molecular absorption methods involve less expensive instrumentation, and are simple to operate with high sensitivity.

Recently, very few reagents and a limited number of methods are reported for spectrophotometric determination of tellurium. According to the review of literature for spectrophotometric determination of tellurium, the methods are based on catalytic kinetic determination [16-19], synergic extraction [20], direct spectrophotometric determination [21-25], solvent extraction spectrophotometric determination [26-31], determination after extraction using molten naphthalene [32-34] and determination by ion-association complex formation [35]. These methods are sensitive, but have the drawback that catalytic kinetic methods need controlled conditions. Most direct determination methods suffer from interferences from associated metal ions and extraction spectrophotometric determination methods require costly and environmentally hazardous organic solvents.

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In our laboratory, work has been carried on for extraction spectrophotometric determination of platinum group metals using OMPT [36-41], ruthenium & osmium [42], selenium [43], palladium [44] and cerium(IV) [45] using OMePT. In extension of this work, solvent-free direct spectrophotometric determination of tellurium with the sensitive chromogenic chelating ligand *o*-methylphenyl thiourea (OMPT) was developed in this work.

EXPERIMENTAL

Apparatus

Elico digital spectrophotometer model SL-159 with 1 cm quartz cells and Contech electronic balance model CA -123 were used for absorption measurements and weighing. Glassware was cleaned by soaking in acidified solution of potassium dichromate followed by washing with soap water and rinsing twice with distilled water.

Standard tellurium(IV) solution

A stock solution of tellurium was prepared by dissolving 0.250 g solid tellurium metal in a nitrating mixture, HCl:HNO_3 (1:3) and diluting up to the mark in a 250 mL standard volumetric flask. A working standard solution (25 µg mL^{-1}) was prepared by diluting an aliquot of the stock solution with distilled water.

o-Methylphenyl thiourea solution

O-Methylphenyl thiourea (OMPT) was synthesized as reported by Frank and Smith [42]. ^{1}H NMR spectrum of *o*-methylphenyl thiourea is given in Fig 1. A 0.01 mol L^{-1} methanolic solution was prepared by dissolving 0.149 g of OMPT in 20 mL of methanol and diluted up to the mark with methanol in a 50 mL calibrated volumetric flask.

Solutions of foreign ions

Standard solutions of different metal ions used to study the effect of foreign ions were prepared by dissolving weighed quantities of their salts in water or dilute hydrochloric acid in a calibrated volumetric flask. Solutions of anions were prepared after dissolving their respective alkali metal salts in water in a calibrated volumetric flask. Distilled water was used throughout the study.

Recommended procedure

An aliquot of a solution containing 25 µg of tellurium(IV), hydrochloric acid (6.2 mL) and 2 mL of 0.018 mol L^{-1} OMPT in methanol was transferred to a 10 mL volumetric flask and diluted up to the mark with water. The absorbance of the tellurium-OMPT complex was measured in the ultraviolet region at 280 nm against reagent blank prepared in a similar manner.

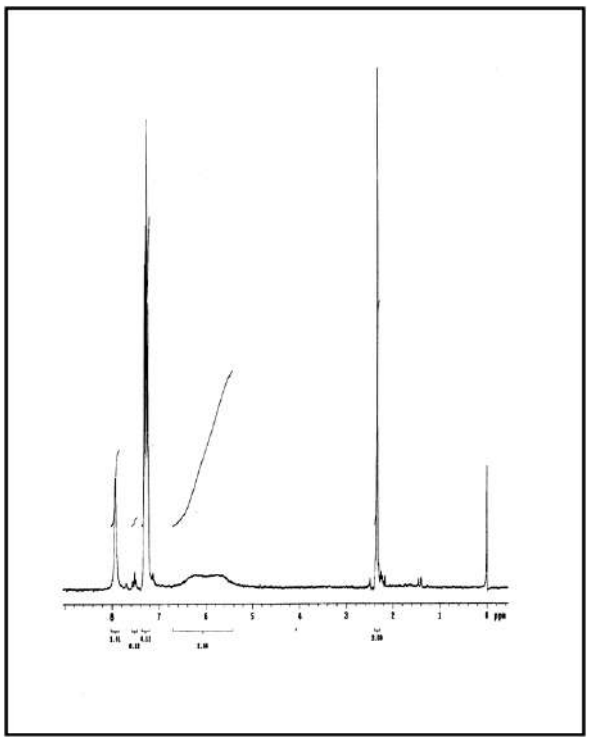

Fig. 1. ^{1}H NMR spectrum of *o*-methylphenyl thiourea (OMPT).

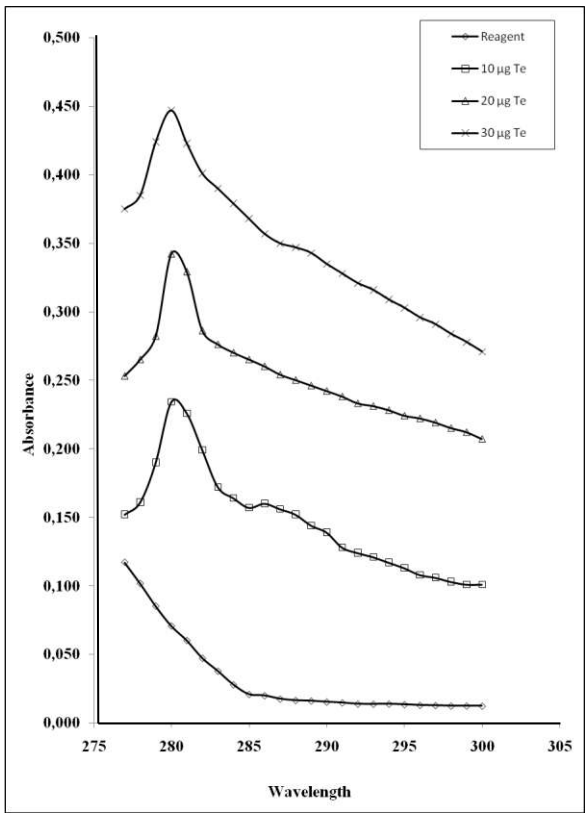

Fig. 2. Absorption spectrum of tellurium (IV)_OMPT-chloride complex vs OMPT reagent blank.

RESULTS AND DISCUSSION

Spectral characteristics

Tellurium(IV) formed 1:1 (tellurium:OMPT) complex in 7.0 mol L^{-1} hydrochloric acid medium. The complex showed maximum absorption at 280 nm. The optimum conditions for determination of tellurium were established by studying the hydrochloric acid concentration, OMPT concentration and interferences by various foreign ions. The proposed method, when compared with other extraction spectrophotometric methods, (Table 1) offers advantages such as reliability, easy reproducibility, and simple operation for determination of tellurium (IV). The spectral and physico-chemical characteristics along with the precision data are reported in Table 2.

Absorption spectra

The absorption spectrum of the tellurium-OMPT complex showed maximum absorbance in the ultraviolet region at 280 nm. Thus, all further spectral measurements of the complex were made at a wavelength of 280 nm (Fig.2).

Effect of hydrochloric acid concentration

Tellurium(IV)-OMPT complex formation was studied in hydrochloric acid, nitric acid, sulphuric acid and perchloric acid. Amongst the acids studied, the tellurium(IV)-OMPT complex formation took place in presence of hydrochloric acid but not in any other acid studied. Maximum absorbance was registered in 7.0 mol L^{-1} hydrochloric acid. Hence, all further measurements were performed in 7.0 mol L^{-1} hydrochloric acid (Fig. 3).

Effect of reagent and extraction solvent

The reagents studied were methanol, dimethylsulphoxide (DMSO), dimethylformamide (DMF) and 1,4-dioxan. There was no complex formation in the presence of DMSO. Complete complexation with maximum absorbance was achieved in methanol. Hence, methanol was chosen for further study. Various extraction solvents were studied, *viz.*, chloroform, benzene, toluene, xylene, isoamyl alcohol and butanol, but none of them was effective for the extraction of the Te-OMPT complex.

Effect of OMPT concentration

The concentration of OMPT in methanol (2.0 mL) was varied in the range of 0.005 - 0.02 mol L^{-1}. It was observed that 2 mL of 0.018 mol L^{-1} reagent was sufficient to ensure complete complexation, (Fig. 4). The excess reagent has no adverse effect on the determination of tellurium(IV).

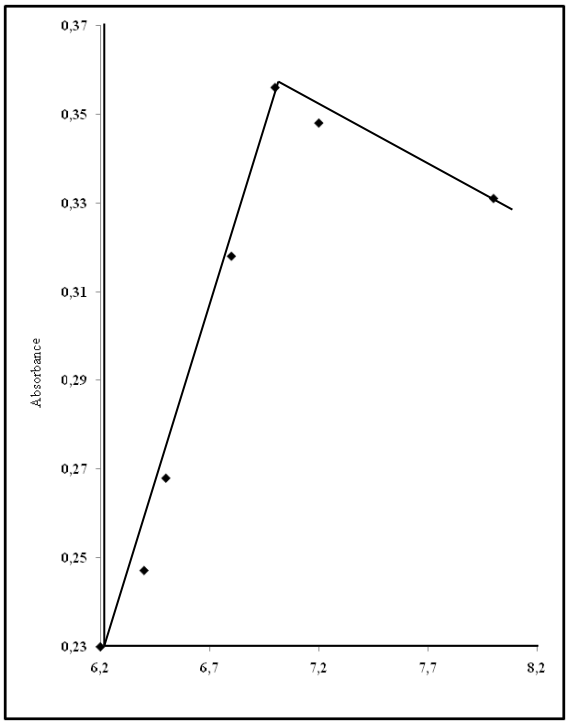

Fig. 3. Effect of hydrochloric acid concentration. Te(IV) 25 µg; OMPT 2.0 ml, 0.01 mol L^{-1}; λ_{max} 280 nm

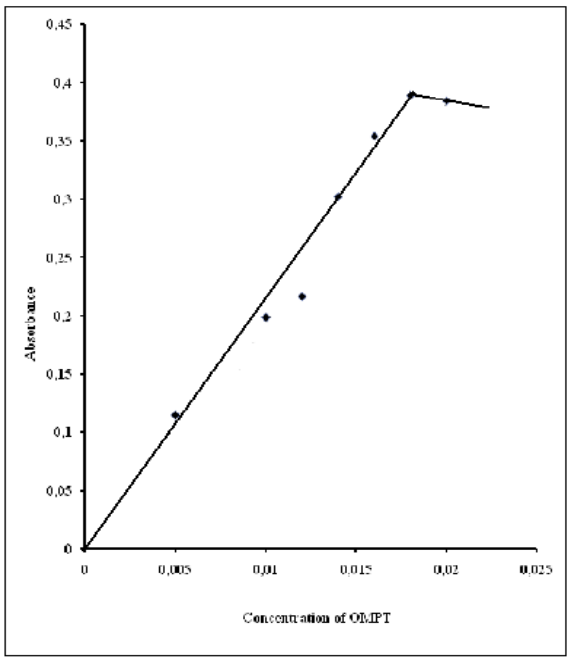

Fig. 4. Effect of *o*-methylphenyl thiourea (OMPT) concentration. Te(IV) 25 µg; HCl 7.0 mol L^{-1}; λ_{max} 280 nm.

Table 1. Comparison of the present method with spectrophotometric determination methods of tellurium.

Reagents	λ_{max} (nm)	Condition	Beer's Law validity range, (µg mL^{-1})	Solvent	Molar Absorptivity, (L mol^{-1}cm^{-1})	Remark	Ref
Gallocyanine	618	pH / 5.0 acetate buffer	2.0 – 200 ng ml^{-1}	water	NR	Interferingions need removal after passing through cation exchange resin	16
Cetyl trimethyl ammoniumbromide	600	pH / 4.0 acetate buffer	0.6 – 500 ng ml^{-1}	water	NR	30 min standing at 35 ^{0}C before initiation reaction	17
Leuco methylene Green	650	pH / 3.0 acetate buffer	0.2 – 2.5 µg ml^{-1}	water	4.9 x10^{4}	Interference study of Se ,Bi, Po not studied	18
Tohuidine blue	630	pH / 7.2 phosphate buffer	0.01 – 0.08 µg ml^{-1}	water	NR	Controlled 25 ^{0}C essential for completion of reaction. Lengthy analysis time 100 sec.	19
p- [4-(3,5-dimethylisoxazolyl)azophenylazo]calix(4)arene	425	3.0 MHNO$_3$	1.0 to 14.0 µg ml^{-1}	1,2 dichloroethane	1.67 x10^{4}	1.0 hour centrifugation and 10 min standing to separate phases	20
Nile blue	580	6.0 M H$_2$SO$_4$	0.004 – 0.006 µg ml^{-1}	water	3.33 x10^{7}	10 min standing before adding reagent and 5 min standing after adding reagent	21
4-bromophenyl-hydrazine	550	4.0 MNaOH	1.0 – 2.5 µg ml^{-1}	water	1.0 x10^{5}	5.0 min standing, test volume restricted to 1.0 ml	22
Chrome azurol S	525	pH / 3.1	Up to 2.0 µg ml^{-1}	water	2.5 x10^{4}	Method is sensitive to order of addition of reagents, 5 min standing, many cations interfere	23
N,N-di(acetoxyethyl)indocarbocyanini	542	4.0 – 5.5 M H$_2$SO$_4$	0.04 – 15.0 µg ml^{-1}	Toulene	4.3 to 11.2 x10^{4}	Hg(II) interferes, No applications studied	26
Hexabromide-diantipyrylmethane	336	2.0 M H$_2$SO$_4$	NR	chloroform	1.82 x10^{3}	Standing 15 min to ensure complexation, lengthy procedure with more number of chemicals required	27
1-(2',3'-dichlorophenyl)-4,6-trimethyl-(1H, 4H)pyrimidine-2-thiol	430	HCl	2.5 – 12.5 µg ml^{-1}	chloroform	7.56 x10^{3}	No real samples analyzed	28
1-(4-Bromophevyl)-4,6-trimethyl-1,6-dihydropyrimidine-2-thiol	440	HCl	1.0 – 15.0 µg ml^{-1}	chloroform	8.1 x10^{3}	No real samples analyzed	29
Morpholine-4-carbodithioate	415	pH / 3.5 – 7.0	0.5 – 12.5 µg ml^{-1}	chloroform	1.07 x10^{4}	Heating at 60 ^{0}C, complex stable on for 3.4 h on chloroform	32
o-Methylphenyl thiourea (OMPT)	280	7.0 M HCl	0.5 – 12.5 µg ml^{-1}	water	1.99 x10^{4}	Minimum reagent required. No need of organic solvent. Higher molar absorptivity. Wide beer's range	PM

NR : Not reported, PM : Present method.

Table 2. Spectral and physico-chemical characteristics along with precision data of the tellurium-OMPT complex.

Spectral characteristics and precision	Parameters
Hydrochloric acid concentration	7.0 mol l^{-1}
Reagent solvent	methanol
Reagent concentration	2 ml, 0.018 mol l^{-1}
λ_{max}	280 nm
Molar absorptivity	1.99 × 10^{4}Lmol^{-1} cm^{-1}
Sandell's sensitivity	0.00641µg cm^{-2}
Beer's law range	up to 70.0 µg ml^{-1}
Ringbom's optimum range	13.0 to 70.0µg ml^{-1}
Limit of detection	0.77µg ml^{-1}
Relative standard deviation	0.004%
Stoichiometry of the complex	1:1 (Te:OMPT)
Stability of complex	1.0 h
Correlation coefficient	0.99

Stability of the complex

The stability of the complex was studied by measuring the absorbance at intervals of 10 min each. Absorbance of the complex was stable for a period of 1.0 h.

Beer's law and sensitivity

Beer's law was obeyed over the concentration range up to 70 µg mL^{-1} (Fig. 5). Ringbom's plot was of sigmoid shape with a linear segment at intermediate absorbance values of 13.0 to 70.0 µg mL^{-1} and with a slope value of 0.576 (Fig. 6). The ratio between the relative error in the concentration and the photometric error was found to be 3.99. The sensitivity of the method as defined by Sandell was 0.00641 µg cm^{-2} and the molar absorptivity was 1.98 × 10^{4} L mol^{-1} cm^{-1}. The correlation coefficient value of the tellurium-OMPT complex with concentration in µg mL^{-1} as independent variable and absorbance as dependent variable was found to be 0.99. The standard deviation calculated from 10 determinations of a solution containing 25 µg tellurium was 0.004.

Stoichiometry of the complex

The composition of the tellurium(IV):OMPT complex was ascertained using the slope ratio method by plotting the graph of log $D_{(Te)}$ against

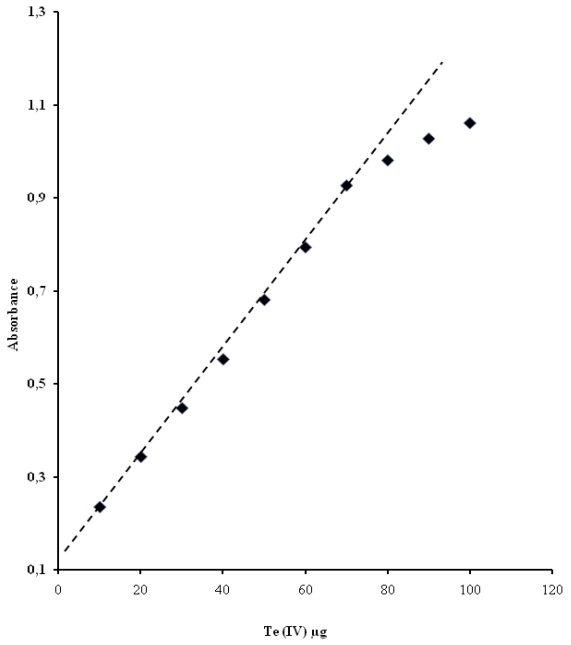

Fig. 5. Beer's law. Te(IV) 25 to 100 µg; HCl 7.0 mol L^{-1}; OMPT 2.0 ml, 0.01 mol L^{-1}; λ_{max} 280 nm

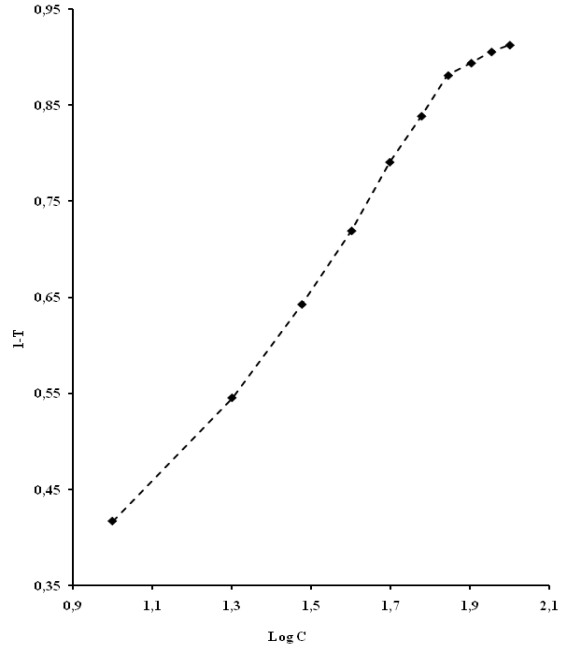

Fig. 6. Ringbom's plot. Te(IV) 25 to 100 µg; HCl 7.0 mol L^{-1} ; OMPT 2.0 ml, 0.01 mol L^{-1}; λ_{max} 280 nm.

log $C_{(OMPT)}$ at 1.0 mol L^{-1} and 3.0 mol L^{-1} hydrochloric acid concentration. These graphs were linear with slope values of 0.89 and 0.98, respectively (Fig. 7). Hence, the probable composition of the extracted species was calculated to be 1:1 (tellurium(IV):OMPT). The composition of the complex was also confirmed by the mole ratio method (Fig. 8) which supported the stoichiometry as 1:1 (tellurium:OMPT). OMPT acts as a multidentate ligand, sulphur from the thio group (-C = S) and nitrogen from the amine group ($-NH_2$) coordinating with tellurium to form a 1:1 (tellurium:OMPT) complex. Based on this investigation the probable structure recommended for the complex is given in Fig. 9.

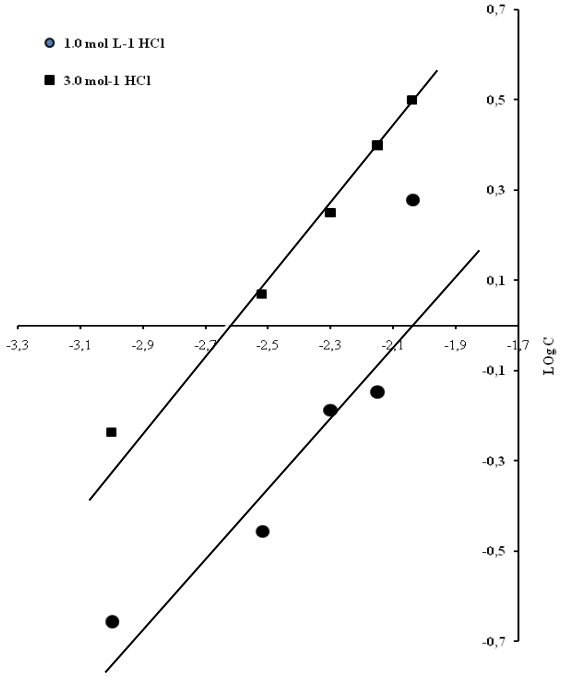

Fig. 7. Stoichiometry by the slope ratio method - log $D_{(Te)}$ against log $C_{(OMPT)}$

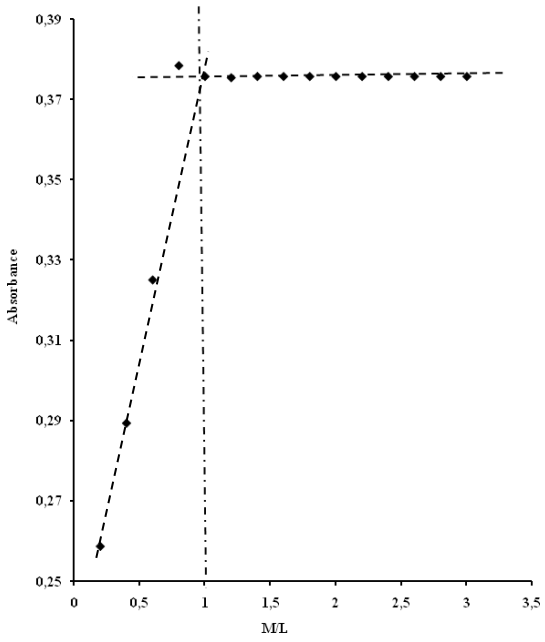

Fig. 8. Mole ratio method.

Te(IV) 25 µg; HCl 1.0 mol L^{-1}, 3.0 mol L^{-1} and 7.0 mol L^{-1}; OMPT 2.0 ml (0.001 mol L^{-1} to 0.01 mol L^{-1}); λ_{max} 280 nm.

Table 3. Effect of foreign ions. Te (IV) 25 µg ; HCl 7.0 mol L^{-1} ; OMPT 2.0 ml, 0.01 mol L^{-1}; λ_{max} 280 nm.

Foreign ion	Added as	Tolerance limit (mg)	Foreign ion	Added as	Tolerance limit (mg)
Mn(II)	$MnCl_2.6H_2O$	0.25	Ca(II)	$CaCl_2.2H_2O$	0.50
Ce(IV)	$Ce(SO_4)_2.4H_2O$	1.00	Tl(III)	Tl_2O_3	0.02
Co(II)	$CoCl_2.6H_2O$	1.00	In(III)	$InCl_3.4H_2O$	0.50
Bi(III)	$BiCl_3$	0.25	Os(VIII)	OsO_4	0.13
Ni(II)	$NiCl_2.6H_2O$	1.00	Ba(II)	$BaCl_2.6H_2O$	10.0
Se(II)	SeO_2	0.10	Ir(III)	$IrCl_3$	0.25
Al(III)	$AlCl_3.6H_2O$	0.80	Os(IV)	OsO_4	0.13
La(III)	$LaCl_3.7H_2O$	3.00	Zr(IV)	$ZrOCl_2.8H_2O$	0.10
Li(I)	LiCl	0.10	As (III)	As_2O_3	0.50
Ti(III)	$(Ti_2SO_4)_3$	0.25	W(VI)	$Na_2WO_4.2H_2O$	0.10
Mg(II)	$MgCl_2.6H_2O$	1.00	Zn(II)	$ZnSO_4.7H_2O$	50.0
Sn(II)	$SnCl_2.2H_2O$	0.10	Be(II)	$BeSO_4.2H_2O$	0.10
Ga(III)	$GaCl_3$	1.00	Sr(III)	$Sr(NO_3)_2$	2.50
Au(III)	$HAuClO_4.H_2O$	1.10	Sulphate	K_2SO_4	0.50
Mo(VI)	$(NH_4)_6MO_7O_{24}.2H_2O$	0.25	Succinate	$(CH_3COONa)_2.6H_2O$	0.25
Sb(III)	Sb_2O_3	1.00	Citrate	$C_6H_8O_7.H_2O$	0.50
V(V)	V_2O_5	0.25	Malonate	$CH_2(COONa)_2$	1.00
Ce(IV)	$Ce(SO_4)_2.4H_2O$	0.25	Acetate	$CH_3COONa.3H_2O$	10.0
U(VI)	$UO_2(CH_3COO)_2.2H_2O$	0.25	E.D.T.A	Na_2EDTA	0.75

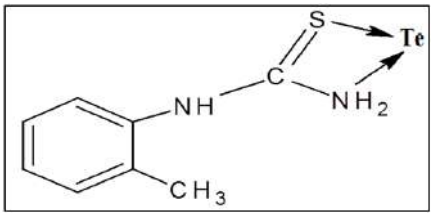

Fig. 9. Probable structure of the tellurium-OMPT (1:1) complex.

Effect of foreign ions

Various foreign ions were tested to determine their tolerance limits in the determination of tellurium(IV) (Table 3). The tolerance limit was defined as the amount of the ion, which does not cause deviations more than ± 2 % in the absorbance of the tellurium-OMPT complex. A large number of foreign ions do not interfere in the method except chromium(VI), lead(II), rhodium(III), copper(II), cadmium(II) and mercury(II).

APPLICATIONS

Analysis of a solar glass plate

The method developed was applied for determination of the tellurium content of solar glass plates present in solar calculators. Known weight of a solar plate containing a thin layer of tellurium below the transparent glass was treated with *aqua regia* to dissolve the tellurium. It was washed with water and the washings were collected in the same container. The clean glass plate was dried and weighed to get the weight of the tellurium coating. The solution containing tellurium, *aqua regia* and washings was evaporated to moist dryness and cooled. The residue was dissolved in water and made up to the mark in a 10 ml volumetric flask. 1.0 ml of this mixture was used for determination of tellurium by the recommended procedure. The results obtained are in good agreement with those obtained using a standard method (Table 4).

Table 4. Determination of tellurium from a solar glass plate. HCl 7.0 mol L^{-1}, OMPT 2.0 ml, 0.01 mol L^{-1}; λ_{max} 280 nm.

Weight of tellurium coating	Tellurium present*	Tellurium content by the recommended method	% Tellurium*
0.0035 g	0.1155	0.1153	99.82

*Six determinations

CONCLUSIONS

O-methylphenyl thiourea (OMPT) is a highly sensitive reagent for determination of tellurium when compared with other spectrophotometric determination methods (Table 1). It was successfully applied to the determination of tellurium in a real sample.

Salient features of the proposed novel method are:

1. Low reagent concentration required for spectrophotometric determination of tellurium.
2. Method is free from interferences from a large number of foreign ions associated with tellurium in its natural occurrence.
3. The method is applicable for analysis of real samples.

4. The proposed method is simple, rapid and reproducible with quantitative recovery of tellurium at a trace level.

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БЪРЗО ОПРЕДЕЛЯНЕ НА ТЕЛУР(IV) ЧРЕЗ УЛТРАВИОЛЕТОВА СПЕКТРОСКОПИЯ С ПОМОЩТА НА *о*-МЕТИЛФЕНИЛТИОКАРБАМИД КАТО НОВ ХРОМОГЕНЕН ЛИГАНД

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(Резюме)

о-Метилфенилтиокарбамидът (OMPT) образува с телур (IV) комплекс в моларно сътношение 1:1 (tellurium(IV)-OMPT) в солно-кисела среда (7.0 mol L^{-1}). Новостта на предложения метод е незабавното образуване на комплекса при стайна температура без нужда от нагряване или престой. Методът е приложим за широк обхват на закона на Beer (до 70 μg ml^{-1}). Изискват се ниски концентрации на реагента (2 ml, 0.018 mol L^{-1} в метанол). Комплексът има максимална абсорбция при дължина на вълната 280 nm. Моларната абсорбция е 1.98×10^4 L mol^{-1} cm^{-1}, а чувствителността по Sandell е 0.00641 μg за телур (IV) cm^{-2}. Предложеният метод бе успешно приложен за анализа на реални проби.

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Socio-economic profile of selected obese school going children

RAJKUMAR M. KAMBLE AND ANURADHA DUBEY

The present study was to assess the prevalence of obesity in school going children and their socio-economic status. The study was carried out in 1500 school going children of 6-16 years of age having different SES from Pune, Nashik and Ahmednagar districtof Maharashtra. The overweight and obesity were considered using BMI reference. The socio-demographic factors were assessed by using self-structured questionnaire. Overweight (16.52)and obesity (7.21)for boys and 43.12 and 23.32 per cent, respectively in girls were found as high and alarming specially in high SES with nuclear families. Therefore nutrition awareness programme should be provided to parents for better and healthy nutrition of their children.

Key Words : Socio-economic, Profile, Children, Obese school

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INTRODUCTION

Obesity can be seen as the first wave of a defined cluster non-communicable disease referred as "New World Syndrome" creating an enormous socio-economic and public health burden in developing (poorer) countries. The World Health Organization has described obesity as one of today's most neglected public health problems, affecting every region of globe. Obesity is a complex problem related to food habits as well as fats accumulated by child which increase his weight more than required. It has been observed that "Childhood obesity is a condition where excess body fat negatively affects a child's health or well-being"(Kopelman,2005).

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Globally, an estimated 43 million preschool children (under age 5) were overweight or obese in 2010, a 60 per cent increase since 1990.The problem affects countries rich and poor, and by sheer numbers, places the greatest burden on the poorest: Of the world's 43 million overweight and obese preschoolers, 35 million live in developing countries (Ramchandran *et al.*,2002). By 2020, if the current epidemic continues unabated, 9 per cent of all preschoolers will be overweight or obese – nearly 60 million children (de Onis and Blossner,2000). Various studies done in India from 2002-2012 inicate a rising trend in the prevalence overweight and obesity in children and adolescents (Chattrejee, 2002; Moha *et al.*, 2004; Khadilkar and Khadilkar, 2004; Marwaha *et al.*,2006 and Chakraborty *et al.*,2012).

Internationally recognized cut off points of BMI for defining overweight is BMI >25.0kg/m and obesity is >30.0kg/m. However percentage of body fat is not uniform among regional populations (Lissner *et al.*,2010). Increase in health related risk factors and co

morbidities associated with obesity occur at lower BMI in Asian populations than in other ethnic groups. Thus lower cut- off points for Asians were identified for overweight (BMI>23.0kg/m) and obesity (BMI>25.0kg/m) (WHO, 2004; Shree G. *et al.*, 2013).

The relation between socio- economic states and weight shows interesting dichotomy. Urban poor I developed countries appear vulnerable due to poor diet and decreased physical activity; urban rich in developing countries remain at risk due to an increased affinity to the western type of lifestyle. Increased prevalence of obesity in high Socio- Economic States private schools could be the result of generous pocket money, availability of domestic help and traveling to school by vehicles (Singh *et al.*, 2008). Against this background, the present study was undertaken to observe the relation between prevalence of overweight and obesity in school going children and socio-demographic factors in the economically, industrially and culturally fast growing districts of *i.e.* Pune, Nashik and Ahmednagar in Western Maharashtra.

METHODOLOGY

An exploratory research has been conducted in three districts such as Pune, Ahmednagar and Nasik of Western Maharashtra. Total 600 children having age between 7 to 12 years including male and female were selected from obese children by (purposive) simple random sampling method. About 200 obese children were randomly selected from each district. Out of 600 obese children 224 were male and 376 were female. The obese children were selectedby calculating BMI through school information of height and weight of the children.

Socio-demographic data were collected in the form of type of family, size of family, parents' educational status,family income, number of family members and Family's surrounding area. All the anthropometric measurements were taken in the school premises with standard procedure described by Jelliffe (1966). Overweight and obesity was assessed by BMI for age. Student who had BMI for age>85th and <95th percentile of reference population were classified as overweight. Students who had BMI for age >95th percentile of reference population were classified as obese. The lower cut- off points for Asians were identified for overweight (BMI>23.0kg/m) and obesity (BMI> 25.0kg/m) (WHO, 2004).The collected data is pooled, tabulated andanalysed statistically.

OBSERVATIONS AND ASSESSMENT

The calculated values of body mass index (BMI) is reported in Table 1 and Fig. 1.

It indicates that 62.22 boys and 68.33 per cent girls were overweight having BMI between 23 to 27 while 37.78 and 31.67 per cent boys and girls were obese having more than 27 BMI.

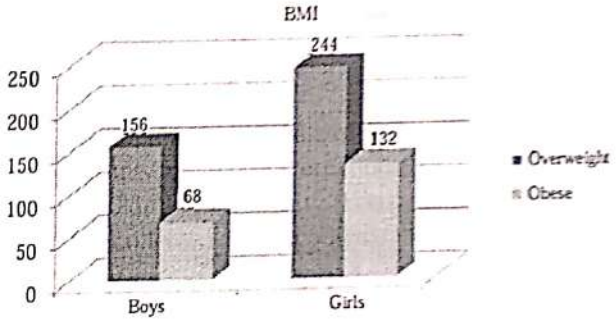

Fig. 1 : Classification of selected obese children on BMI

BMI of overweight and obese children:

Hypothesis: there is no significant difference between boys and girls with respect to BMI

H0: Oi = Ei H1: Oi ≠ Ei (Oi: observed frequency, Ei: expected frequency of BMI)

Calculated value of $\chi^2 = 1.07$, Critical value of χ^2 at 5 per cent level of significance = 3.841,

As Calculated value of χ^2 lies in the acceptance region, accept H0.

Therefore, there is no significant difference between boys and girls with respect to BMI.

The data about the type of family of the obese children is presented in Table 2 and Fig. 2.Socio demographic variables of overweight and obese children revealed that majority of children *i.e.* 64.44 and 62.9 per cent boys and girls were from nuclear families, respectively, while 35.56 and 34.84 per cent boys and girls were from joint family.

Table 1 : BMI of obese school going children

BMI	Boys (90)	Percentage	Girls(221)	Percentage
Overweight	56	62.22	151	68.32
Obese	34	37.78	70	31.67

Table 2 : Demographic profile of selected obese school going children

Demographic details	Boys(224)	Girls(376)
Type of family		
Joint	79 (35.27)	131(34.84)
Nuclear	143(63.84)	237(63.03)
Extended	02(7.14)	8(2.13)
Size of family		
Small	61 (27.23)	41 (10.90)
Medium	106 (47.32)	212(56.38)
Big	57 (25.45)	123(32.71)
Living surrounding of family		
Urban	97(43.30)	173(46.01)
Semi-urban	42(18.75)	55(14.62)
Slum	02(.89)	08(2.13)
Rural	83(37.05)	140(45.21)
Religion of the Family		
Hindu	202(90.18)	349(92.82)
Muslim	12(5.36)	14(3.72)
Christian	08(3.57)	09(2.39)
Jain	02(0.8)	4(1.06)
Mother's Education		
Higher secondary	47(20.98)	68(18.09)
Graduate	153(68.30)	182(48.40)
Post graduate	24(10.71)	126(33.51)
Father's Education		
Higher secondary	19(8.48)	61(16.22)
Graduate	116(51.78)	203(53.99)
Post graduate	89(39.73)	112(29.79)
Annual Income		
Up to 2 lacs	49(21.88)	87(2.14)
2-5 lacs	78(34.82)	119(31.65)
More than 5 lacs	97(43.30)	170(45.21)
BMI		
Overweight	156(61.64)	244(64.89)
Obese	68(30.36)	132(35.11)

Figures in parenthesis indicate percentage

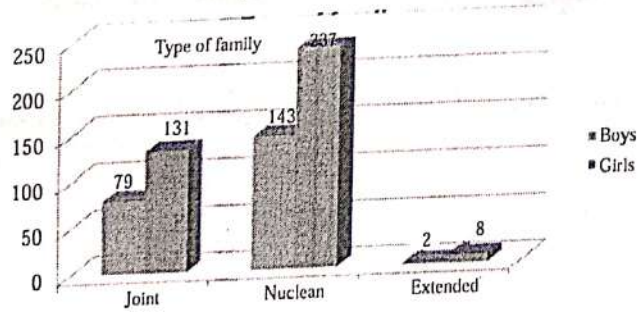

Fig. 2 : Type of family of obese children

Data of the size of the family of obese children is given in Fig. 3.It is depicted from Table 2 that 46.67per cent boys sand 56.11 per cent girls were from medium size of family having 3 to 6 members in family. Nearly 32 per cent boys and girls were from big size family more than 6 members in family.

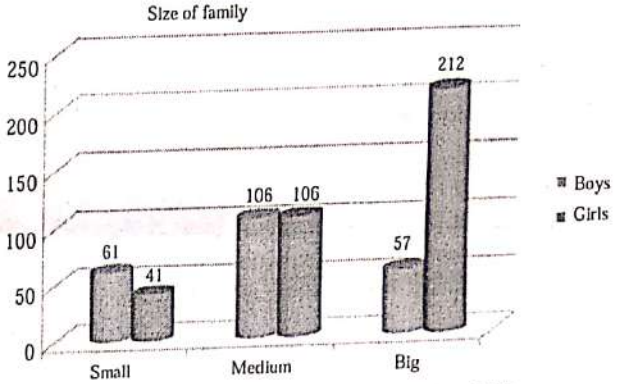

Fig. 3 : Size of family of selected obese school going children

Fig. 4 indicates that mostly children were belonging with hindureligion (76 to 85 %) from rural area 43 and 47 per cent boys and girls, respectively, followed by 34.44 per cent boys and 33.03 per cent girls semi- urban background.

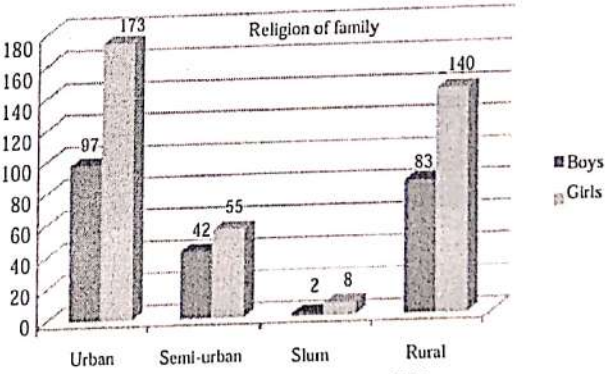

Fig. 4 : Religion of family of selected obese children

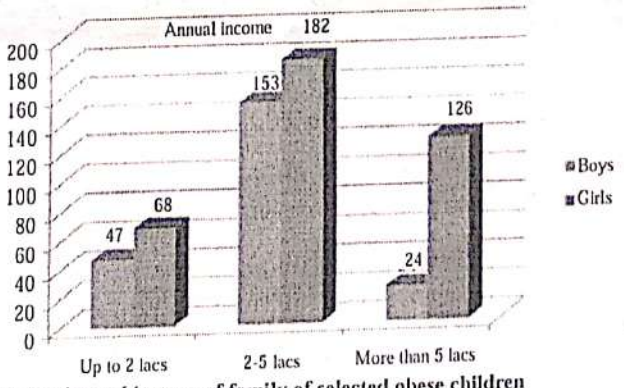

Fig. 5 : Annual income of family of selected obese children

It is observed that 41 and 56 per cent families having better jobs and income more than 5 lacs, while 46.67 and 34.84 per cent families of boys and girls, respectively having annual income between 2 to 5 lacs (Fig. 5). The results of Singh *et al.* (2008) study among Delhi school children in the age group of 10-16 years had shown that increase in prevalence of obesity is inhigher income group. The results are also confirmed with the results of Goyal *et al.* (2010), Kotian and Kotian (2010), Sharma *et al.* (2007) and Sangha *et al.* (2006).

Conclusion:

From the above data, it is concluded that majority of obese children were from nuclear family, medium size of family, urban living background, hindu religion, graduate parents and higher income(>5 lacs/year).

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Research Paper

A study on eating habits of selected obese school going children

■ RAJKUMAR M.KAMBLE AND ANURADHA DUBEY

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■ **ABSTRACT :** Nutritional status of obese school going children were assessed in Western Maharashtra *i.e.* Pune, Nashik and Ahmednagar districts. For this study, 600 obese school going children were selected, from which 224 boys and 376 were girls in 6- 16 age group of 6-16 years. The obesity of these children were assessed by using BMI. Eating habits of these children were examined by using questionnaire and dietary recall method. It is found that eating habits like preference for junk food, skipping meal and eating in front of TV marked as correlating factors for its effect on overweight and obesity.

■ **KEY WORDS:** Eating habits, Obese school, BMI, TV marked

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Obesity is a global nutrition concern confined not only in adults but also in children and adolescents. With changing life-style and growing urbanization, there has been a rapid increase in health problems related to over nutrition such as overweight and obesity in developing countries worldwide (Bhave *et al.*, 2004). Childhood obesity is a condition where excess body fat negatively affects a child's health or well being (Briefel and Johnson, 2004). The prevalence rate of overweight and obesity in India are 12.8 and 10.3 per cent, respectively and about 30 per cent of obesity begins in childhood (Centers for disease controland prevention, 2009). This may have major implications towards increasing prevalence of non-communicable diseases like diabetes, hypertension and cardiovascular disease in early adulthood (Chakraborty *et al.*, 2012 and Kopelman, 2005). The negative life style, lack of physical activity and consumption of unhealthy foods are contributing factors for childhood over weight and obesity (Kumar *et al.*, 2007). Studies in the US have observed a change across the age groups that they consume a large proportion of their daily food intakevia snacks rather than sit- down meals , favouring quick, easy –often non-nutritious-foods and high-calorie treats be it in the form of processed foods, street foods, fast foods or junk foods (McMaster *et al.*, 2005). Against this background, the present study was undertaken to assess the nutritional status especially eating habits of overweight and obese children and reasons for accepting junk food always.

RESEARCH METHODS

An exploratory research has been conducted in three districts such as Pune, Ahmednagar and Nasik of Western Maharashtra. Total 600 (obese) children among obese children having age between 7 to 12 years including male and female were selected by (purposive) simple random sampling method. About 200 obese children were randomly selected from each district. Out of 600 obese children 224 were male and 376 were female. The obese children were selected by calculating BMI through school information of height and weight of children with prior permission of principal.

All the anthropometric measurements were taken in the school premises with standard procedure. We have recorded body weight to the nearest 0.1 kg using a standard balance scale with subjects barefoot and wearing light indoor clothing. Body height was measured by scale was used up to an accuracy of 1 mm. Body Mass Index (BMI) is defined as the ratio of body weight to body height squared, expressed as kg/m^2. Overweight and obesity was assessed by BMI for age. Student who had BMI for age>85th and <95th percentile of reference population were classified as overweight. Students who had BMI for age >95th percentile of reference population were classified as obese. The lower cut- off points for Asians were identified for overweight (BMI>23.0kg/m) and obesity (BMI>25.0kg/m) (WHO, 2004). The collected data were pooled, tabulated and analysed statistically.

Table 1 : Eating habits of selected obese children

Particulars	Male (224)		Female (376)	
	Frequency	Per cent	Frequency	Per cent
Eating pattern				
Vegetarian	68	30.36	157	41.76
Non-vegetarian	156	69.64	219	58.24
Diet frequency				
2 times	97	43.30	139	36.96
3 times	82	36.60	172	45.74
4 times	45	20.08	65	17.28
Type of food in tiffin				
Bread based	82	36.60	49	13.03
Fried foods	39	17.41	63	16.75
Chiwada	21	9.37	28	7.44
Laddu	19	8.48	21	5.58
Thalipith	7	3.12	19	5.05
Chapati bhaji	56	25.00	196	52.12
Outside food in lunch time				
Wada Pav	102	45.53	94	25.00
Kurkure	154	68.75	177	47.07
Wafers	87	38.63	134	35.63
Choclates/Cadburry	39	17.41	89	23.67
Bhel	47	20.98	79	21.01
Type of meal eating with family				
Breakfast	31	13.83	84	22.34
Lunch	18	8.04	27	9.18
Dinner	48	21.42	98	26.06
Activity during food intake				
Watching TV	134	59.82	269	71.54
Playing on mobiles	71	31.69	58	15.42
Reading	13	05.80	28	7.45
Listening to stories	06	02.68	21	5.58

■ RESEARCH FINDINGS AND DISCUSSION

The present study was conducted in Nashik, Pune and Ahmednagar districts of Western Maharashtra on randomly selected 600 overweight and obese children, among them 224 were boy and 376 were girls of 6-17 years of age. From which 69 per cent and 65 per cent boys and girls were overweight, respectively while 30and 35 per cent boys and girls were obese, respectively. It has been seen that the prevalence of obesity was higher in girls when compared with that of boys. These findings are in confirmation with the study of Kumar *et al.* (2007); McMaster *et al.* (2005) and Kavitha Shree *et al.* (2013) who observed the prevalence of obesity and overweight was higher in school going girls than boys.

Majority of boys and girls *i.e.* 69.64 per cent and 58 per cent were non- vegetarian, respectively. Many studies suggested that type of diet is responsible factor for weight gain. This result is in confirmation with Ramachandran *et al.*(2002) in Kerala who reported slightly higher prevalence in obesity among non-vegetarian than vegetarian. The children consuming vegetarian diet tend to be lighter than non–vegetarian. It is also observed that 43 and 37 per cent boys and girls were taking only 2 times diet, respectively while 37 and 46 per cent boys and girls were taking diet 3 times, respectively. Only 20 per cent boys and 17 per cent girls were following 4 time meal pattern. This indicates that skipping meal is more common. Similarly WHO reported that skipping breakfast may lead to over consumption in next meal.

It can be concluded that skipping meal was common for both boys and girls.

Majority of the children were carrying tiffin in school. The content of tiffin was chapatti-bhaji mostly in girls (52.12%). But 72 per cent boys were having bread based food item, fried foods, chiwada and laddoo as a tiffin content. Instead of tiffin both boys and girls were interested in eating out side food like wada pav, kurkure, wafers, chocolates/Cadbury and bhel. Girls were more interested in chocolates/Cadbury. Some times children eat more foods which are high in sugar and energy rich foods. Hence energy intake is higher than expenditure and contributing to weight gain (WHO, 2003).This is also a serious issue which was observed only in 43 per cent boys and 58 per cent girls were taking at least one meal with family members. While having food or meal 61 per cent boys and 72 per cent girls were watching TV and 32 per cent boys were playing games on mobiles. TV viewing while eating is a contributing factor to childhood obesity. These results are in confirmation with the findings of Kavitha Shree *et al.* (2013).

Hypothesis: there is no significant different between male and female children with respect to obesity and overweight.

Response	Male	Female	Total
Overweight	156	244	400
Obesity	68	132	200
Total	224	376	600

H_0: Oi = Ei v/s H_1: Oi ≠ Ei (Oi: observed, Ei: expected frequency of response)

Calculated value of $\chi^2 = 1.424$, critical value of $\chi^2 = 3.841$.

Frequency of diet	Male	Female	Total
2	97	139	236
3	82	172	254
4	45	65	110
Total	224	376	600
Mean	2.77	2.80	
S.D.	0.763	0.711	
C.V.	27.57	25.35	

As calculated value of χ^2 lies in the acceptance region, accept H_0.

Therefore, there is no significant difference between male and female children with respect to obesity and overweight.

Table 2 indicates the preferences given to junk food by selected overweight and obese children. The children preferred mostly Kurkure, fried snacks, wafers and magi noodles by both genders.But it seems that boys preferred cold drinks and girls preferred chocolates mostly.

Table 3 indicates that the reasons given by children for preferences of junk food. It was found that all children were habitual for junk foods.

There is no difference between male (224) and female (376) children in the preference to junk food which is habitual, all *i.e.* 100 per cent children responses that it is habitual.

H_0: $P_1 = P_2$ v/s H_1: $P_1 > P_2$ (P: Population proportion of reason of preferences)

Sample proportions: $p_1 = 0.882$, $p_2 = 0.863$

Table 2 : Junk food preferences given by overweight and obese children

Sr. No.	Type of foods	Preferences of food items			
		Male		Female	
		Likes	Dislikes	Likes	Dislikes
1.	Chips/wafers	88.8	11.2	93.6	6.4
2.	Fried snacks	95.5	4.5	91.5	8.5
3.	Pizza /burger	80.4	19.6	77.1	22.9
4.	Chocolates	85.7	14.3	85.4	14.6
5.	Cold drinks	93.3	6.7	77.1	22.9
6.	Cake and pastries	77.7	22.3	80.1	19.9
7.	Chinese food	75.5	24.5	78.7	21.3
8.	Fruit juices	79.9	20.1	74.5	25.5
9.	Kurkure	93.8	6.2	91.5	8.5
10.	Magi noodles	91.1	8.9	83.5	16.5

Table 3 : Reasons behind preferences for junk food

Reason of preferences	Response	
	Male (%)	Female (%)
Habitual	100	100
Impact of advertisement	84.8	85.4
Easily available	85.7	80.31
Peer pressure	89.7	87.0
Convenient to eat	92.4	92.6

Calculated value of Z = 92.66, critical value of Z at 5 per cent level of significance = 1.64 (one sided test).

As calculated value of Z lies in the critical region, hence reject H_0.

Therefore, the preferences to junk food by male students are more than that of female students.

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Nutritional status of selected obese school going children in Western Maharashtra

RAJKUMAR M. KAMBLE AND ANURADHA DUBEY

Nutritional status of obese school going children were assessed in Western Maharashtra *i.e.* Pune, Nashik and Ahmednagar districts. For this study, 600 obese school going children were selected, from which 224 boys and 376 were girls in 6-16 age group of 6-16 years. The obesity of these children were assessed by using BMI. The nutritional status of these children were examined by using questionnaire and dietary recall method. It is found that the food intake especially cereals, pulses and fat based foods are found significantly excess and vegetables and fruits consumption noted less by these children. However, the nutrients intake like energy and protein were noticed excess than that of their standard level. Whereas vitamins and minerals intake were found less among these children which were as correlating factors for its effect on overweight and obesity in children.

Key Words : Childhood obesity, School going obese children, Nutritional status, Food intake

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INTRODUCTION

Obesity is a complex problem related to food habits as well as fats accumulated by child which increase weight more than normal. It has been observed that "Childhood obesity is a condition where excess body fat negatively affects a child's health or well-being" (Kopelman, 2005).

Obesity is a universal problem having different ramifications national, regional and local. The pace at which the obesity epidemic is threatening the world's children and adolescents has raised immediate public health concern. Scholars have studied obesity and overweight in their own perspective. "The term overweight rather than obese is often used in children as it is less stigmatizing"(Bessesen, 2008). Due to availability of square food and affinity of parents the school children are provided more nutritious food than they require, which leads to complex situation of obesity.

According to the estimation of prevalence of overweight and obesity among school aged children aged 5-17 years collected by the international association for the study of obesity, one in five children is affected by excess body weight across all countries and in Greece, United States and Italy, the figure is closer to one third.Only in China, Korea and Turkey 10 per cent or less of children are overweight. In most countries, boys have higher rates of overweight and obesity than girls (International Association for the study of obesity, 2014). It seems in most of the countries the problem of obesity and fatness is prevailing and it requires scientific treatment. In the last few decades, the childhood obesity has tripled and it has reached epidemic levels in

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developed countries (Ogden *et al.*, 2010). Thus in developed countries nutrition facilities are available and parents do not care regarding square meals and balanced calories. About 10 per cent of school children aged between 5 to 17 years around the globe are overweight, out of which 70 per cent grow up to become obese adults (Kuczmarski and Flegal, 2000 and Flegal *et al.*, 2002). It shows the problem is critical and burning in all the parts of the world. The negative life style, lack of physical activity and consumption of unhealthy foods are contributing factors for childhood over weight and obesity (Kumar *et al.*, 2007). Studies in the US have observed a change across the age groups that they consume a large proportion of their daily food intake via snacks rather than sit- down meals, favouring quick, easy –often non-nutritious-foods and high-calorie treats be it in the form of processed foods, street foods, fast foods or junk foods (McMaster *et al.*, 2004). Hence, nutritional profile of the children is very important factor In other words young children are making unhealthy eating choices and are not getting enough physical activity (Wechsler *et al.*, 2004). Recent data from (World Health Organization, 2007) revealed that the prevalence of childhood obesity worldwide is 16.5 per cent and in India it accounts ti 12.4 per cent in boys and 9.9 per cent in girls. According to Knoon (2002), the prevalence rates of overweight(12.8 %) and obesity (10.3 %) among children in India is an alarming situation due to improper nutritional profile (Knoon, 2002).

Against this background, the present study was undertaken to assess the nutritional status especially eating habits of overweight and obese children and reasons for accepting junk food always.

METHODOLOGY

An exploratory research has been conducted in three districts such as Pune, Ahmednagar and Nasik of Western Maharashtra. Total 600 (obese) children among obese children having age between 7 to 12 years including male and female were selected by (purposive) simple random sampling method. About 200 obese children were randomly selected from each district. Out of 600 obese children 224 were male and 376 were female. The obese children were selected by calculating BMI through school information of height and weight of children with prior permission of principal.

All the anthropometric measurements were taken in the school premises with standard procedure. We have recorded body weight to the nearest 0.1 kg using a standard balance scale with subjects barefoot and wearing light indoor clothing. Body height was measured by scale was used up to an accuracy of 1 mm. Body Mass Index (BMI) is defined as the ratio of body weight to body height squared, expressed as kg/m^2. Overweight and obesity was assessed by BMI for age. Student who had BMI for age>85th and <95th percentile of reference population were classified as overweight. Students who had BMI for age >95th percentile of reference population were classified as obese. The lower cut- off points for Asians were identified for overweight (BMI>23.0 kg/m) and obesity (BMI>25.0kg/m) (WHO, 2004). The collected data were pooled, tabulated and analysed statistically.

The 24 hours dietary recall method is commonly used method in large nutritional surveys to collect dietary intake information of the individuals. The food intake within 24 hours were recorded in the structured questionnaire. The type of food consumed, amount of food, method used for food preparation, type of food consumption and other details related to food intake were asked to the mothers of school going children and their memorable replies were recorded. The 24 hours dietary recall was taken for subsequent three days and means of each ingredient was taken as24 hours dietary recall. From the raw ingredients amounts, the nutritive value of each food item was calculated by using the nutritive values given by Gopalan (2006). It was compared with Recommended Dietary Allowances (RDA) of nutrients for those of specific age groups. Along with nutritive value amount of each food group was calculated, recorded and compared with Balanced Dietary Allowance (BDA).

OBSERVATIONS AND ASSESSMENT

The data regarding food intake pattern of school going obese boys of 7 to 9 years age is given in Table 1. It explained that cereal intake by obese boys was noted 207.5g. The per cent of adequacy of cereal was excess as compared with RDA (115.3). The average pulses and legumes were also observed excess *i.e.* 106.7 per cent. However average intake of green leafy vegetables was found very poor as 15g. As compared with their daily requirement, the green leafy vegetables intake was found very inadequate level. Intake of roots and tubers was also

found excess as compared with daily requirements (135g). The intake of fruits and milk were noticed very low adequate level *i.e.* 10 and 42 per cent, respectively. The intake of sugar and jaggery was observed as 49.5g and was found in excess *i.e.* 247.5 per cent. Fats and oils in the diet of school going boys was found 62.5g which was found excess (208.3%). Consumption of non-vegetarian foods *i.e.* eggs, meat/fish/poultry among these school going obese children found non-significantly more than their RDA. It is observed from table that calculated Z values of average intake of cereals, pulses, green leafy vegetables, roots and tubers, fats and oils and sugar and jaggery are negatively significant which may be the leading factors for the obesity among school going boys.

The data regarding food intake pattern of school going obese girls of 7 to 9 years age is given in Table 2. It reveals that cereal intake by obese girls was noted 215g. The per cent of adequacy of cereal was excess as compared with RDA (119.4%) and negatively significant. The average intake of pulses and legumes were also observed excess *i.e.* 102.5 per cent. However, average intake of green leafy vegetables and other vegetables were found to be very poor as 21g and 75g, respectively. As compared with their daily requirement, the green leafy vegetables intake was found very inadequate level (21 %). Intake of roots and tubers was also found excess as compared with daily requirements (122.5g). The intake of fruits and milk were noticed to be very low adequate level *i.e.* 15 and 58 per cent, respectively when compared with RDA. The intake of sugar and jaggery was observed as 50g and was found in excess *i.e.* 250 per cent. Fats and oils in the diet of school going girls was found 60g which was found excess (200%) when compared with RDA. Whereas, non-significantly more consumption of non-vegetarian foods *i.e.* eggs (32.0g) and meat/ fish/ poultry (33.8g) are noticed in these children. Hence, statistically also it is found that the intake of cereal, pulses, roots and tubers, fats and oils, and sugar and

Table 1 : Average intake of food groups by obese boys of 7-9 years age

Food groups	RDA	Average food intake	Z Value	Percent of adequacy
Cereals(g)	180	207.5	-(8.1)**	115.3
Pulses(g)	60	64	-(1.3)NS	106.7
Green leafy vegetables(g)	100	15	-(13.1)**	15
Other vegetables(g)	100	80	(4.9)**	80
Roots and tubers(g)	100	135	-(6.4)**	135
Fruits(g)	100	10	(15.1)**	10
Milk(ml) and milk product	500	210	(8.7)**	42
Fats and oils(g)	30	62.5	-(7.4)**	208.3
Sugar and jaggery (g)	20	49.5	-(8.3)**	247.5
Eggs (g)	30	35.1	-(1.6)^{NS}	117.0
Meat/fish/poultry(g)	30	34.1	-(1.3)^{NS}	113.7

** indicates significance of value at P=0.01, NS=Non-significant

Table 2 : Average intake of food groups by obese girls of 7-9 years age

Food groups	RDA	Average food intake	Z Value	Per cent of adequacy
Cereals(g)	180	215	-(15.6)**	119.4
Pulses(g)	60	61.5	-(0.5)^{NS}	102.5
Green leafy vegetables(g)	100	21	(12.3)**	21
Other vegetables(g)	100	75	(13.9)**	75
Roots and tubers(g)	100	122.5	-(4.4)**	122.5
Fruits (g)	100	15	(13.1)**	15
Milk (ml) and milk product	500	290	(7.1)**	58
Fats and oils(g)	30	60	(-8.1)**	200
Sugar and jaggery(g)	20	50	-(9.8)**	250
Eggs (g)	30	32.0	-(0.8)^{NS}	106.7
Meat/fish/poultry(g)	30	33.8	-(0.9)^{NS}	112.7

** indicates significance of value at P=0.01, NS=Non-significant

jaggery are negatively significant with RDA.

The Table 3 reveals the information about average intake of food groups consumed by obese boys of 10 to 12 years of age.It is observed that cereal intake by obese boys was noted 325g. The per cent of adequacy of cereal was excess as compared with RDA (108.3%) and negatively significant. The average intake of pulses and legumes were also observed excess *i.e.* 115 per cent when compared with RDA. However average intake of green leafy vegetables was found to be very poor as 27.5g. As compared with their daily requirement, the green leafy vegetables intake was found very inadequate level (27.5 %). Intake of other vegetables and roots and tubers were also found excess as compared with daily requirements *i.e.* 155 and 170 per cent, respectively. The intake of fruits and milk were noticed to be very low adequate level *i.e.* 27.5 and 60 per cent, respectively when compared with RDA. The intake of sugar and jaggery was observed as 62.5g and was found in excess *i.e.* 208.3 per cent. Fats and oils in the diet of school going boys was found 60g which was found excess(171.4%) when compared with RDA. Non-vegetarian intake *i.e.* eggs and meat/fish/ poultry was noted non-significantly more in this age group of obese boys. Hence, statistically also it is found that the intake of cereal, pulses, other vegetables, roots and tubers, fats and oils, and sugar and jaggery are negatively significant with RDA.

The Table 4 reveals the information about average intake of food groups consumed by obese girls of 10 to 12 years of age.It is observed that cereal intake by obese girls was noted 275g. The per cent of adequacy of cereal was excess as compared with RDA (114.6%) and negatively significant. The average intake of pulses and legumes were also observed excess *i.e.* 110.8 per cent when compared with RDA. However average intake of green leafy vegetables and other vegetables were found to be poor as 30g and 150g, respectively. As compared with their daily requirement, the green leafy vegetables

Table 3 : Average intake of food groups by obese boys of 10-12 years age

Food groups	RDA	Average food intake	Z Value	Per cent of adequacy
Cereals(g)	300	325	-(8.0)**	108.3
Pulses(g)	60	69	-(1.8)^{NS}	115
Green leafy vegetables(g)	100	27.5	(12.1)**	27.5
Other vegetables(g)	200	310	-(16.5)**	155
Roots and tubers(g)	100	170	-(12.7)**	170
Fruits(g)	100	27.5	(14.6)**	27.5
Milk(ml) and milk product	500	300	(5.7)**	60
Fats and oils(g)	35	60	-(5.5)**	171.4
Sugar and jaggery(g)	30	62.5	-(9.2)**	208.3
Eggs (g)	30	31.9	-(0.6)^{NS}	106.3
Meat/fish/poultry(g)	30	37.1	-(1.6)^{NS}	123.7

** indicates significance of value at P=0.01, NS=Non-significant

Table 4 : Average intake of food groups by obese girls of 10-12 years age

Food groups	RDA	Average food intake	Z Value	Per cent of adequacy
Cereals(g)	240	275	-(16.1)**	114.6
Pulses(g)	60	66.5	-(4.4)**	110.8
Green leafy vegetables (g)	100	30	(4.3)**	30
Other vegetables(g)	200	150	(2.8)**	75
Roots and tubers(g)	100	165	-(2.6)**	165
Fruits (g)	100	30	(2.8)**	30
Milk (ml) and milk product	500	220	(5.9)**	44
Fats and oils (g)	35	57.5	-(3.9)**	164.3
Sugar and jaggery (g)	30	56.5	-(5.1)**	188.3
Eggs (g)	30	38.3	-(3.4)**	126.7
Meat/fish/poultry(g)	30	32.7	-(1.3)^{NS}	109

**indicates significance of value at P=0.01, NS=Non-significant

intake was found very inadequate level (30 %) and intake of other vegetables was 75 per cent. Intake of roots and tubers were also found excess as compared with daily requirements *i.e.*165 per cent. The intake of fruits and milk were noticed to be very low adequate level *i.e.* 30 and 44 per cent, respectively when compared with RDA. The intake of sugar and jaggery was observed as 56.5g and was found in excess *i.e.* 188.3 per cent. Fats and oils in the diet of school going girls was found 57.5g which was found excess (164.3%) when compared with RDA. Consumption of eggs found significantly more *i.e.*38.3g/ day among 10 to 12 years in age obese girls. Whereas, meat/fish/poultry intake reported slightly and non-significantly more than RDA in these girls. Hence, statistically also it is found that the intake of cereal, pulses, roots and tubers, fats and oils, and sugar and jaggery are negatively significant with RDA.

The nutrients intake by school going obese children was calculated from their food intake by use of the standard method. The averages were calculated, compared with RDA of specific age group. The data is depicted in Table 5 to 8.

The data about average nutrients intake by school going obese boys in the age of 7 to 9 years can be seen from Table 5. It indicates that the average calorie intake by school going boys was noted 2200 Kcal. When this calorie intake is checked at per cent of adequacy level, it was found in excess (*i.e.* 130.2 %). There is negatively significant difference when compared with standards. The amount of protein consumption by school going obese boys was reported 51.5g which is noticed negatively significant more (174.6 %) than that of normal standard. Fat consumption in boys was recorded as 47g and per cent of fat consumption was reported as in excess (156.7%). There is also noticed negatively significantly more than that of their normal RDA.

B-complex vitamins like Vitamin B_1(mg), Vitamin B_2(mg) and Vitamin B_3(mg), Vitamin C(mg) and β-carotene (μg) were also calculated in comparison with their Standards. About 0.9mg of vitamin B_1, 0.9mg of Vitamin B_2 and 11.0mg of Vitamin B_3 consumption were seen in boys. There is no significant difference when

Table 5 : Average nutrients intake by obese boys (7 to 9 years)

Nutrients	RDA	Average nutrient intake	Z value	Per cent of adequacy
Calories(Kcal)	1690.0	2200.0	--(7.8)**	130.2
Protein(g)	29.5	51.5	-(6.6)**	174.6
Fat(g)	30.0	47.0	-(7.6)**	156.7
Vitamin B_1 (mg)	0.8	0.9	$(0.9)^{NS}$	112.5
Vitamin B_2(mg)	1.0	1.0	$(0.01)^{NS}$	100
Vitamin B_3(mg)	13.0	11.0	$(1.4)^{NS}$	84.6
Vitamin C(mg)	40.0	34.0	(5.1)**	85
β-carotene(μg)	4800.0	3850.0	(8.9)**	80.2
Calcium(mg)	600.0	390.0	(2.4)*	65
Iron(mg)	16.0	16.5	$(0.7)^{NS}$	103.1

* and ** indicate significance of values at P=0.05 and 0.01, respectively NS=Non-Significant

Table 6 : Average nutrients intake by obese girls (7 to 9 years)

Nutrients	RDA	Average nutrients intake	Z Value	Per cent of adequacy
Calories(Kcal)	1690.0	2025.0	--(8.1)**	119.8
Protein(g)	29.5	46.5	-(6.8) **	253.1
Fat(g)	30.0	44.0	-(8.7)**	146.7
Vitamin B_1 (mg)	0.8	0.88	$(0.09)^{NS}$	84.6
Vitamin B_2(mg)	1.0	0.95	$(0.01)^{NS}$	110
Vitamin B_3(mg)	13.0	11.0	$(1.8)^{NS}$	95
Vitamin C(mg)	40.0	38.5	(1.6)**	84.6
β-carotene(μg)	4800.0	4180.0	(7.3)**	96.3
Calcium(mg)	600.0	385.0	(3.2)*	87.1
Iron(mg)	16.0	15.0	$(0.01)^{NS}$	93.8

* and ** indicate significance of values at P=0.05 and 0.01, respectively NS=Non-Significant

compared with RDA. The vitamin B_3 consumption in boys was noticed in poor adequate level. The consumption of vitamin C (mg) and β-carotene (μg) were 34 and 3850, respectively. The consumption were notice in poor adequate level *i.e.* 85 and 80.2 per cent, respectively when compared with RDA.

The mineral intake such as calcium (mg) and iron (mg) among school going boys were noted 390 and 16.5, respectively. The intake level of calcium was very less and did not reach their daily intake recommendations. This may be due to many boys showed very less intake of milk.

On the whole, it is seen that the average consumption of major nutrients were excess and minor nutrients were on their borderline or inadequate than their recommended dietary allowances among 7 to 9 years school going obese boys. A similar data about 7 to 9 years school going obese girls was put in Table 6.

Table 6 reveals that the average calorie intake by school going girls was noted as 2025 Kcal. When this calorie intake is examined at per cent of adequacy level, it was found in excess. There is negatively significant difference when compared with their standards. The amount of protein consumption by school going obese girls was reported as 46.5g which is noticed negatively significant difference. The per cent of adequacy level for protein was noted excess *i.e.* 253.1 per cent. Fat consumption in girls was recorded as 44g and per cent of fat consumption was reported as in excess(146.7%). There is also noticed negatively significant difference.

In case of consumption of B-complex vitamins like Vitamin B_1(mg), Vitamin B_2(mg) and Vitamin B_3(mg), Vitamin C(mg) and β-carotene(μg)were found non-significantly lower than that of their Standards. Vitamin B_1(0.88mg), Vitamin B_2 (0.95mg) and 11.0mg Vitamin B_3(11.0mg) consumption were seen in boys. However intake of vitamin B_3 in girls was noticed more poor adequate level. The consumption of vitamin C (mg) and β-carotene (μg) were 38.5 and 4180, respectively. The consumption was noticed in poor adequate level *i.e.* 84.6 and 96.3 per cent, respectively when compared with their RDA.

Table 7 : Average nutrients intake by obese boys of 10 to 12 years

Nutrients	RDA	Average nutrients intake	Z values	Per cent of adequacy
Calories(Kcal)	2190.0	2475.0	--(5.5)**	113.0
Protein(g)	39.9	51.5	-(4.0)**	129.1
Fat(g)	35.0	52.0	-(4.1)**	148.6
Vitamin B_1 (mg)	1.1	0.85	$(0.2)^{NS}$	77.3
Vitamin B_2(mg)	1.3	1.1	$(0.5)^{NS}$	84.6
Vitamin B_3(mg)	15.0	12.6	(2.6)*	84.0
Vitamin C(mg)	40.0	31.5	(3.5)**	78.8
β-carotene(μg)	4800.0	3400.0	(8.5)**	70.8
Calcium(mg)	800.0	560.0	(2.9)**	70.0
Iron(mg)	21.0	20.5	$(1.8)^{NS}$	97.6

* and ** indicate significance of values at P=0.05 and 0.01, respectively NS=Non-Significant

Table 8 : Average nutrients intake by obese girls of 10 to 12 years

Nutrients	RDA	Average nutrients intake	Z cal	Per cent of adequacy
Calories(Kcal)	2010.0	2340.0	--(10.4)**	116.4
Protein(g)	40.4	47.5	-(3.0)**	117.6
Fat(g)	35.0	48.0	-(4.1)**	137.0
Vitamin B_1 (mg)	1.0	0.85	$(0.7)^{NS}$	85.0
Vitamin B_2(mg)	1.2	1.05	$(0.3)^{NS}$	87.5
Vitamin B_3(mg)	13.0	11.95	$(0.7)^{NS}$	91.9
Vitamin C(mg)	40.0	37.0	$(1.2)^{NS}$	92.5
β-carotene(μg)	4800.0	3400.0	(8.5)**	70.8
Calcium(mg)	800.0	455.0	(5.6)**	56.9
Iron(mg)	27.0	22.0	$(2.3)^{NS}$	81.5

** indicate significance of value at P=0.01 NS= Non-significant

The mineral intake such as calcium (mg) and iron (mg) among school going girls were noted 385 and 15 respectively. The intake level of calcium and iron were less and did not reach their daily intake recommendations. This may be because many girls showed very less intake of green leafy vegetables and milk.

In the same way as boys, the schools going obese girls are also noticed excess consumption of major nutrients such as calories, protein and fats whereas minor nutrients intake was noted at inadequate level.

The data about average nutrients intake of school going obese children of age in 10 to 12 years was kept in Table 7 and 8.

Data presented in Table 7 is clearly stated that the average calorie intake by school going boys was noted 2475 Kcal. When this calorie intake is checked at per cent of adequacy level, it was found in excess (113%). There is negatively significant difference when compared with standards. The amount of protein consumption by school going obese boys was reported 51.5g which is noticed negatively significant difference. Whereas Fat consumption in boys was recorded as 52g and per cent of fat consumption was reported as in excess (148.6%). There is also noticed negatively significant difference.

A non-significant difference was noticed as compared with their RDA of B-complex vitamins like vitamin B_1 (mg), vitamin.B_2 (mg) and vitamin B_3 (mg), Vitamin C (mg) and β-carotene (µg) were also calculated in comparison with their Standards. About 0.85mg of vitamin B_1, 1.1 mg of vitamin. B_2 and 12.6mg of vitamin B_3 consumption were seen in boys. The vitamins consumption in boys was noticed in poor adequate level *i.e.* 77.3, 84.6 and 84 per cent for vitamin B_1, B_2 and B_3, respectively. The consumption of vitamin C (mg) and β-carotene (µg) were 31.5 and 3400, respectively. The consumption was notice in poor adequate level *i.e.* 78.8 and 70.8 per cent, respectively when compared with RDA.

The mineral intake such as calcium (mg) and iron (mg) were noted less adequate level among school going boys. The calcium intake was reported as 560 mg, whereas only 20.5 mg iron intake was found among 10-12 years obese boys.

The data given in Table 8 exhibits the average nutrients intake by 10-12 years in age school going obese girls.

Table 8 reveals that the average caloric intake by school going girls was noted 2340 Kcal. When this calorie intake is checked at per cent of adequacy level, it was found in excess (116.4). There is negatively significant difference found it was when it was compared with their standards. The amount of protein consumption by school going obese girls was reported 47.5g which is noticed negatively significant difference. The per cent of adequacy level for protein was noted excess *i.e.* 117.6 per cent. Fat consumption in girls was recorded as 48g and per cent of fat consumption was reported as in excess (137.1%). There is also noticed negatively significant difference.

B-complex vitamins like Vitamin B_1 (mg), Vitamin B_2(mg) and Vitamin B_3(mg), Vitamin C(mg) and β-carotene (µg) consumption were also calculated in comparison with their Standards.it shoes that 0.85mg of Vitamin B_1, 1.05mg of Vitamin B_2 and 11.95mg of Vitamin B_3 consumption were in boys. There is no significant difference when compared with RDA. The vitamin Bcomplex consumption in girls was noticed in poor adequate level. The consumption of vitamin C (mg) and β-carotene (µg) whereas 37 and 3400, respectively. This consumption was noticed in poor adequate level *i.e.* 92.5 and 70.8 per cent, respectively when compared with RDA.

Conclusion:

On the whole it can be concluded that the food intake especially cereals, pulses and fat based foods are found significantly excess in these school going children. Vegetables and fruits consumption noted less by these children. However the nutrients intake *i.e.* energy and protein were noticed excess than that of their standard level. Whereas vitamins and minerals intake were found less among these children.

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ORIGINAL ARTICLE

Extraction spectrophotometric determination of rhodium(III) with *o*-methylphenyl thiourea

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Mutual separation: palladium(II), rhodium(III), platinum(IV) and iridium(III);
Synthetic mixtures

Abstract Trivalent rhodium was determined spectrophotometrically as its 1:2 rhodium *o*-methylphenyl thiourea (OMPT) complex, extracted into chloroform from aqueous acetate buffer media at pH 5.4. The complex exhibits maximum absorption at 320 nm (Molar absorptivity 9.76×10^3 L mol^{-1} cm^{-1}), Sandell's sensitivity 0.0105 μg of rhodium(III) cm^{-2}. Beer's law obeyed up to 10.0 μg/ml. The method is free from a large number of interferences from cations and anions. The method is simple, selective and reproducible. It permits separation and determination of rhodium(III) from synthetic mixtures corresponding to alloys. A scheme for mutual separation of palladium(II), rhodium(III), platinum(IV) and iridium(III) has been developed.

1. Introduction

Rhodium is a precious element usually found in ores mixed with other elements viz. platinum, palladium, silver and gold. Its abundance in earth's crust is only 0.001 ppm. It has application in catalysis, corrosion, electrical and electronic apparatus. The major medicinal use of rhodium is in radiotheorapy using ^{106}Rh isotope to treat retinoblastoma, rhodium(II) carboxylates as antitumor agents and rhodium(II) pyrimidine derivatives with bacteriostatic and bactericidal properties.

Literature survey reveals that many extractants are used for the separation of rhodium(III) but very few of them give quantitative results with positive merits. Hence low abundance, high price, low natural occurrence, and a wide range of applications, demand a novel method for separation and determination of rhodium.

Rhodium(II) was complexed with 1-(2-pyridylazo)-2-naphthol(PAN) in the pH range 3.2–4.7, adsorbed on modified multiwalled carbon nanotubes (MMWCNT's) eluted with *N*,*N*-dimethylformamide and determined by FAAS (Ghaseminezad et al., 1999). PAN was used for the determination of rhodium by laser induced thermal lense spectrometry (Li-TLS) however use of surfactant and phase separation at 50 °C demerits the method (Shokoufi and shemirani, 2007). High performance liquid chromatography was applied for the separation of platinum, palladium and rhodium (Quinfen et al., 2005) but it requires long time. 2-(5-Bromo-2-pyridylazo)-5-diethylaminophenol was used for the determination of rhodium(III) with FAAS, The method needs preconcentration of samples (Molaakbari et al., 2011). Rhodium along with platinum and gold was determined from archeological specimens

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by ICPMS after fire assay treatment (Pillai and Punyadeera, 2001). Rhodium(III) was determined from road dust and water samples by FAAS but the method needs preconcentration of rhodium(III) and suffers from interferences by large number of cations (Afzali et al., 2011).

Various analytical techniques are available for the determination of rhodium still most of them have some drawbacks. Comparatively solvent extraction technique is the most efficient method of separation technology with high simplicity, speed and applicability to both tracer as well as macro amount of metal ions.

N-*n*-octylaniline is used for the quantitative extraction of rhodium(III) from sodium malonate media (Anuse and Kolekar, 2002). Extraction of rhodium(III) was carried out from bromide media in the presence of stannous chloride using cyanex 471X and cyanex 923. (Duche et al., 2002). *N*,*N*' dimethyl*N*,*N*'diphenyltetradecylmalonamide (DMDPHTDMA) extracts rhodium(III) in the presence of tin (Malik and Ana paula, 2008). Rhodium(III) was separated from iridium(III) and ruthenium(III) using different concentrations of alamine 336 in kerosene using hydrochloric acid media (Goralsa et al., 2007).

Rhodium(III) complexes with water soluble porypyrin 5, 10, 15, 20 – tetrakis(4-*N*-methylpyridyl)Porphine(TMPYM) in acetate buffer at pH 3.9, complexation enhanced in the presence of ethanol by heating at 100 °C for 15 min (Kunio et al., 2006).

In the present investigation we have reported a novel method for extractive spectrophotometric determination of rhodium(III) from acetate buffer media, using *o*-methylphenyl thiourea in chloroform as a solvent. The method is proved to be selective and sensitive as compared to other existing extractive spectrophotometric determination methods for rhodium(III) (Table 1).

2. Experimental

2.1. Apparatus

An elico make UV–visible spectrophotometer model SL-159 with matched 10 mm quartz cells was used for absorbance measurements and pH meter make control dynamic was used for pH measurements. Equilibration of two phases was carried out using wrist action shaker. Standardized glasswares were used for volumetric measurements.

2.2. Reagents

All the reagents used were of analytical reagent grade unless otherwise stated, double distilled water was used throughout the experimental work.

o-Methylphenyl thiourea (OMPT) was synthesized as per the method reported by Frank and Smith (Frank and Smith, 1995). Ethanolic solution (0.01 M) of *o*-methylphenyl thiourea (OMPT) was prepared by dissolving 0.166 g of OMPT in distilled ethanol and made up to the mark in a 100 ml standard volumetric flask with distilled ethanol.

A standard stock solution of rhodium(III) was prepared by dissolving 1.0 g of rhodium chloride ($RhCl_3.4H_2O$) (Loba.Chemie.Pvt.Ltd.India) in 15–20 ml, 1.0 M hydrochloric acid, diluted up to 250 ml mark in a standard volumetric flask with distilled water and this solution was standardized by gravimetric method (Beamish and van loon, 1977). A working standard solution of rhodium(III), 50 μg/ml was prepared by further dilution from standard stock solution with distilled water.

Buffer solution (pH 5.4) was prepared by mixing 88 ml of acetic acid (0.2 M), 412 ml of sodium acetate (0.2 M) and diluted to 1000 ml with double distilled water in a 1000 ml standard volumetric flask (Sidney and Nathan, 1955).

Standard solutions of different metal ions used for interference study were prepared by dissolving weighed quantity of their respective salts in double distilled water or dilute hydrochloric acid and diluted with double distilled water. Solutions of anions were prepared by dissolving their respective alkaline metal salts in distilled water and diluted with double distilled water.

2.3. General procedure for extraction spectrophotometric determination of rhodium(III)

The aliquot of solution containing 50 μg rhodium(III) is transferred to a 25 ml standard volumetric flask, 2 ml of 0.01 M OMPT in ethanol is added to it and the mixture was diluted up to the mark with acetate buffer(pH 5.4). The mixture was heated in boiling water bath for 4 min. The yellow colored solution containing rhodium(III)–OMPT complex is cooled, transferred into 125 ml separatory funnel and extracted with 10 ml chloroform by single extraction. The phases are allowed to separate and the yellow colored rhodium(III)–OMPT complex is dried over 1.0 g anhydrous sodium sulfate. Rhodium(III)–OMPT complex in chloroform is transferred into a 10 ml volumetric flask The absorbance of rhodium(III)–OMPT complex is measured at 320 nm against the reagent blank in chloroform.

3. Results and discussion

3.1. Absorption spectra

Rhodium(III) forms yellow colored rhodium(III)–OMPT complex in acetate buffer media at pH 5.4 after heating for 4 min in water bath. The absorption spectra of rhodium(III)–OMPT complex against reagent blank in chloroform is shown in Fig. 1. The spectra obtained reveal that the rhodium(III)-OMPT complex in chloroform has the maximum absorbance at 320 nm while the absorption spectrum due to reagent blank is negligible. It indicates the reagent does not interfere in the determination of rhodium(III). Thus all further absorbance measurements were made at 320 nm wavelength against reagent blank for spectrophotometric determination of rhodium(III).

3.2. Effect of various buffers and pH

The color development of rhodium(III) by the formation of rhodium(III)–OMPT complex was studied using various buffer solutions. Recommended procedure was followed for color development using different buffer solutions. To an aliquot of solution containing 50 μg rhodium(III), 2 ml of 0.01 M OMPT in ethanol was added and it was diluted up to the mark in a 25 ml in standard volumetric flask using various buffer solutions (viz: sodium acetate + acetic acid, citric acid + diso-

Table 1 Comparison of present method with other extractive spectrophotometric determination methods of rhodium(III).

Reagents	λ_{max} (nm)	Condition	Beer's Law validity range (ppm)	Solvent	Molar Absorptivity (L mol^{-1} cm^{-1})	Remark	References
Cyclohexylthioglycolates	345	pH 9.0–12.5	0.2–4.1	Chloroform	1.60×10^4	2.5 min heating at 60–70 °C	Avasarala et al., 1986.
Diphenylcarbazide + -picoline	560	1.0 ml, 0.5 % picoline	1.0 – 3.0	Isobutl methyl ketone	4.01×10^4	Complex stabliLy less than 2 h, interference by large number of cations	Saramah and Das, 1985
1,5-Diphenylcarbazide	–	pH 5.0	0.56–2.8	Isobutanol	–	Low beer's range, complexation at 70 °C	Krystna and Urzula, 1984.
25,26,27,28-Tetrahydroxy-5,11,17,23-tetra1-[4-(*N*-hydroxy-3-phenylprop-2-						(nimidamido)phenylazo)calyx[4]arene	–
3.0 M HNO_3	1.2–10.0	30%, 1,2 Dichloroethane in dimethylformamide	9.8×10^3	Synergestic extraction	Kumar et al., 2008.		
Isonitro-*p*-methylacwtophenone	370	pH 4.5 acetate buffer	0.05–6.0	Carbontetrachloride	$2.47 \times 1\ 0^4$	30 min heating	Mahajan and Patil, 1992.
2-(5-Bromo-2-pyridylazo)-5-diethylaminophenol)-tetraphenylborate)	–	pH 5.0–6.5	0.03–2.5	Molten naphthalene: dimethylformamide	–	Second derivative spectrophotometry	Puri and Patric, 1999.
3-hydroxy-2-methyl-1,4-napthoquinone monoxime	430	pH 5.5–7.0	6.06	Molten naphthalene: dimethylformamide	2.15×10^4	Interference by thiourea, thiosulfate, ruthenium, platinum	Sharma and Sindhwani, 1988.
N-Hydroxy-*N*,*N*′-diphenylbenzamidine + 5-Br-PADAP	460	pH 5.8–6.5	0.6	Dichloromethane	2.8×10^4	Low beer's range	Thakur et al., 2005
o-Methyl phenyl thiourea(OMPT)	320	pH 5.4 acetate buffer	10.0	Chloroform	9.76×10^3	Selective and sensitive	PM

PM: Present method.

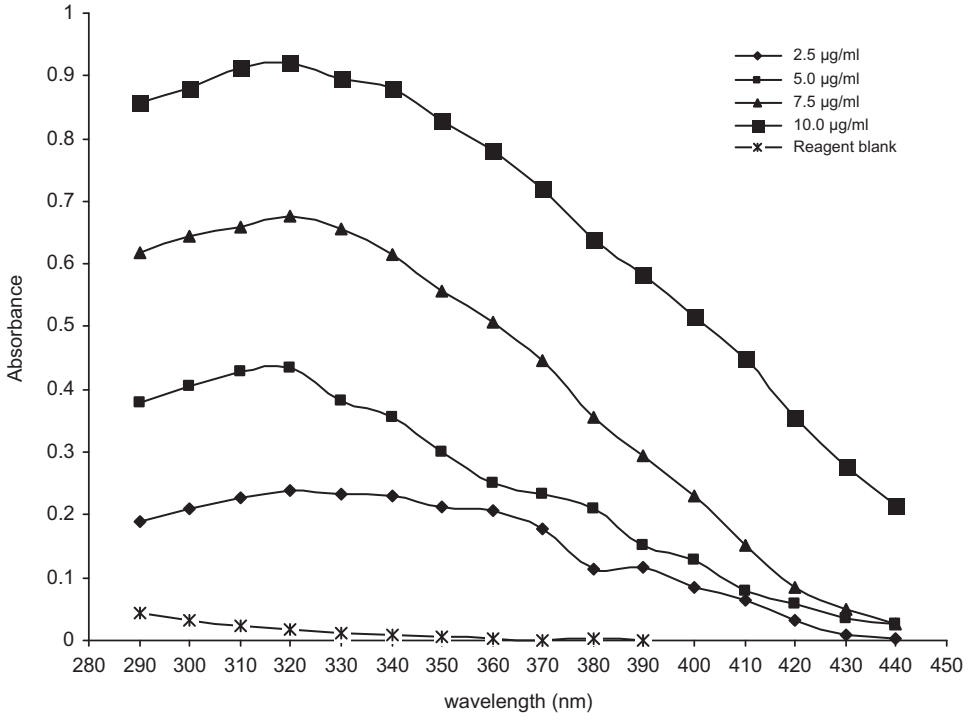


Figure 1 Absorption spectra of Rh(III)–OMPT complex vs OMPT reagent blank Rh(III) 2.5 µg/ml; 5.0 µg/ml; 7.5 µg ml, 10.0 µg/ml; acetate buffer pH 5.4; OMPT 2.0 ml, 0.01 M in ethanol, heating time 4.0 min.

dium hydrogen phosphate, succinic acid + borax, boric acid + sodium hydroxide, phosphoric acid + sodium hydroxide, sodium succinate + succinic acid, borax + hydrochloric acid) The color was developed by heating in water bath for 4 min. Absorbance of extracted complex in chloroform was measured at λ_{max} 320 nm. The absorbance increases up to

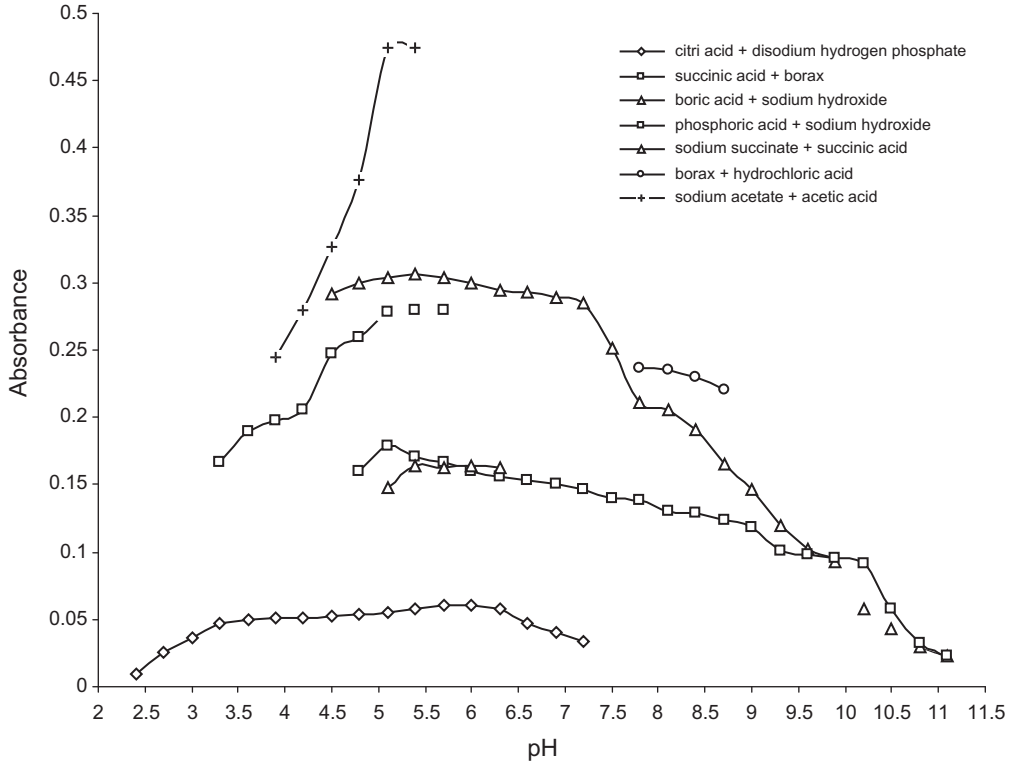


Figure 2 Effect of pH on extraction of Rh(III)–OMPT complex Rh(III) 5.0 µg/ml; OMPT 2.0 ml, 0.01 M in ethanol; heating time 4.0 min; λ_{max} 320 nm.

pH 5.0 where the absorbance values are maximum and remain steady for different buffer solutions in the pH range 5.0–6.0 (Fig. 2). The complete extraction of rhodium(III) with maximum absorbance is observed in acetate buffer system. Hence acetate buffer at pH 5.4 was used for further studies.

3.3. Effect of reagent concentration

The effect of reagent concentration on the formation of rhodium(III)–OMPT complex for color development was studied by varying the OMPT concentration from 0.001 M to 0.1 M. The result shows that absorbance increases with increase in OMPT concentration from 0.001 to 0.01 M OMPT in ethanol and further it remained constant up to 0.1 M. Hence 0.01 M OMPT in ethanol (2 ml volume used) was sufficient for quantitative extraction and determination of rhodium(III) (Table 2, Fig. 3).

Table 2 Effect of reagent concentration Rh(III) 5.0 μg/ml; OMPT 2 ml, 0.001–0.01 M in ethanol, heating time 4.0 min, λ_{max} 320 nm; pH 5.4.

Reagent concentration (M)	Extraction (%)	Distribution ratio(D)
0.001	8.4	0.23
0.003	40.0	1.66
0.005	65.5	4.75
0.007	79.6	9.75
0.010	99.9	2497.5

3.4. Effect of heating time and stability of complex

There was no color development at room temperature while yellow color of rhodium(III)–OMPT complex was observed on heating the mixture in water bath. The absorbance of rhodium(III)–OMPT complex increases with increase in heating time from one minute to four minutes and further it remains constant with no adverse effect on the color development up to 60 min (Fig. 4). The stability of the complex was studied for more than 48 h with absorbance measurements in the interval of one hour. The results obtained show, rodium(III)–OMPT complex is stable for more than 48 h.

3.5. Effect of ethyl alcohol concentration

The amount of ethyl alcohol (solvent) in aqueous phase in terms of percentage was varied, keeping other optimum conditions constant. The results obtained show that the absorbance of rhodium(IIII)–OMPT complex remained constant from 5% to 20% (V/V) of ethyl alcohol in aqueous phase. The absorbance further decreases above 20% concentration of ethyl alcohol. The percentage of ethyl alcohol in aqueous phase was fixed as 10% (V/V). Along with ethyl alcohol the color development was also studied by varying the solvents for OMPT in aqueous phase viz: *N*,*N*-dimethylformamide, dimethylsulfoxide and 1,4 dioxan, the maximum color development was seen in the presence of ethyl alcohol and complexation was poor in the presence of dimethyl formamide, dimethlysulfoxide and 1,4 dioxan (Fig. 5).

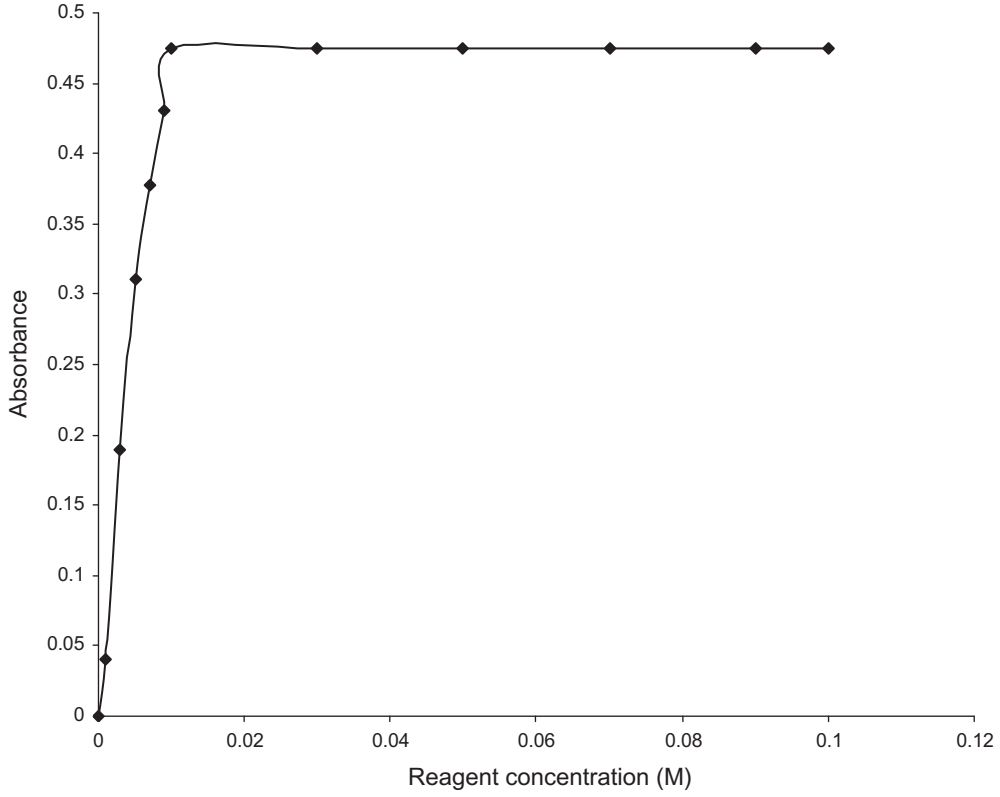


Figure 3 Effect of reagent concentration on formation of rhodium(III)–OMPT complex Rh(III) 5.0 μg/ml; acetate buffer pH 5.4; OMPT 2.0 ml, 0.001 M to 0.1 M in ethanol; heating time 4.0 min; λ_{max} 320 nm.

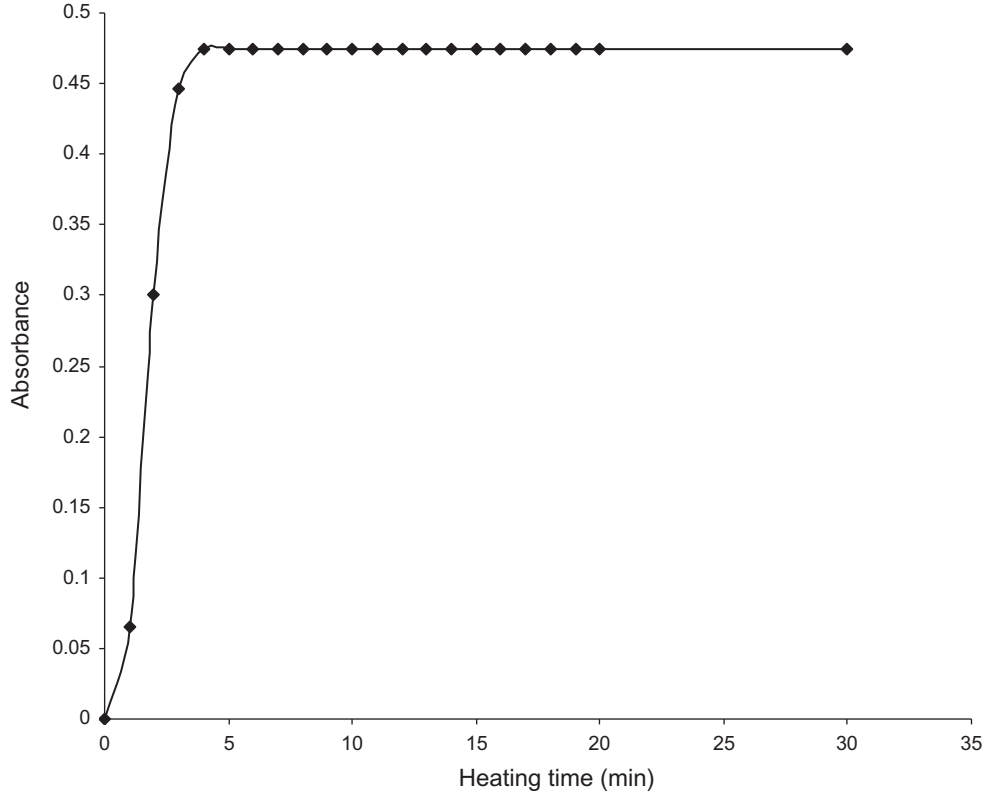


Figure 4 Effect of heating time on formation of rhodium (III)–OMPT complex Rh(III) 5.0 μg/ml; acetate buffer pH 5.4; OMPT 2.0 ml, 0.01 M in ethanol; heating time 1 to 30 min; λ_{max} 320 nm.

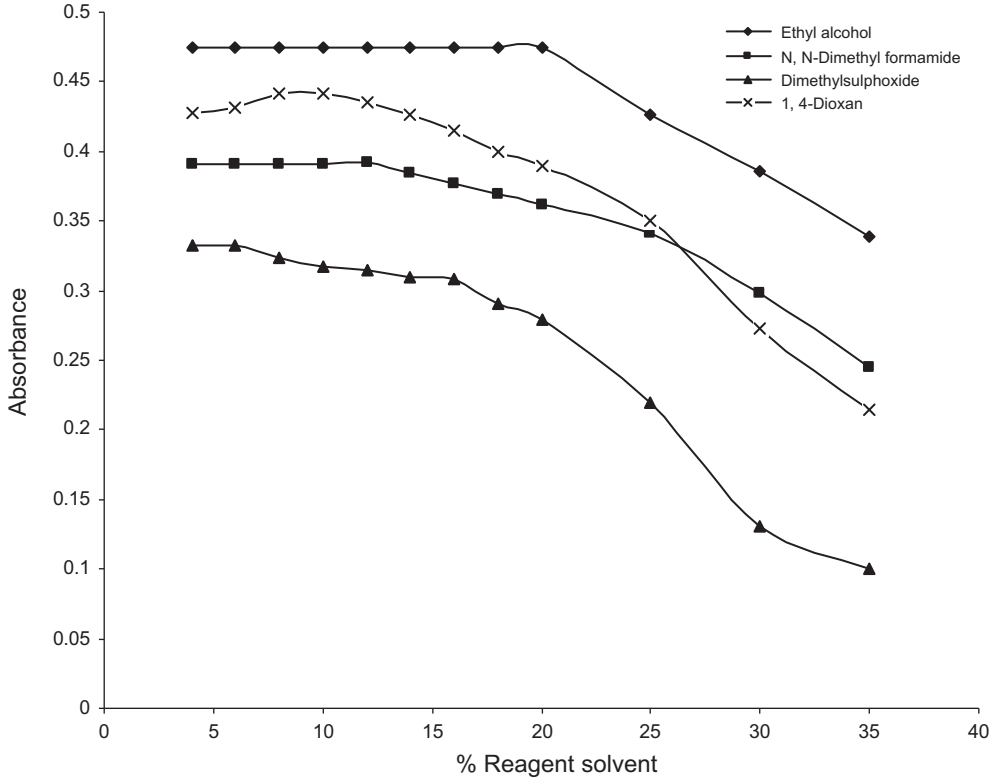


Figure 5 Effect of reagent solvent on formation of rhodium(III)–OMPT complex Rh(III) 5.0 μg/ml; acetate buffer pH 5.4; OMPT 2.0 ml, 0.01 M in ethanol; heating time 4 min; λ_{max} 320 nm.

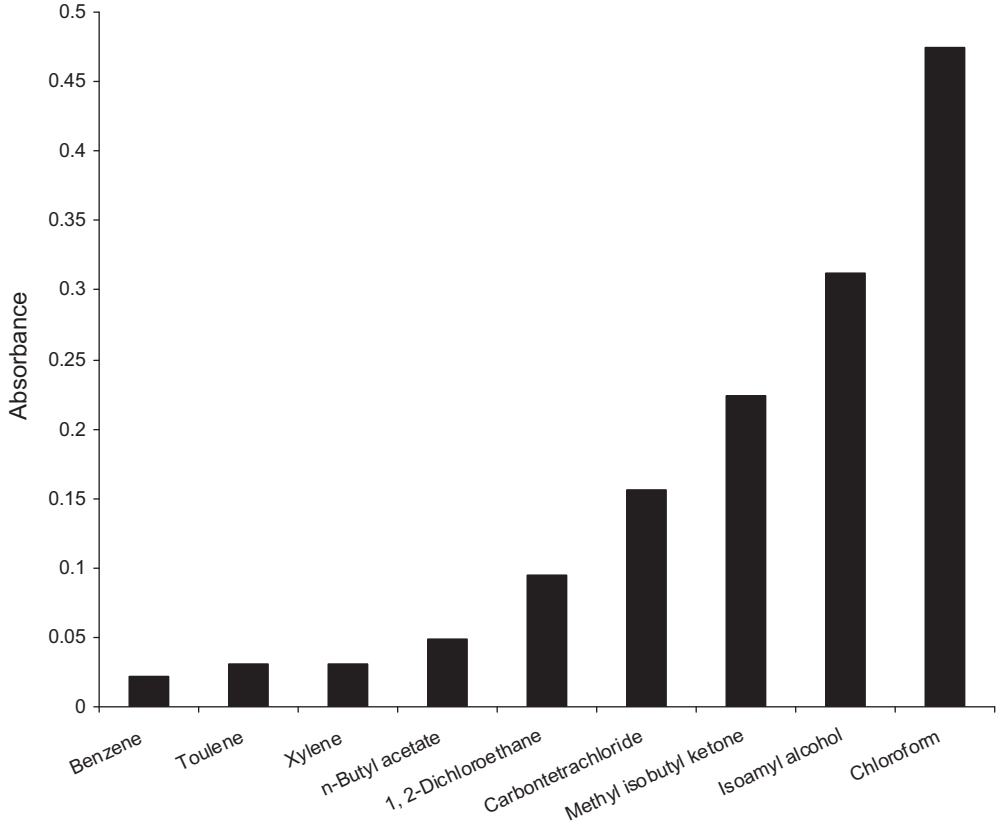


Figure 6 Effect of extracting solvent on extraction of rhodium(III)–OMPT complex Rh(III) 5.0 μg/ml; acetate buffer pH 5.4; OMPT 2.0 ml, 0.01 M in ethanol; heating time 4 min; λ_{max} 320 nm.

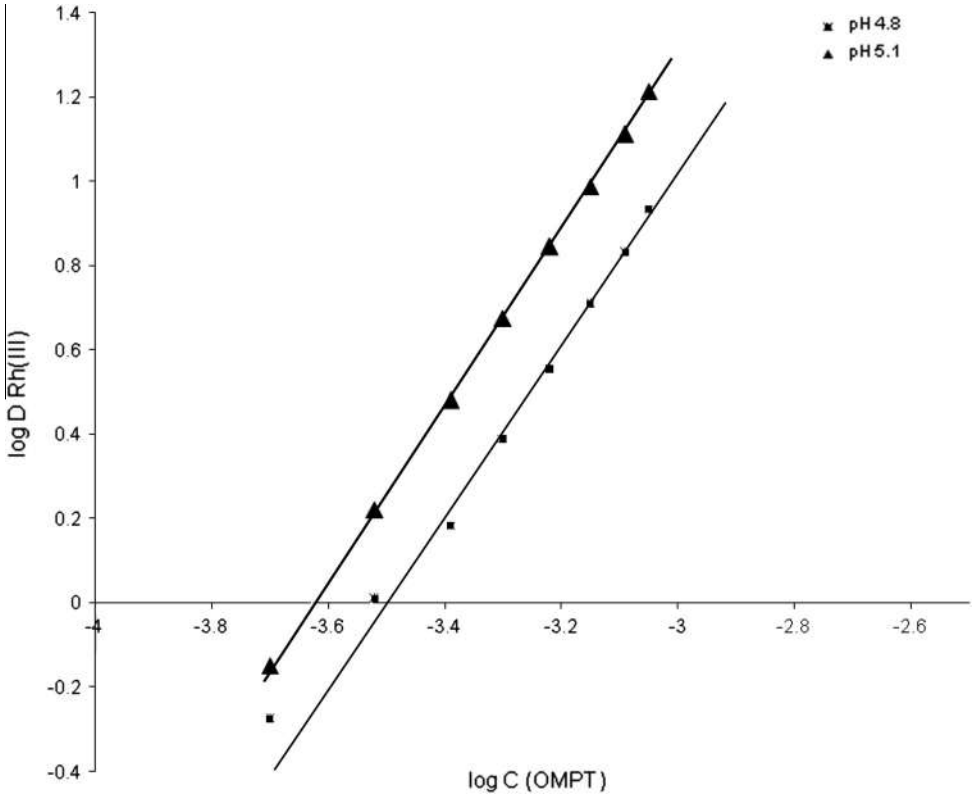


Figure 7 Plot of $\log D_{Rh(III)}$ vs $\log C_{(OMPT)}$ Rh(III) 5.0 μg/ml; acetate buffer pH 4.8 & 5.1; OMPT 2.0 ml, 0.002 to 0.009 M in ethanol; heating time 4 min; λ_{max} 320 nm.

3.6. Choice of extraction solvent

Various solvents were tested for the extraction of rhodium(IIII)–OMPT complex from acetate buffer media viz. benzene, toluene, xylene, carbontetrachloride, isoamyl alcohol, 1,2-dichloroethane, *n*-butyl acetate, methyl isobutyl ketone and chloroform. Among the solvents studied, complete extraction with maximum absorbance was observed in chloroform (Fig. 6).

3.7. Composition of extracted species

The composition of rhodium(IIII)-OMPT complex was ascertained from log–log plot (Miller and Miller, 1993) as log of *o*-methylphenyl thiourea concentration versus log of distribution ratio of rhodium(III) at pH 4.8 and pH 5.1 gave a slope of 1.85 and 1.95 respectively. It confirms that the probable composition of extracted species is 1:2 (Rh(III):OMPT) (Fig. 7).

3.8. Beer's law, molar absorptivity, sandell's sensitivity and correlation coefficient

Beer's law is obeyed over the concentration range up to 10.0 μg for rhodium(III)–OMPT complex in chloroform at 320 nm (Fig. 8). The molar absorptivity and sandell's sensitivity of the complex are 9.76×10^3 L mol^{-1} cm^{-1} and 0.0105 μg cm^{-2} respectively. The ringbom's plot is applied as a standard method to determine the optimum range of concentration for a system that obeys beer's law (Ringbom, 1939). Ringbom's plot was drawn as log C of rhodium(III) versus (1−T) where T is the transmittance (Fig. 9). This plot has a sigmoid shape with a linear segment at intermediate absorbance values 3.0–7.4 μg/ml and has slope 0.833. The ratio between the relative error in concentration and photometric error is 2.764. The correlation coefficient values of rhodium(IIII)–OMPT complex with an independent variable as concentration in μg/ml and dependent variable as absorbance was found to be 0.99, indicates clear linearity between these two values. The slope and intercept for the best fitted line are 0.08713 and 0.0086. Hence the content of rhodium(III) in the real samples can be determined using the straight line equation $Y = 0.08713X + 0.0086$.

3.9. Precision, accuracy and detection limit

To access the reproducibility of results and accuracy of the method, absorbance measurements with ten identical solutions containing 50 μg rhodium(III) were carried out by proposed method. The average of these ten readings and standard deviation were determined. The standard deviation was found to be 0.001 and the relative standard deviation was 0.299%. It is evident from these results that the method is precise and accurate. The detection limit of rhodium(III) for the proposed method is as the amount corresponding to thrice the standard deviation of blank value, which is 0.021 μg/ml.

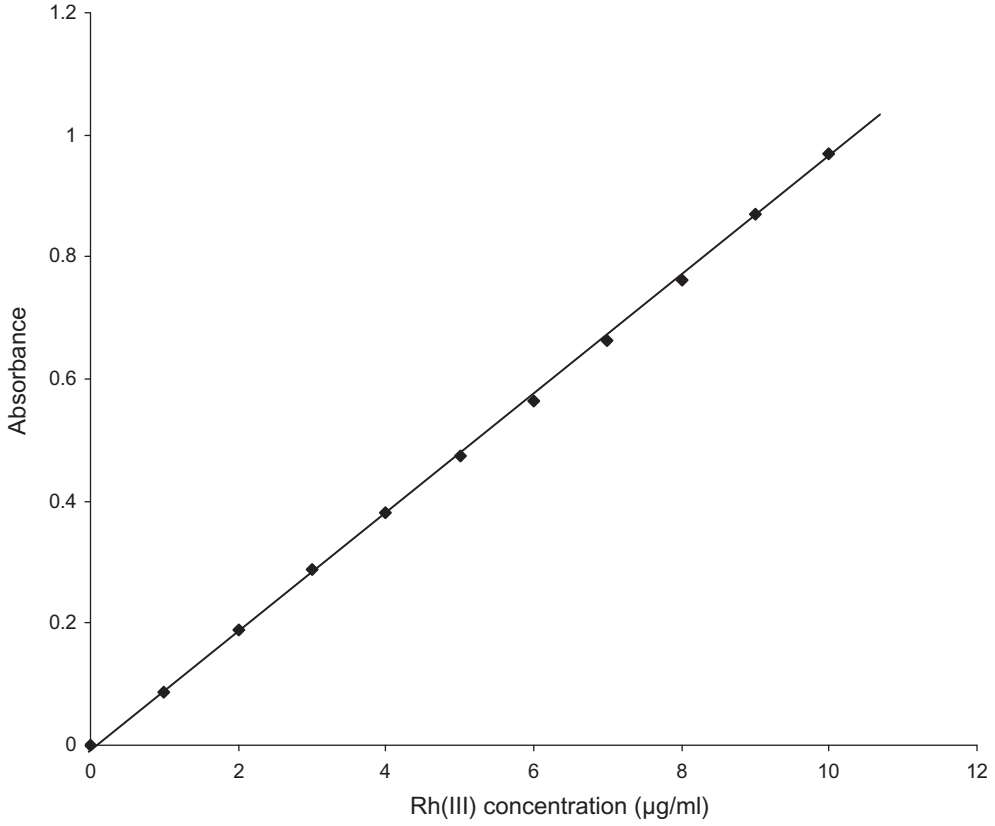


Figure 8 Applicability of beer's law to rhodium(III)–OMPT complex Rh(III) 1.0 to 10.0 μg/ml; acetate buffer pH 5.4; OMPT 2.0 ml, 0.01 M in ethanol; heating time 4 min; λ_{max} 320 nm.

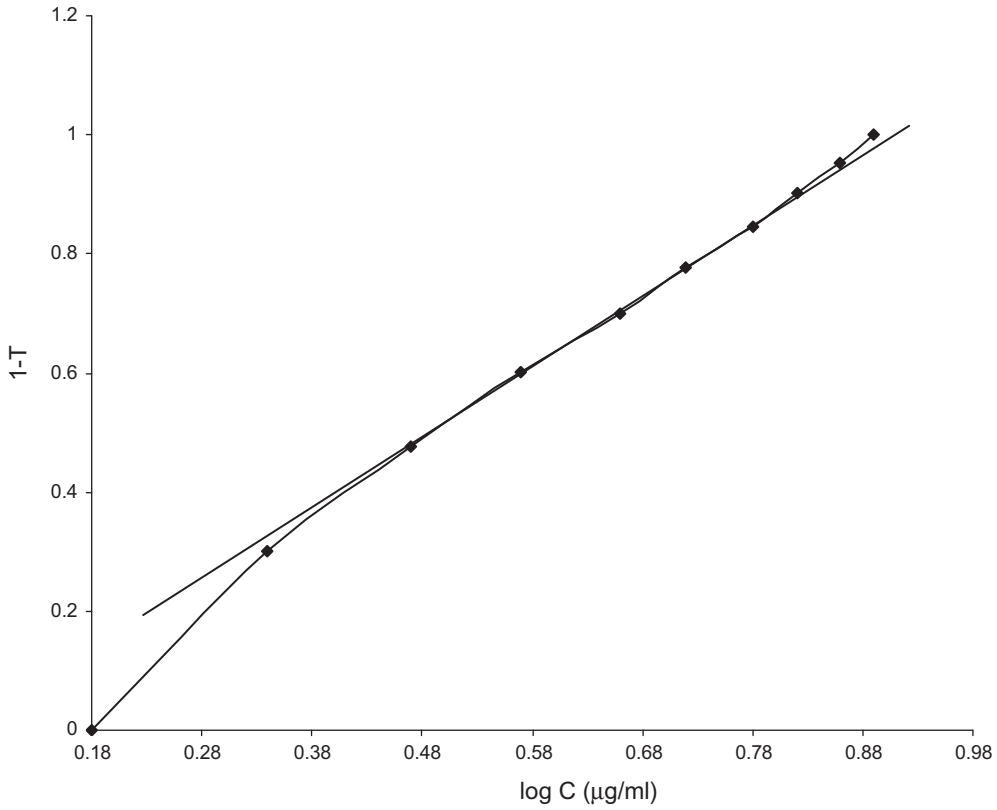


Figure 9 Ringbom's plot for Rhodium(III)-OMPT complex Rh(III) 1.0 to 10.0 µg/ml; acetate buffer pH 5.4; OMPT 2.0 ml, 0.01 M in ethanol; heating time 4 min; λ_{max} 320 nm.

Table 3 Effect of foreign ions Rh(III) 5.0 µg/ml; OMPT 2 ml, 0.01 M in ethanol, heating time 4.0 min, λ_{max} 320 nm; pH 5.4.

Foreign ion	Added as	Tolerance limit (mg)	Foreign added as ion	Tolerance limit (mg)
Mn(II)[a]	$Mncl_2{\cdot}6H_2O$	5	Os(VIII) OsO_4	0.7
Cd(II)	$Cdcl_2{\cdot}2H_2O$	10	Ir(III) $IrCl_3$	1
Fe(III)[a]	$(NH_4)Fe(SO_4)_2{\cdot}12H_2O$	4.5	Ru(III) $RuCL_3{\cdot}6H_2O$	0.2
Hg(II)	$Hgcl_2$	1	Pt(IV) $H_2PtCl_6{\cdot}H_2O$	0.5
Bi(III)[a]	$BiCl_3$	4	Ce(IV)[a] $Ce(SO_4)_2{\cdot}4H_2O$	3
Ni(II) [a]	$NiCl_2{\cdot}6H_2O$	5	Pb(II) $PbCl_2$	2
Cu(II)[a]	$CuSO_4{\cdot}5H_2O$	2	V(V) V_2O_5	15
Al(III) [a]	$AlCl_3{\cdot}6H_2O$	3	U(VI) $UO_2(CH_3COO)_2$	10
Cr(III)	$CrCl_3$	1.5	Co(II) [a] $CoCl_2{\cdot}6H_2O$	5
Zn(II)	$ZnSO_4{\cdot}7H_2O$	7	Ba(II) $BaCl_2{\cdot}6H_2O$	15
Se(IV)	SeO_2	1	Ca(II) $CaCl_2{\cdot}2H_2O$	10
La(III)	$LaCl_3{\cdot}7\ H_2O$	1	Sr(III) $SrCl_3{\cdot}6H_2O$	20
Li(I)	LiCl	8	Tl(III)[b] Tl_2O_3	6
Ti(III)	$(Ti_2SO_4)_3$	1	Bromide KBr	100
Pd(II)	$Pdcl_2$	0.3	Fluoride NaF	100
Mg(II)	$MgCl_2{\cdot}6H_2O$	15	Phosphate Na_3PO_4	50
Sn(II)	$SnCl_2{\cdot}2H_2O$	0.2	Sulfate K_2SO_4	80
Ga(III)[b]	$GaCl_3$	3	Succinate $(CH_3COONa)_2{\cdot}6H_2O$	100
Au(III)	$HAuClO_4{\cdot}H_2O$	0.5	Citrate $C_6H_8O_7{\cdot}H_2O$	50
Mo(VI) [a]	$(NH_4)_5MO_7{\cdot}2H_2O$	2.5	Malonate $CH_2(COONa)_2$	100
Sb(III)	Sb_2O_3	10	Tartrate $(CHOH:COOH)_2$	50
Be(II)	$BeSO_4{\cdot}4H_2O$	0.3	Oxalate $(COOH)_2{\cdot}2H_2O$	100
In(III)[b]	$InCl_3{\cdot}4H_2O$	4	EDTA. Na_2EDTA	50

[a] Masked with 50 mg EDTA.
[b] Masked with 50 mg tartrate.

3.10. Effect of foreign ions

The effects of various foreign ions were investigated in order to determine the tolerance limits of the ions in extraction spectrophotometric determination of rhodium(III). The method is free from a large number of cations and anions. The interference from manganese(II), iron(III), nickel(II), bismuth(III), copper(II), aluminium(III), molybdenum(VI), cobalt(III) and cerium(IV) was removed by masking these ions with EDTA. The interference from gallium(III), indium(III) and thallium(III) was removed by masking with tartrate (Table 3).

4. Applications

4.1. Analysis of synthetic mixtures corresponding to alloys, catalyst and thermocouple wire

The selectivity of the method was confirmed by applying it for the determination of rhodium(III) in synthetic mixtures corresponding to alloys, catalyst and thermocouple wire. The composition of synthetic mixtures corresponding to iridium alloy, osmoiridium alloy, platinum-palladium-rhodium catalyst and platinum–rhodium thermocouple wire was prepared in laboratory. The amount of rhodium(III) was determined using recommended procedure. The results are in good agreement with those obtained by direct atomic absorption spectrometry. These results are reported in Table 5.

4.2. Mutual separation of palladium(II), rhodium(III), platinum(IV) and iridium(III)

Method permits mutual separation of palladium(II), rhodium(III), platinum(IV) and iridium(III) from their mixture by taking advantage of the difference in their reactivity with *o*-methylphenyl thiourea (Scheme 1, Table 4). Aqueous solutions containing a mixture of palladium(II), rhodium(III), platinum(IV) and iridium(III) in the ratios of 1:1:2:1 were mixed. The solution was made 0.8 M with respect to hydrochloric acid at 25 ml in a standard volumetric flask. It was transferred to 125 ml separatory funnel and palladium(II) was extracted in 10 ml, 1.0×10^{-4} M OMPT in chloroform. After separation of phases, the yellow colored organic phase containing palladium(II)–OMPT complex was dried over 1.0 g anhydrous sodium sulfate and absorbance of palladium(II)–OMPT complex was measured at λ_{max} 340 nm (Shelar et al., 2011). The aqueous phase containing rhodium(III), platinum(IV) and iridium(III) was evaporated to moist dryness. After cooling, 2 ml, 0.01 M OMPT in ethanol was added and diluted to 25 ml with acetate buffer pH 5.4 in a 25 ml standard volumetric flask. This solution was heated for 4 min on a boiling water bath. The yellow colored rhodium(III)–OMPT complex was cooled and extracted into 10 ml chloroform by single extraction. It was dried over 1.0 g anhydrous sodium sulfate and transferred to 10 ml volumetric flask. The absorbance of rhodium(III)–OMPT complex was measured at λ_{max} 320 nm. The aqueous phase containing platinum(IV) and iridium(III) was evaporated to moist dryness and after cooling the residue was dissolved into distilled water. The aqueous phase was made 0.1 M with respect to Potassium iodide in a 25 ml standard volumetric flask. This solution was transferred to 125 ml separatory funnel and equilibrated with 10 ml, 0.1 M OMPT in chloroform for 30 s, platinum(IV) gets extracted into organic phase as yellow colored platinum(IV)–OMPT complex. It was measured at λ_{max}360 nm after drying over 1.0 g anhydrous sodium sulfate. The raffinate containing iridium(III) was evaporated to moist dryness, dissolved in hydrochloric acid and distilled water. It was again evaporated to moist dryness and the residue dissolved in distilled water. Iridium(III) was estimated by the stannous chloride-hydrobromic acid method (Sandell, 1962).

Table 4 Mutual separation of palladium(II), rhodium(III), platinum(IV) and iridium(III).

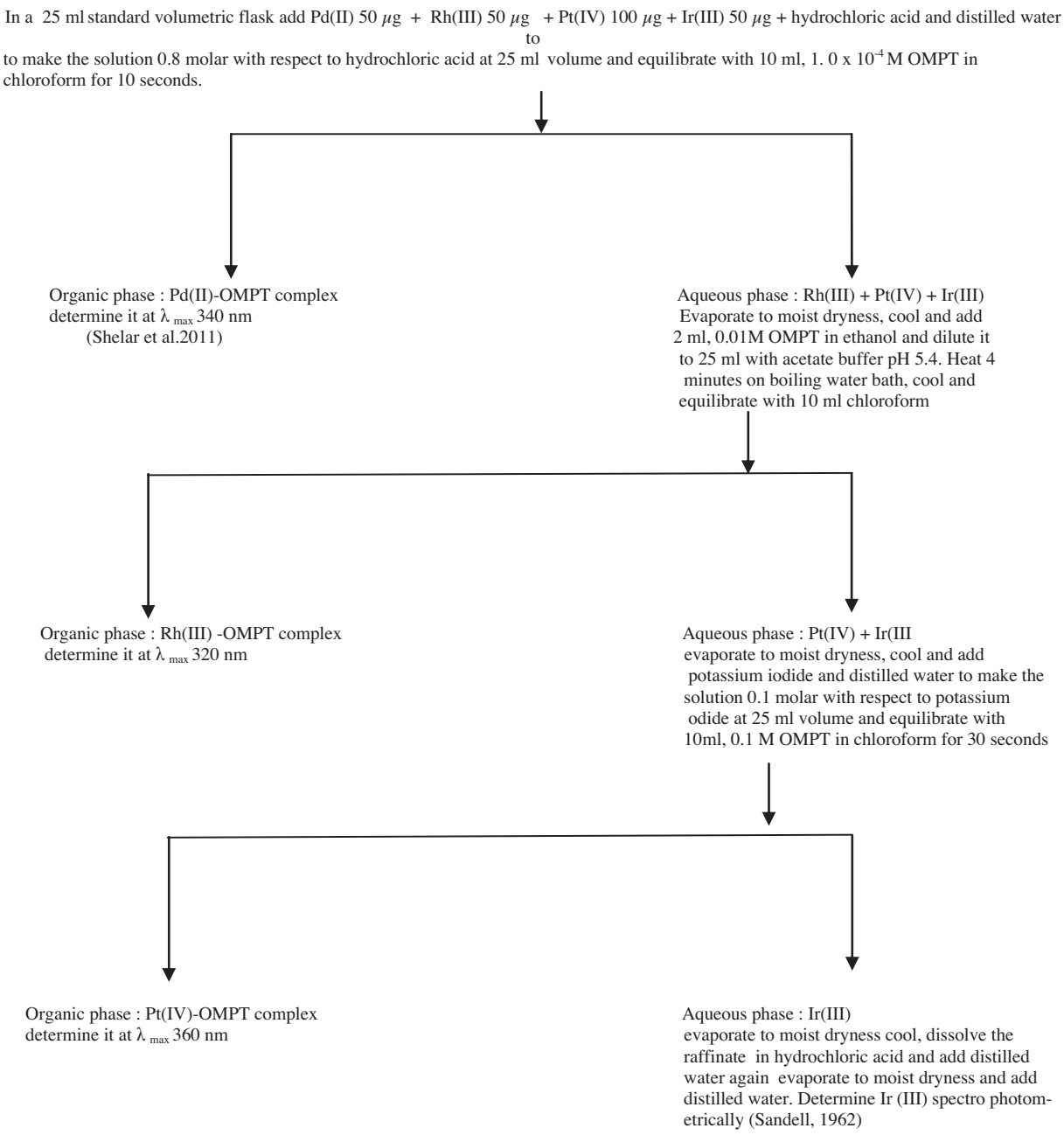
Metal ion	Amount taken (μg)	Chromogenic ligand	% Recovery [a]	% RSD
Pd (II)	50	OMPT	98.8	1.61
Rh (III)	50	OMPT	98.9	1.54
Pt (IV)	100	OMPT	98.1	1.71
Ir (III)	50	HBr + $Sncl_2$	99.4	0.40

[a] Average of three determinations.

Table 5 Separation of rhodium(III) from synthetic mixtures corresponding to alloys, catalyst and thermocouple wire.

Composition of alloy, catalyst and thermocouple wire	Amount of rhodium(III)			S.D	R.S.D (%)
	Taken (μg)	Found (μg)			
		AAS	PM*		
Iridium alloy Rh 7. 0, Pd 3.5, Cu [a] 8. 01, Pt 55. 51, Fe [a] 3. 51, Ir 8. 01	50	49.90	49.76	0.18	0.36
Osmoiridium alloy Rh 110, Os 325, Pt 100, Ru 80, Ir 450, Au 10	50	49.95	49.60	0.22	0.43
Pt-Pd-Rh catalyst Rh 0. 005–0. 05, Pd 0.03–0.15, Pt 0. 03–0. 20	50	49.90	49.78	0.19	0.39
Pt–Rh thermocouple wire Rh 13, Pt 87	50	49.87	49.73	0.13	0.27

[a] Masked with 50 mg EDTA.
* PM-Present method, average of four determinations.



Scheme 1 Mutual separation of palladium(II), rhodium(III), platinum(IV) and iridium(III).

5. Conclusions

o-Methylphenyl thiourea (OMPT) has been proved to be a sensitive and selective spectrophotometric reagent for rhodium(III). The method developed is simple, sensitive, selective, reproducible and rapid with low reagent concentration. The quantitative extraction was carried out in a single step. Method is free from interferences from a large number of cations and anions. A scheme for mutual separation of palladium(II), rhodium(III), platinum(IV) and iridium(III) has been developed. The rhodium(III)–OMPT complex is stable for more than 48 h. Separation of rhodium(III) from synthetic mixtures corresponding to iridium alloy, osmoiridium alloy, platinum-palladium catalyst and thermocouple wire is carried out.

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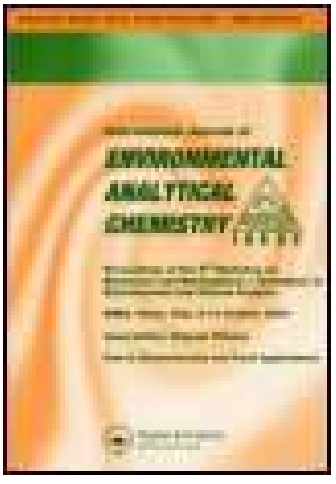

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Selective determination of selenium(IV) from environmental samples by UV-visible spectrophotometry using O-methoxyphenyl thiourea as a chelating ligand

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Selective determination of selenium(IV) from environmental samples by UV-visible spectrophotometry using *O*-methoxyphenyl thiourea as a chelating ligand

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A selective extraction–spectrophotometric method has been developed for determination of selenium(IV) using *O*-methoxyphenyl thiourea (OMePT) as a chelating agent. The basis of the proposed method is the spectrophotometric determination of selenium(IV)–OMePT complex obtained after extraction of selenium(IV) from 3.5 M hydrochloric acid media using OMePT in chloroform solvent. The complex shows maximum absorbance at 350 nm against the reagent blank. The Beer's law was obeyed over the concentration range 5–60 μg mL^{-1} of selenium(IV). The optimum concentration range was 20–50 μg mL^{-1} as evaluated from Ringbom's plot. The molar absorptivity and Sandell's sensitivity of the selenium(IV)–OMePT complex in chloroform were 3.312×10^2 L $mol^{-1}cm^{-1}$ and 0.2384 μg cm^{-2}, respectively. The composition of selenium(IV)–OMePT complex was 1:2 established from slope ratio method, mole ratio method and Job's continuous variation method. The complex was stable for more than 72 h. The interfering effect of various foreign ions was studied and suitable masking agents were used wherever necessary to enhance the selectivity of the developed method. The proposed method was successfully applied for the determination of selenium(IV) from real samples, viz. pharmaceutical formulations, shampoo, vegetable sample, synthetic mixtures and environmental samples. Repetition of the method was checked by finding the relative standard deviation (RSD) for 10 determinations which was 0.35%.

Keywords: *O*-methoxyphenyl thiourea; pharmaceutical samples; environmental samples; selenium; solvent extraction; spectrophotometry

1. Introduction

Selenium is an essential trace element. It has importance in human biology and human health. It is essential for the prevention of a variety of diseases. The selenium content in the human body is widely distributed in all the tissues in which it is bound to proteins. Selenium deficiency causes several reproductive and obstetric complications, including male and female infertility, miscarriage, pre-eclampsia, foetal growth restriction, preterm labour, gestational diabetes and obstetric cholestasis [1]. Recent studies showed that supplemental selenium in human diets may reduce cancer risk [2]. Selenium supplementation for patients undergoing different pathologies is necessary as selenium is a structural component of the active centre of the enzyme glutathione peroxidase (GSH-Px) connected with a protective activity against free radicals [3]. In the agriculture organo-selenium compounds are reported as bactericides, fungicides and herbicides [4–7].

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Though selenium is essential to life, but its excess quantity is toxic. Dermatologic effects, such as nail and hair loss and dermatitis, occur after exposure to high levels of environmental selenium [8]. An excess of selenium in food or pharmaceutical preparations is hazardous to human health. Selenium and its compounds are listed as the Basel convention on the control of transboundary movements of hazardous waste and their disposal [9]. Trace abundance, human health applications, bactericide and herbicidal applications create a background for a need of development of selective method for the determination of selenium at trace level for its quantitative determinations.

Different methods are available for determination of Se(IV) including neutron activation analysis [10], atomic absorption spectroscopy (AAS) [11], high performance liquid chromatography [12], capillary electrophoresis [13], stripping voltammetry [14] and catalytic kinetic spectrophotometry [15]. These methods have limitations, viz. it requires more time for sample preparation, less sensitivity, instrumental set-up, maintenance of instruments, etc.

In routine analysis, spectrophotometric method is versatile and economical. Spectrophotometric methods have received considerable attention because of their significant advantages in the determination of various components at trace levels. Many methods and large variety of reagents are reported for spectrophotometric determination of selenium. A solid phase extraction multi-syringe flow injection system was used for the spectrophotometric determination of selenium with 2,3-diaminonaphthalene [16]. However, this method involves the number of steps with the laborious and lengthy procedure. A spectrophotometric method was developed for the determination of selenium in cosmetic and pharmaceutical preparations after pre-concentration with cloud point extraction [17]; the method suffers from drawbacks, viz. it requires standing time of 15 min for complete colour development, further heating is required for 10 min at 40°C and phase separation was accelerated by centrifuging in the test tube at 3500 rpm for 15 min. Methdilazine hydrochloride was reported as a reagent for the spectrophotometric determination of selenium [18]. The method lacks with extended 10 minutes for colour development and higher hydrochloric acid concentration. 3,3′-Diaminobenzidine hydrochloride was used as chromogene for spectrophotometric determination of selenium, it requires 20 min heating at 70°C [19]. A large number of methods are reported for the determination of selenium(IV). The comparison of the present method with reported methods for spectrophotometric determination of selenium(IV) is presented in Table 1 [18,20–26].

The proposed method offers several advantages over the reported methods, viz. simple and precise complex formation at room temperature, high Beer's range, low reagent concentration (0.012 mol L^{-1}) and single extraction. The proposed method was applied for the determination of selenium in synthetic mixtures, pharmaceutical and toilet preparations and environmental sample.

2. Experimental

2.1. *Apparatus*

A double beam UV-VIS 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 were cleaned by soaking in dilute nitric acid followed by washing with soap water and rinsed two times with water.

2.2. *Reagents*

2.2.1. *Standard selenium(IV) solution*

All the reagents used were of analytical reagent grade unless otherwise stated. A standard stock solution of 1 mg mL^{-1} selenium(IV) was prepared by dissolving 1.404 g of selenium dioxide

Table 1. Comparison of present method with other extraction–spectrophotometric determination methods of Se (IV).

Reagents	λ_{max} (nm)	Condition	Beer's law validity range (μg mL^{-1})	Solvent	Molar absorptivity (L $mol^{-1}cm^{-1}$)	M:L	Remark	Ref.
J-acid (6-ammo-I-naphthol-3-sulphonic acid)	520	5 mL of cone sulphuric acid	0.03–0.3	Butanol	18.5×10^3	1:2	Initially low pH (1–1.5) with concentrated sulphuric acid	[20]
Cetylpyridinium chloride (CPC)	510	pH 2.5 acetate buffer	50–1000 ng mL^{-1}	Aqueous	1.8×10^4	NM	Beyond 1.7×10^{-5} mol L^{-1} CPC, co-precipitation takes place. Limited application.	[21]
2′,4′-Dichlorophenylfluorone (p -CPF)	480	Potassium bromate, HNO_3, heating −10 min	0.4–15	Aqueous	NM	NM	High heating time at 80°C for 10 min	[22]
1,3,3-Trimethyl-2-[3-(1,3,3-trimethyl-1,3-dihydroindol-2ylidene)propenyl]-3 H-indolium chloride	556	2.2 mol dm^{-3} H_2SO_4 pH 7	0.01 to 3.84	toluene	2.4×10^5	NM	Limited applications	[23]
Methdilazine hydrochloride	513	10 M HCl (20 mL)	0.1–2.3	Aqueous	9.32×10^4	NM	High acid concentration, Low Beer's range	[18]
2,4-Dinitrophenyl hydrazine hydrochloride (2,4-DNPH)	520	5 mL conc HCl	0.03–3.5	Aqueous	3.10×10^4	NM	10 min standing time required	[24]
Furfuraldehyde thiocarbohydrazone (FATCH)	400	0.5 M HCl	5−25	Dichloromethane (DCM)	4.026×10^3	1:1	Long shaking time of 7 min	[25]
N-1-naphthyl-ethylenediamine dihydrochloride (NEDA)	545	Hydroxylamine hydrochloride, *p*-nitroaniline	0.01 to 2.50	Aqueous	2.85×10^4	NM	High heating time in two steps at 50°C for 80 min and at 50°C for 15 min	[26]
O-Methoxyphenylthiourea (OMePT)	350	3.5 M HCl	5–60	Chloroform	3.312×10^2	1: 2	Simple and precise, complex formation at room temperature, large Beer's range, low reagent concentration (0.012 M L^{-1}), single extraction	PM

Note: NM, not mentioned; PM, proposed method.

(Fluka) in concentrated hydrochloric acid (11.1 mL) and diluted to 1000 mL with water. This solution was standardised by the reported method [27]. The working standard solution of selenium(IV) was prepared after diluting the standard stock solution with water.

2.2.2. *Solution of foreign ions*

Standard solutions of different metal ions used for interference study were prepared after dissolving exactly weighed quantity of their respective salts in distilled water or dilute hydrochloric acid. Standard solutions of anions were prepared after dissolving their respective alkaline metal salts in distilled water. Different synthetic mixtures were prepared by combining their definite compositions. Double distilled water was used throughout the experimental study.

2.2.3. *O-methoxyphenyl thiourea solution*

OMePT was synthesised as per the method reported by Frank and Smith [28]. The 0.012 mol L^{-1} solution of OMePT was prepared after dissolving 0.219 g OMePT in 25 mL chloroform and diluted to the mark with chloroform in a 100 mL calibrated volumetric flask.

2.3. *Recommended procedure*

Hydrochloric acid was added to an aliquot of solution containing 400 µg selenium(IV) in a 25 mL volumetric flask, to maintain the acidity 3.5 mol L^{-1} on dilution up to mark with distilled water. This solution was equilibrated with 10.0 mL, 0.012 mol L^{-1} OMePT in chloroform for 3 min in a 125 mL separatory funnel. The two phases were allowed to separate, and the organic phase containing selenium(IV)–OMePT complex was dried over anhydrous sodium sulphate. It was transferred in a 10 mL volumetric flask and volume was adjusted to the mark with chloroform. Absorbance of selenium(IV)–OMePT complex in organic phase was measured at 350 nm against the reagent blank.

3. Results and discussion

3.1. *Absorption spectra*

The absorption spectra of the selenium(IV)–OMePT complex in chloroform shows maximum absorbance at 350 nm. The reagent blank has a negligible absorbance at the maximum absorbance wavelength of selenium(IV)–OMePT complex (Figure 1). Thus, all further absorption measurements of the complex were made at 350 nm.

3.2. *Effect of acid type and concentration*

Selenium(IV)–OMePT complex formation takes place in mineral acid media like hydrochloric acid, sulphuric acid and perchloric acid (Figure 2). Though selenium(IV)–OMePT complex formation takes place in various mineral acids, it was observed that the maximum absorbance is obtained in 3.5 mol L^{-1} hydrochloric acid concentration. Therefore, 3.5 mol L^{-1} hydrochloric acid concentration was used for this work.

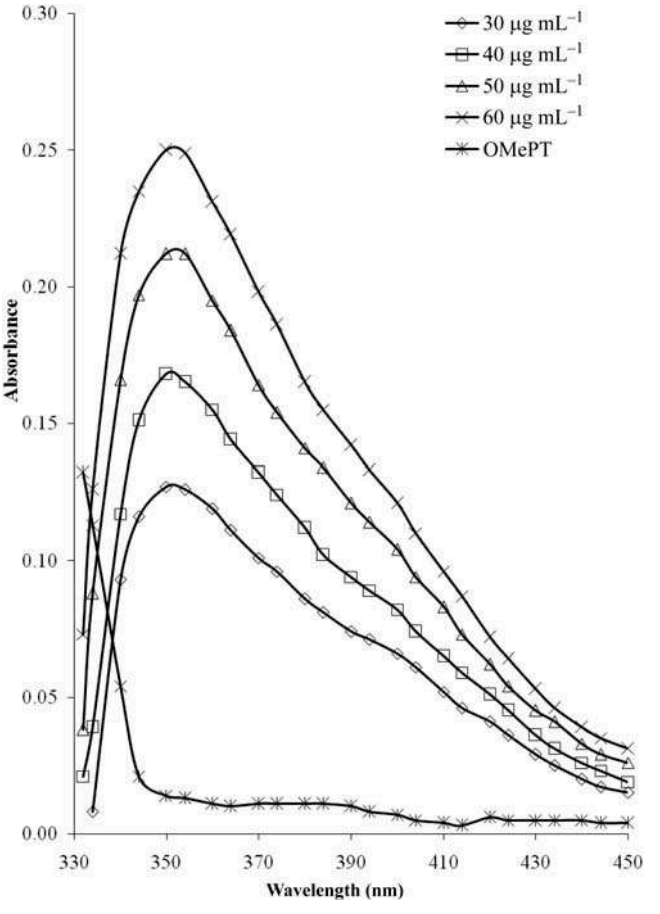

Figure 1. Absorbance spectra of Se(IV)–OMePT versus OMePT reagent blank. Se(IV): 30.0 µg mL^{-1}, 40.0 µg mL^{-1}, 50.0 µg mL^{-1}, 60.0 µg mL^{-1}; OMePT: 10.0 mL of 0.012 mol L^{-1} OMePT in chloroform; hydrochloric acid: 3.5 mol L^{-1}; shaking time 3 min.

3.3. *Effect of OMePT concentration*

Different molar concentrations of OMePT in chloroform (10 mL) in a range of 0.001 to 0.2 mol L^{-1} were varied using a fixed selenium(IV) concentration (40.0 µg mL^{-1}) and absorbance measurements were performed as per the recommended method. A 10 mL, 0.012 mol L^{-1} OMePT was sufficient for complete complex formation with selenium(IV). Absorbance increases up to 0.012 M OMePT and further remains constant. The excess of reagent does not have any adverse effect (Figure 3).

3.4. *Effect of extraction solvent*

Various extraction solvents, viz. toluene, xylene, benzene, isoamyl alcohol, MIBK and chloroform, were studied for quantitative extraction of selenium(IV)–OMePT complex. Amongst the extraction solvents studied, quantitative extraction with maximum absorbance was obtained in chloroform as a solvent.

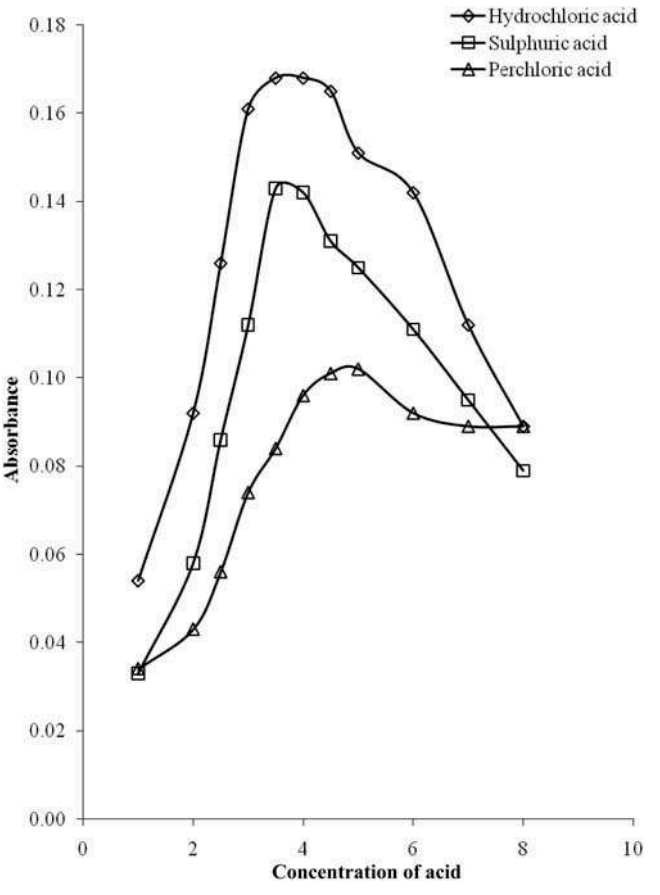

Figure 2. Effect of acid concentration on Se(IV)–OMePT complex. Se(IV): 40.0 µg mL^{-1}; acid concentration: 1.0–8.0 mol L^{-1}; OMePT: 10.0 mL, 0.012 mol L^{-1} in $CHCl_3$; λ_{max}: 350 nm.

3.5. *Effect of equilibration time and stability of complex*

The study of change in absorbance with variation in equilibration time was carried out over 30 s to 30 min. It was observed that extraction of selenium(IV) was complete in 3 min and there was no any adverse effect of prolonged equilibration on extraction of selenium(IV) up to 30 min. Hence, 3 min equilibration time was fixed for further study.

The absorbance of the complex remained stable and constant for more than 72 h. The spectral and physico-chemical characteristic of the selenium(IV)–OMePT complex is given in Table 2.

4. Analytical figures of merit

4.1. *Validity of Beer's law*

The Beer's law was obeyed over the concentration range of 5–60 µg mL^{-1} selenium(IV) (Figure 4). The Ringbom's plot was sigmoid shape with linear segment at intermediate absorbance values of 20–50 µg mL^{-1} (Figure 5) [29].

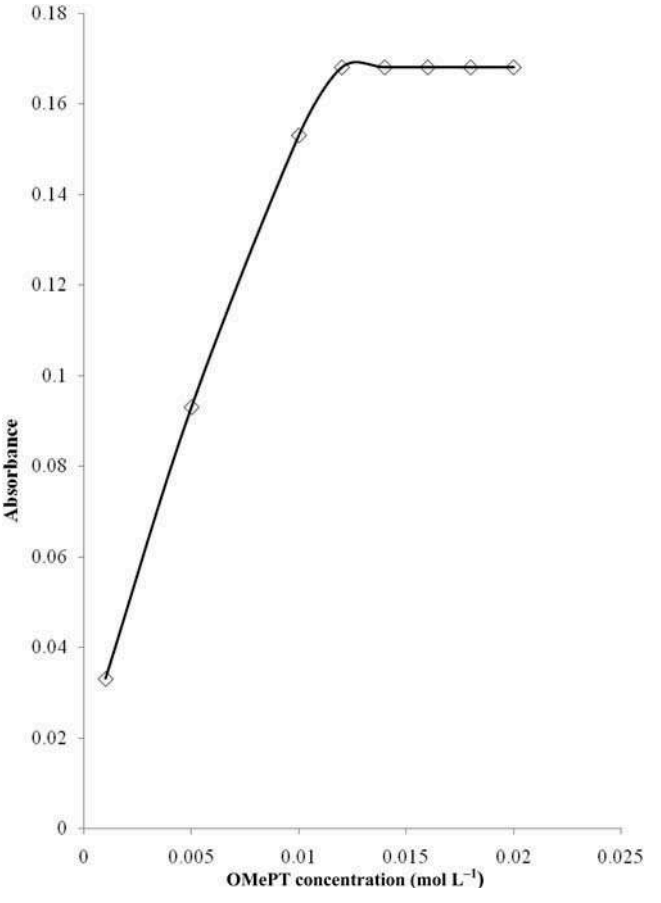

Figure 3. Effect of reagent concentration Se(IV)–OMePT complex.

Table 2. Spectral and physico-chemical characteristics along with precision data of selenium(IV)–OMePT complex.

Spectral characteristics and precision	Parameters
Hydrochloric acid concentration	3.5 mol L^{-1}
Reagent concentration	10.0 mL, 0.012 mol L^{-1}
Extraction solvent	Chloroform
Equilibration time	3 min
λ_{max}	350 nm
Molar absorptivity	3.312×10^2 L mol^{-1} cm^{-1}
Sandell's sensitivity	0.2384 μg cm^{-2}
Beer's law range	5 to 60 μg mL^{-1}
Ringbom's optimum	20 to 50 μg mL^{-1}
Limit of detection	0.6121 μg mL^{-1}
Relative standard deviation	0. 35%
Stoichiometry of the complex	1:2 (Se(IV):OMePT)
Stability of complex	>72 h
Correlation coefficient	0.99

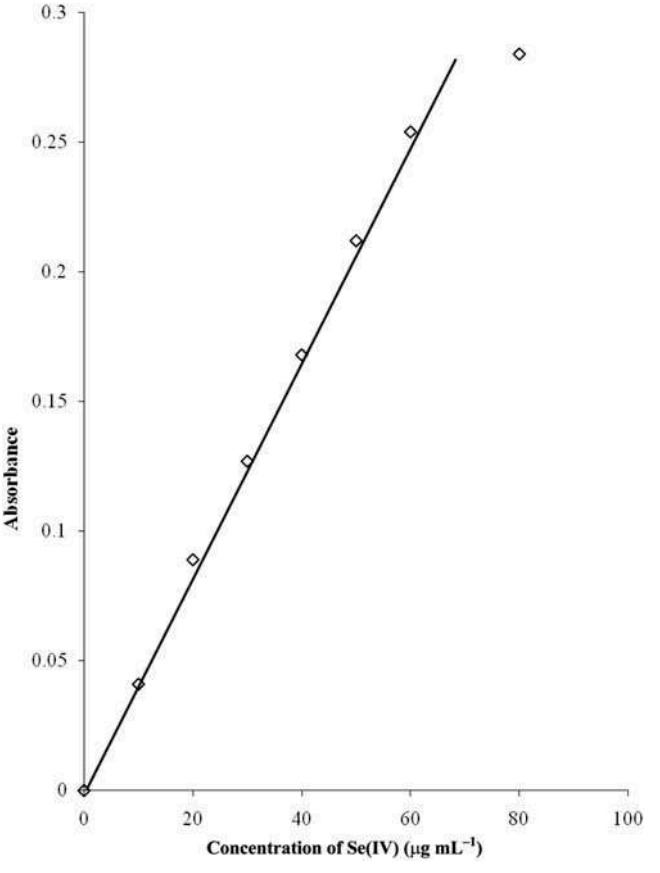

Figure 4. Validity of Beer's law for Se(IV)–OMePT complex. OMePT: 10.0 mL, 0.012 mol L^{-1}; HCl concentration: 3.5 mol L^{-1}; λ_{max}: 350 nm.

4.2. *Precision accuracy and detection limit*

The molar absorptivity and Sandell's sensitivity of the selenium(IV)–OMePT complex were found to be 3.312×10^2 L mol^{-1} cm^{-1} and 0.2384 μg cm^{-2}, respectively. The optimum conditions and other analytical parameters were evaluated. The ratio of relative error to photometric error in concentration was found to be 4.34. The limit of detection for the developed method was 0.61 μg mL^{-1} in terms of thrice the standard deviation of the blank value. The correlation coefficient value of selenium(IV)–OMePT complex with an independent variable as concentration in μg mL^{-1} and a dependent variable as absorbance was found to be 0.99, it indicates a clear linearity between these two variables. The slope value and intercept for the best-fitted line were 0.0036 and 0.018, respectively. The content of selenium(IV) in real samples can be determined using the straight line equation $Y = 0.0036X + 0.018$.

4.3. *Stoichiometry of selenium(IV)–OMePT complex*

The composition of selenium(IV)–OMePT complex was ascertained using the slope ratio method in which the graph of $\log(D_{Se(IV)})$ against $\log(C_{OMePT})$ at 1.0, 2.0 and 3.0 mol L^{-1} hydrochloric acid concentrations were plotted. The plots were linear, having slope value 1.90,

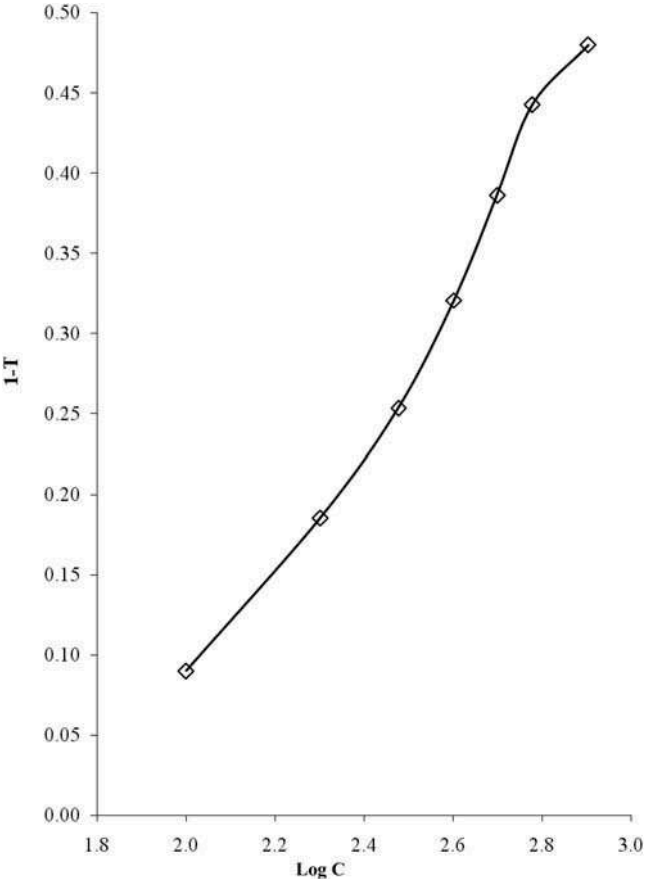

Figure 5. Ringbom's plot for optimum concentration of Se(IV)–OMePT complex. OMePT: 10.0 mL, 0.012 mol L^{-1}; HCl concentration: 3.5 mol L^{-1}; λ_{max}: 350 nm.

1.93 and 1.99, respectively (Figure 6). Hence, the probable composition of the extracted species was 1:2 (Se(IV):OMePT). This composition of the complex was confirmed by the mole ratio method (Figure 7) and Job's continuous variation method (Figure 8).

OMePT acts as a multidentate ligand; sulphur from thio group (–C=S) and nitrogen from the amino group ($–NH_2$) coordinate with selenium(IV) to form a 1:2 (Se(IV):OMePT) complex. Based on this investigation, probable structure recommended to complex is reported (Figure 9).

4.4. *Effect of interfering ions*

The selectivity of the proposed method was checked for the determination of selenium(IV) (40 μg mL^{-1}) in the presence of high concentration of various foreign ions. The tolerance limit was fixed for the ions which do not cause deviation more than ±2% in the absorbance of yellow coloured selenium(IV)–OMePT complex. The interference of cations was removed by using suitable masking agents. Tolerance limit for various interfering ions is reported in Table 3.

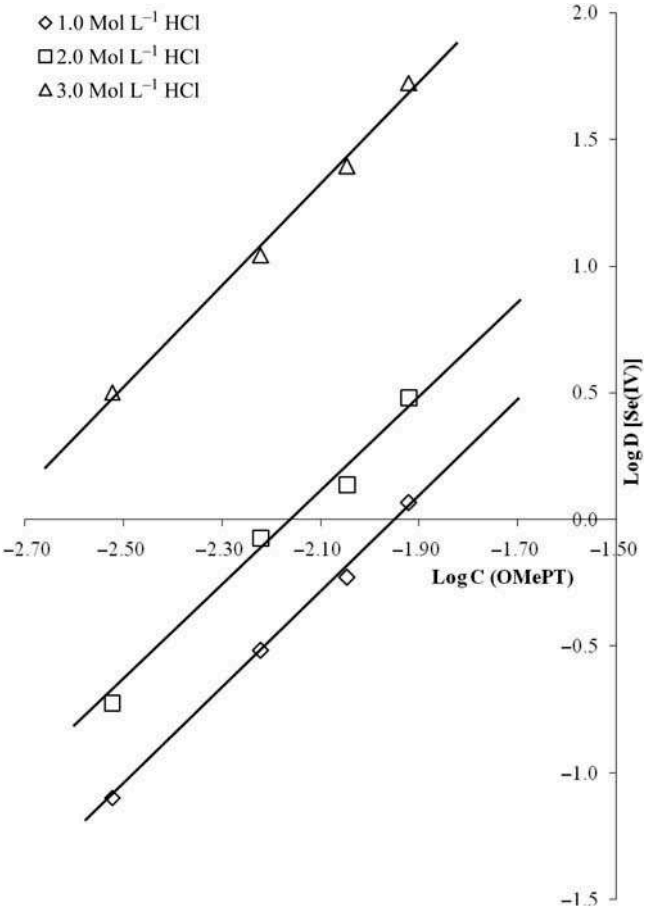

Figure 6. Plot of log C $_{(OMePT)}$ versus log D $_{[Se(IV)]}$. Se(IV): 40.0 µg mL^{-1}; OMePT: 10.0 mL, 0.003 to 0.012 mol L^{-1}; HCl concentration: 1.0 mol L^{-1}, 2.0 mol L^{-1}, 3.0 mol L^{-1}; shaking time: 3 min; λ_{max}: 350 nm.

5. Applications

5.1. *Separation and determination of selenium(IV) from binary synthetic mixtures*

The proposed method was applied for separation and determination of selenium(IV) from different metal ions, viz. Ni(II), Au(III), Bi(III), Al(III) and Sb(III). After quantitative extraction of selenium(IV), the aqueous phase was evaporated to moist dryness followed by 3.0 mL concentrated hydrochloric acid. The residue obtained was cooled, dissolved in water and added metal ions were determined by reported methods [30]. To enhance the extraction of selenium(IV) in the presence of Ni(II) it was masked with EDTA. It was de-masked after treatment with 3.0 mL nitric acid, evaporated to moist dryness, followed by 3.0 mL hydrochloric acid. The residue obtained was cooled, dissolved in water and Ni(II) was determined spectrophotometrically as per the reported method [30] (Table 4).

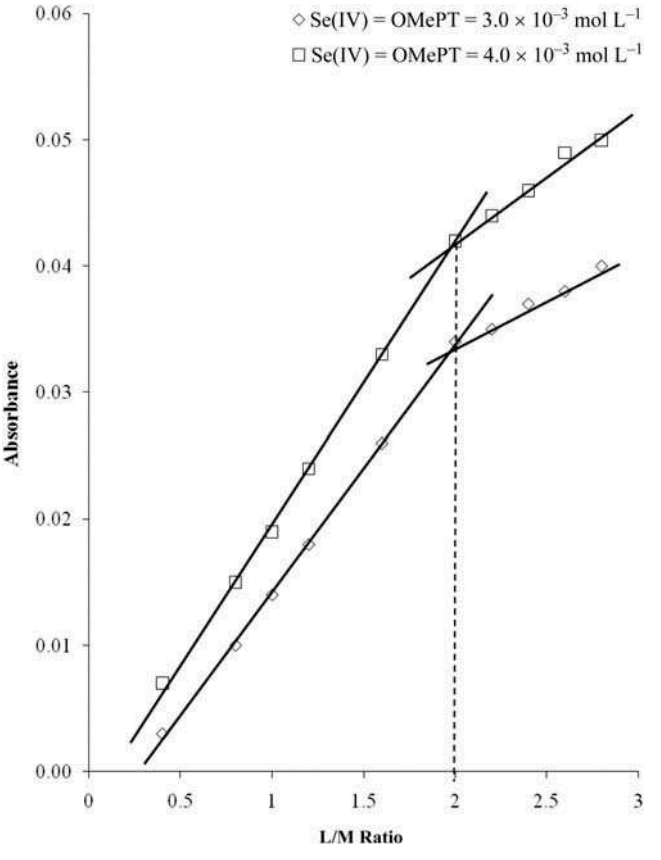

Figure 7. Mole ratio method for Se(IV)–OMePT complex. Se(IV) = OMePT: 3.0×10^{-3} mol L^{-1} and 4.0×10^{-3} mol L^{-1}; HCl concentration: 3.5 mol L^{-1}; λ_{max}: 350 nm.

5.2. *Determination of selenium(IV) from pharmaceutical samples*

The proposed method was also applied for separation and determination of selenium(IV) from pharmaceutical samples, viz. Menopace ISO, Cardio-Vit plus, Betared, Lyco-First, EC-350, Casera and toilet preparation Selsun shampoo. The pharmaceutical sample (5 to 15 tablets or capsules) was heated with the minimum amount of concentrated hydrochloric acid followed by the addition of 1 mL of concentrated nitric acid. The organic matter was destroyed by treatment with 5 mL of 60% perchloric acid. The solution was slowly evaporated to moist dryness. The residue obtained was dissolved in hot dilute hydrochloric acid and made up to 25 mL volume with distilled water. An aliquot (5 mL) of this solution was extracted and selenium(IV) was determined by the proposed method. The results are in good agreement with the certified values provided by respective manufacturer of pharmaceutical and toilet preparation.

The toilet preparation, medicated shampoo (Selsun, Pfizer Ltd.), 1 mL, was transferred in a 100 mL beaker and a mixture of 1:1 perchloric acid and nitric acid was added. The solution was heated to moist dryness. The residue was treated with dilute hydrochloric acid and finally diluted to 50 mL with water. A definite aliquot (5 mL) was extracted and determined by the proposed method. The results obtained were precise and accurate with that of reported data by manufacturer (Table 5; supplemental data).

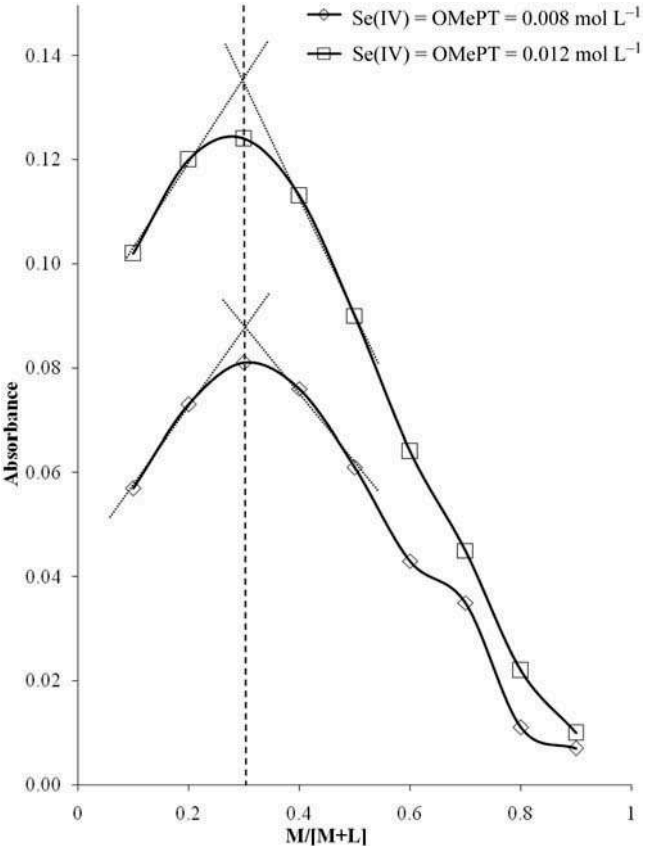

Figure 8. Job's continuous variation method for Se(IV)–OMePT complex. Se(IV) = OMePT: 0.008 mol L^{-1} and 0.012 mol L^{-1}; HCl concentration: 3.5 mol L^{-1}; shaking time: 3 min: λ_{max}: 350 nm.

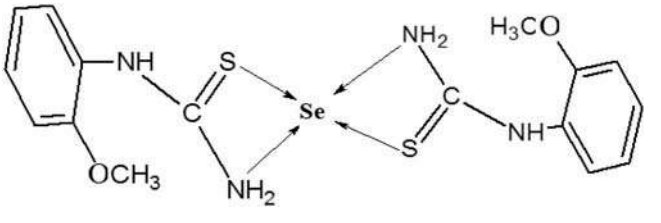

Figure 9. Probable structure of selenium(IV)–OMePT complex.

5.3. *Analysis of selenium(IV) in environmental sample*

5.3.1. *Vegetable*

A 25.0 g finely chopped fresh cabbage (*Brassica oleracea* var. *capitata*) sample, from local village in Ahmednagar district, was placed in a 250 mL beaker. It was digested with 10–20 mL concentrated nitric acid for 20 min. After cooling 0.5 mL perchloric acid was added and heating was continued for another 10 min. The residue was cooled and 10 mL water and 5 mL of concentrated hydrochloric acid were added. This mixture was boiled for 10 min to convert

Table 3. Effect 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	Ca(II)	$CaCl_2.2H_2O$	50.0
Cd(II)	$CdCl_2.2H_2O$	12.0	Tl(III)	Tl_2O_3	2.00
Fe(III)	$(NH_4)Fe(SO_4)_2.12H_2O$	13.0	In(III)	$InCl_3.4H_2O$	4.00
Hg(II)	$HgCl_2$	1.00	Rh(III)	$RhCl_3$	1.00
Bi(III)	$BiCl_3$	11.0	Pt(IV)	H_2PtCl_6	1.50
Ni(II)[a]	$NiCl_2.6H_2O$	3.00	Ir(III)[b]	$IrCl_3$	0.40
Cu(II)[a]	$CuSO_4.5H_2O$	1.80	Os(IV)	OsO_4	0.05
Al(III)	$AlCl_3.6H_2O$	12.0	Ru(III)	$RuCl_3,3H_2O$	0.60
La(III)	$LaCl_3.7H_2O$	1.00	Pd (II)[c]	$PdCl_2$	0.125
Li(I)	LiCl	15.0	Zr(IV)	$ZrOCl_2.8H_2O$	18.0
Ti(III)	$(Ti_2SO_4)_3$	12.0	As (III)	As_2O_3	4.00
Mg(II)	$MgCl_2.6H_2O$	18.0	W(VI)	$Na_2WO_4.2H_2O$	15.0
Sn(II)	$SnCl_2.2H_2O$	2.00	Zn(II)	$ZnSO_4.7H_2O$	50.0
Ga(III)	$GaCl_3$	2.00	Be(II)	$BeSO_4.2H_2O$	18.0
Au(III)	$HAuClO_4.H_2O$	1.00	Fluoride	NaF	100
Mo(VI)	$(NH_4)_6MO_7O_{24}.2H_2O$	12.0	Phosphate	Na_3PO_4	100
Sb(III)	Sb_2O_3	3.00	Sulphate	K_2SO_4	100
V(V)	V_2O_5	25.0	Succinate	$(CH_3COONa)_2.6H_2O$	100
Ce(IV)	$Ce(SO_4)_2.4H_2O$	0.50	Citrate	$C_6H_8O_7.H_2O$	100
Pb(II)	$PbCl_2$	7.00	Malonate	$CH_2(COONa)_2$	100
U(VI)	$UO_2(CH_3COO)_2.2H_2O$	16.0	Tartrate	$(CHOH:COOH)_2$	100
Co(II)	$CoCl_2.6H_2O$	10.0	Acetate	$CH_3COONa.3H_2O$	100
Ba(II)	$BaCl_2.6H_2O$	50.0	Oxalate	$Na_2C_2O_4.2H_2O$	100
Sr(III)	$Sr(NO_3)_2$	50.0	E.D.T.A	Na_2EDTA	100

Note: [a]Masked with 100 mg EDTA. [b]Prior extraction of Ir(III). [c]Prior extraction of Pd (II).

Table 4. Separation of selenium(IV) from binary synthetic mixtures.

Mixture	Amount taken (μg)	Recovery (%)[a]	RSD (%)	Chromogenic ligand	Ref.
Se(IV)	400	99.33	0.44	OMePT	–
Ni(II)[b]	100	99.13	0.52	DMG	[30]
Se(IV)	400	99.65	0.44	OMePT	–
Au(III)	200	99.51	0.62	Rhodamine-B	[30]
Se(IV)	400	99.62	0.27	OMePT	–
Bi(III)	300	99.76	0.13	Iodide (KI)	[30]
Se(IV)	400	99.60	0.21	OMePT	–
Al(III)	50	99.51	0.39	8-Hydroxy quinoline	[30]
Se(IV)	400	99.54	0.24	OMePT	–
Sb(III)	300	99.77	0.22	Iodide (KI)	[30]

Note: [a]Average of six determinations.
[b]Masked with 100 mg EDTA.

selenium (VI) into selenium (IV). The solution was evaporated to moist dryness and the residue was dissolved in hot dilute hydrochloric acid and diluted to 50 mL with distilled water. An aliquot (10 mL) of this solution was analysed for selenium(IV) according to the recommended method (Table 6). A Systronics 8130 atomic absorption spectrometer equipped with a hydride generator was used for comparative purposes.

Table 5. Analysis of pharmaceutical and toilet preparation samples.

Sample	Composition	Certified value of Se(IV) (μg/Tab)	Amount of Se(IV)[a] found (μg/Tab)	(μg g^{-1})	RSD (%)
Menopace ISO	Nicotinamide 10 mg, Vit-C 75 mg, Vit-E 20 mg, iron 5 mg, selenium 100 μg	100	98.87	36.06	0.40
Cardio-Vit plus	Pyridoxine hydrochloride 3 mg, nicotinamide 100 mg, cyanocobalmin 15 μg, folic acid 1.5 mg, chromium picolinate 250 μg, selenium 100 μg, zinc sulphate monohydrate 61.8 mg	100	98.82	28.41	0.44
Betared	Vit-C 100 mg, Vit-E 25 IU, manganese 1.5 mg, beta carotene 10.33 mg, selenium 75 μg	75	74.11	45.49	0.10
Lyco-First	Lycopene 6% 5000 μg, Vit-A 2500 IU, Vit-E 10 IU, Vit-C 50 mg, selenium 70 μg	70	69.76	23.91	0.33
EC-350	Vit-C 150 mg, Vit-E 25 mg, alpha lipoic acid 100 mg, selenium 75 μg	75	73.79	28.03	0.33
Casera	Vit-A 2500 IU, Vit-C 100 mg, alphatocophenyl acetate 25 IU, beta carotene 6 mg, selenium 55 μg, zinc 7.5 mg, molybdenum 25 μg	55	54.29	17.42	0.68
Selsun shampoo	Selenium sulphide 2.5% w/v	275[b]	273.39 [b]		0.19

Note: [a]Average of six determinations. [b]μg of Se(IV) per 2 mL of diluted solution.

Table 6. Analysis of environmental sample.

Sample	Amount of selenium(IV) added ($\mu g\ g^{-1}$)	Amount of selenium(IV) found ($\mu g\ g^{-1}$ or $\mu g\ mL^{-1}$)		RSD (%)
		PM[a]	AAS	
Cabbage	–	10.53	10.61	1.36
Soil	50.0	50.06	50.15	1.56
Water	–	0.031	0.035	1.17

Note: [a]Average of four determinations.

5.3.2. *Soil*

A known amount of selenium was mixed with 20 g of soil sample, and extracted with hydrochloric acid and nitric acid mixture three times. The filtrate of the extract was evaporated to moist dryness and the residue was treated with 20 mL of 10 mol L^{-1} hydrochloric acid and then heated to convert all selenium into selenium(IV). The solution was further diluted with water to give a suitable concentration of selenium. The selenium content was determined from an aliquot of this solution following the recommended method. Results are in good agreement with that of the analysis by AAS.

5.3.3. *Water from Bhandardara Dam*

One litre of water from Bhandardara Dam (Maharashtra) was filtered through Whatman filter paper and concentrated to about 60 mL by heating on a hot plate. Concentrated nitric acid, 10 mL, was added in this solution. The mixture was heated on a hotplate and evaporated to moist dryness. The residue was dissolved in 10 mL hot dilute hydrochloric acid and the solution was boiled to convert all selenium into selenium(IV); after cooling the solution was transferred into a 25 mL calibrated flask, and analysed by the proposed method. Results are in good agreement with that of the analysis by AAS.

6. Conclusion

O-Methoxyphenyl thiourea (OMePT) is a sensitive and selective reagent for the spectrophotometric determination of selenium(IV). Low concentration (0.012 mol L^{-1}) of the OMePT is required for quantitative extraction of selenium(IV). The selenium(IV)–OMePT complex is highly stable. Rapid determination of selenium(IV) at room temperature with low interference of foreign ions is achieved by the recommended method.

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Disclosure statement

No potential conflict of interest was reported by the authors.

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Supplemental data

Supplemental data for this article can be accessed at http://dx.doi.org/10.1080/03067319.2015.1046057

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Separation and Spectrophotometric Determination of Osmium(IV) and Ruthenium(III) with O-methoxyphenyl Thiourea as Chromogenic Legand: Sequential Separation of Osmium(IV), Ruthenium(III), and Platinum(IV)

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Separation and Spectrophotometric Determination of Osmium(IV) and Ruthenium(III) with *O*-methoxyphenyl Thiourea as Chromogenic Legand: Sequential Separation of Osmium(IV), Ruthenium(III), and Platinum(IV)

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A precise and selective method has been developed for extraction spectrophotometric determination of osmium(IV) and ruthenium(III) using *o*-methoxyphenyl thiourea (OMePT) as a chromogenic ligand. The basis of the proposed methods are osmium(IV)-OMePT complex was formed in 0.8 mol L^{-1} at room temperature while ruthenium(III)-OMePT complex was formed in 3.4 mol L^{-1} aqueous hydrochloric acid media after 5.0 min heating in boiling water bath. The osmium(IV)-OMePT and ruthenium(III)-OMePT complex were measured at 518 and 640 nm against the reagent blank, respectively. Complexes were also extracted in 10 mL chloroform and showed comparable absorbance values. Beer's law was obeyed up to 110.0 μg mL^{-1} for osmium(IV)-OMePT complex and up to 50.0 μg mL^{-1} for ruthenium(III)-OMePT complex. Molar absorptivity and Sandell's sensitivity of osmium(IV)-OMePT and ruthenium(III)-OMePT complexes were 2.12 × 10^3 L mol^{-1} cm^{-1}, 0.089 μg cm^{-2} and 2.34 × 10^3 L mol^{-1} cm^{-1}, 0.043 μg cm^{-2}, respectively. The stoichiometry of osmium(IV)-OMePT and ruthenium(III)-OMePT complex was 1:1 and 1:2, respectively. Stability of osmium(IV)-OMePT complex was > 8 days and that of ruthenium(III)-OMePT complex was > 48 h. The proposed method was successfully applied for determination of osmium(IV) and ruthenium(III) from synthetic mixtures corresponding to platinum-osmium alloy and fissium alloy, respectively. The method was successfully applied for sequential separation of osmium(IV), ruthenium(III), and platinum(IV).

Keywords osmium; ruthenium; sequential separation; fissium alloy; platinum-osmium alloy

INTRODUCTION

Osmium and ruthenium are rare metals found in metallic state together with other platinum group metals and coinage metals. The abundance of osmium in earth's crust is 0.005 ppm (1) while ruthenium is 0.0001 ppm by weight (1). About 34 isotopes of osmium are discovered; out of seven occur naturally (2). Both osmium(IV) and ruthenium(III) has widespread applications. The most significant application of osmium is as an oxidizing agent for many organic substances. It has many applications as used to biosensor for glucose determination in alcoholic beverages (3), and determination of manganese (4). Osmium complex $(Os(bpy)_2pyCl)^+$ was used as co-substrate for determination of catalysis and inhibition reaction between horseradish-peroxidase and hydrogen peroxide (5). Many osmium compounds showed specific catalytic activity as hydrogenation (6), oxidative cleavage (7), and atom transfer radical addition (8). Osmium complexes have recently been studied as potential anticancer drugs (9). Thus, strongly catalytic property, oxidizing agent, toxic in nature, minimum natural abundance, antitumor activity, and widespread applications signifies the necessity of simple and rapid separation and determination method for the osmium.

Ruthenium complexes are used for site specific chemo selective labelling of proteins (10), potential models for iron-sulphur bond in heme-protein (11), determination of amino acids (12), cholorophenaramine (13), and determination of cephalosporins in pharmaceutical preparations (14). Ruthenium chloroquine complexes exhibit enhanced anti-malarial activity (15). Ruthenium carboxylates act as potential anti-microbial agents (16). Ruthenium complexes have also shown promise for future development as effective anticancer drugs (17). It plays a vital role in catalysis (18). Trace abundance along with closely associated platinum group metals, enhanced properties, and significant biological and catalytic applications demand the

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effective and selective analytical method for separation and determination of ruthenium.

A large number of methods are reported for determination of osmium and ruthenium. The comparison of the present method with reported methods for spectrophotometric determination of osmium(IV) and ruthenium(III) is reported in Table 1. Literature survey reveals that the existing spectrophotometric determination methods lack a large number of drawbacks such as sensitivity, precision, and large number of interferences from foreign ions (19–30).

In our laboratory we have developed extraction and spectrophotometric determination methods for palladium(II) (31), rhodium(III) (32), and platinum(IV) (33) using *o*-methylphenyl thiourea (OMPT). Current study reports the analytical applications of *o*-methoxyphenyl thiourea (OMePT) for spectrophotometric determination of osmium(IV) and ruthenium (III).

The present method overcomes the limits of reported methods. The new reagent *o*-methoxyphenyl thiourea (OMePT) forms pink colored complex with osmium(IV) at room temperature and a blue-green colored complex with ruthenium(III) after heating in boiling water bath for 5.0 min.

EXPERIMENTAL

Apparatus and Reagents

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

O-Methoxyphenyl thiourea (OMePT) was synthesized as per method reported by frank and smith (34). The stock solution of reagent, OMePT (0.1 mol L^{-1}) was prepared after dissolving 0.911 g OMePT in 20 mL ethanol and was made up to 50 mL with ethanol. Its working solution was prepared from the stock solution using ethanol as a solvent.

Metal Solutions

A standard stock solution of osmium(IV) was prepared after dissolving 1.0 g osmium tetroxide (Loba Chemie Pvt Ltd, Mumbai, India, Purity = 99.9%) with carefully crushing a hermetically closed ampoule containing osmium tetroxide in glass bottle containing 1.0 mol L^{-1} hydrochloric acid and was made up to mark in a 250 mL volumetric flask with water. The stock solution was standardized using the gravimetric method (35). Quantitative conversion of osmium into the stable $OsCl_6^{2-}$ as H_2OsCl_6 species was carried out by heating the solution for 20 min at 90-100°C (36, 37). Standard working solution of osmium(IV) was prepared by diluting an aliquot of osmium(IV) initial stock solution in 1.0 mol L^{-1} hydrochloric acid. Osmium(IV) present in the form $OsCl_6^{2-}$ does not undergo hydrolysis at room temperature at the concentration greater than 0.5 mol L^{-1} of hydrochloric acid (38). The stock solution of ruthenium(III) was prepared by dissolving 1.0 g ruthenium trichloride ($RuCl_3.3H_2O$) in 1.0 mol L^{-1} hydrochloric acid and diluted to 250 mL and standardized by the reported method (39). A working solution (200 μg mL^{-1}) was prepared after further dilution of the stock solution.

Standard solutions of different metal ions used for interference study were prepared after dissolving exactly weighed quantity of their respective salts in distilled water or dilute hydrochloric acid. Standard solutions of anions were prepared after dissolving their respective alkaline metal salts in distilled water. Different synthetic mixtures were prepared by combining their definite compositions. Double distilled water was used throughout the experimental study.

Recommended Procedure

In a 10 mL volumetric flask, an aliquot of solution containing 150 μg osmium(IV) and 2 mL, 0.009 mol L^{-1} OMePT in ethanol was added. This solution was made 0.8 mol L^{-1} with respect to hydrochloric acid, and after dilution with water, it gives pink colored osmium(IV)-OMePT complex instantly at room temperature. This pink colored complex was measured in aqueous phase at 518 nm and the complex was also extracted into 10 mL chloroform and the absorbance was measured at 518 nm against the reagent blank.

An aliquot of solution containing 200 μg of ruthenium(III) and 2.0 mL, 0.012 mol L^{-1} OMePT in ethanol were transferred in a 10 mL volumetric flask and solution was made 3.4 mol L^{-1} with respect to hydrochloric acid. After dilution with water the solution was kept in boiling water bath for 5 min. The mixture was cooled and the blue-green colored ruthenium(III)-OMePT complex was measured at 640 nm or extracted into 10 mL chloroform and the absorbance was measured at 640 nm against the reagent blank.

RESULTS AND DISCUSSION

Absorption Spectra

The absorption spectrum of osmium(IV)-OMePT and ruthenium(III)-OMePT complexes showed maximum absorbance at 518 nm and 640 nm (Figs. 1 and 2). The reagent blank has negligible absorbance at 518 and 640 nm wavelengths for both the absorption spectrum.

Effect of Hydrochloric Acid Concentration

Osmium(IV)-OMePT and ruthenium(III)-OMePT complex formation were took place in hydrochloric acid media and it depends upon the hydrochloric acid concentration. The hydrochloric acid concentration was varied from 0.02 to 5.0 mol L^{-1} for osmium(IV), it showed complete complex formation and maximum absorbance in the range of 0.8 to 1.0 mol L^{-1}, for ruthenium(III) the hydrochloric acid concentration was

TABLE 1
Comparison of present method with other extraction spectrophotometric determination methods of Os(IV) and Ru(III)

Reagents	λ_{max} (nm)	Condition	Beer's Law validity range, ($\mu g\ mL^{-1}$)	Solvent	Molar Absorptivity, ($L\ mol^{-1}cm^{-1}$)	M: L	Remark	Ref
4-Hydroxy 3, 5-dimethoxy benzaldehyde 4-hydroxy benzoyl hydrazone	410	pH 5.0	0.285−2.853	chloroform	5.16×10^4	1: 1	low beer's range	19.
Tropeolin O,	540,	pH 5.2	0.57−28.67	Aqueous	NM	NM	Heating at 95°C, limited	20.
Tropiolin OOO-I,	364,	pH 8.0	0.01−1.15				applications0.	
Eriochrome Black T	400,	pH 10.0	2.8−142.7					
Congo Red (CR)	490	pH 3.5	7.0×10^{-7}-8.5×10^{-5}	Aqueous	NM	1: 1	Very low beer's range, heating at 98°C	21.
Thiocynatochrome Ethyl thiourea + $NH_4[Cr(CHS)_4$(aniline)]	535−340	0.1M HCl	68.4−548	Acetone	793.067	NM	Heating, filtration using G_4 crucible 15-20 minutes for development of complex	22.
Orange G	540	pH 5.80	0.01−7.70	Chloroform	1.1×10^4	1: 1	30 min heating in boiling water bath	23.
Ethylisobutrazine hydrochloride	519	2M HCl	0.25−7.5	Chloroform	2.4×10^3	NM	Analysis of synthetic syserkite mineral	24.
o-Methoxyphenylthiourea (OMePT)	518	0.8 M HCl	Up to 110	Chloroform and in aqueous medium same absorbance	2.028×10^3	1: 1	Simple and precise, instant complex formation at room temperature, large beer's range, low reagent concentration, single extraction.	PM
Quercetin Quercetin 5'-sulfonic acid	291	0.04 m HCl	up to 30	Methanolic-aqueous (1:1) solution	5.0×10^3	NM	Limited applications	25.
4-hydroxy 3,5 dimethoxybenzaldehyde 4 hydroxybenzoylhydrazone	400	pH 3.0−5.0	0.252−5.053	Acidic surfactant of C-TAB (5%)	1.79×10^4	1: 1	Low beer's range, limited applications	26.
3-(2-pyridyl)-5,6-diphenyl-as-triazine (PDT) and	475	pH 3.0	NM	EtOH-H_2O	3.5×10^4	1: 3	Colour development time 1 Hr	27.
ferrozine	478	pH 3.0		Aqueous Medium	3.56×10^4	1: 3	Colour development time 1 Hr	
Sodium periodate	350	pH 2.4−3.6	0.1−5	Chloroform	NM	NM	Long complex formation time	28.
p-chloror and p-bromobenzoylacetoneoxime	475	pH 5.0	20−200	Ethylacetate	3.8×10^3	1: 2	Two stage extraction	29.
propericiazine	511	6-8 M HCl	0.2−9.4	Aqueous	1.1×10^4	NM	High acid concentration	30.
o-Methoxyphenylthiourea (OMePT)	640	3.4 M HCl	Up to 50.0	Chloroform and in aqueous medium same absorbance	2.32×10^4	1: 2	Simple and precise, 5.0 min heating, large beer's range, low reagent concentration, single extraction.	PM

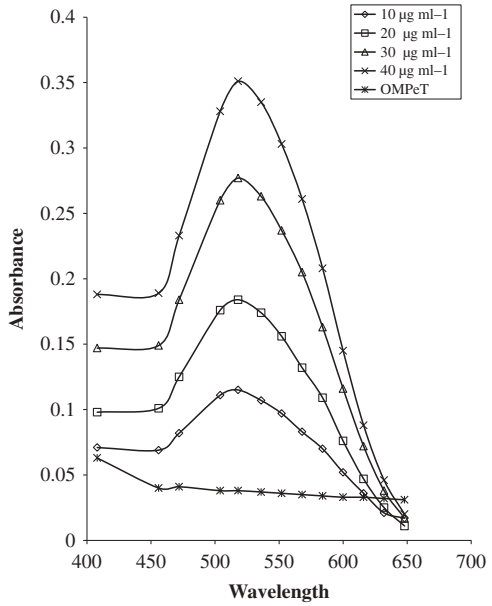


FIG. 1. Absorption spectra of Os(IV)-OMePT complex: Os(IV): 10.0 µg mL^{-1}; 20.0 µg mL^{-1}; 30.0 µg mL^{-1}, 40.0 µg mL^{-1}; OMePT: 2.0 mL, 0.009 mol L^{-1}; HCl concentration: 0.8 mol L^{-1}.

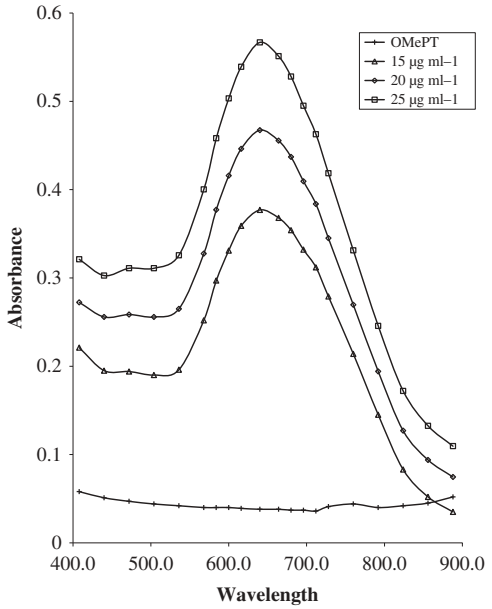


FIG. 2. Absorption spectra of Ru(III)-OMePT complex: Ru(III): 15.0 µg mL^{-1}; 20.0 µg mL^{-1}; 25.0 µg mL^{-1}; OMePT: 2.0 mL, 0.015 mol L^{-1}; HCl concentration: 3.4 mol L^{-1}; heating time: 5.0 min.

varied from 0.2 to 8.0 mol L^{-1} showed maximum absorbance in the range of 3.4 to 6.0 mol L^{-1} and further the absorbance decreases (Fig. 3).

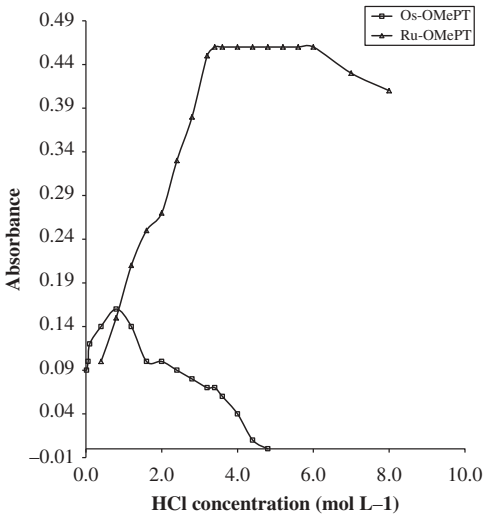


FIG. 3. Effect of hydrochloric acid concentration on Os(IV)-OMePT and Ru(III)-OMePT complex: Os(IV): 15.0 µg mL^{-1}, Ru(III): 20.0 µg mL^{-1}; OMePT: 2.0 mL, 0.009 mol L^{-1} and 0.012 mol L^{-1}; HCl concentration: 0.02 mol L^{-1} to 8.0 mol L^{-1}; λ_{max}: 518 nm and 640 nm.

Effect of Ethyl Alcohol, DMF, and Dimethylsulfoxide Concentrations

The chromogenic reagent was used in ethyl alcohol, dimethylformamide (DMF), and dimethylsulphoxide (DMSO) with concentration [from 1.0% to 50.0% (V/V)] keeping other parameters constant. It was found that maximum absorbance was obtained for both the complexes in presence of ethyl alcohol. For osmium(IV) maximum absorbance was obtained in the range of 4.0% to 36.0% (V/V) ethyl alcohol and for ruthenium(III) it was obtained above 8.0% (V/V) ethyl alcohol. Thus, substantially in order to ensure complete complex formation, excess reagent medium 20% (V/V) ethanol in aqueous phase was fixed for both osmium(IV) and ruthenium(III).

Effect of OMePT Concentration

Different molar concentrations of OMePT (2.0 mL) using ethanol as a solvent in the range of 0.0002 to 0.2 mol L^{-1} was added to a fixed osmium(IV) (150 µg) or ruthenium(III) (200 µg) and absorbance measurements was performed as per the recommended procedure. A 2.0 mL, 0.009 mol $L^{-1,}$ and 0.012 mol L^{-1} OMePT was sufficient for complete complex formation with osmium(IV) and ruthenium(III), respectively. The excess of reagent does not have any adverse effect.

Effect of Heating Time

Osmium(IV)-OMePT complex forms at room temperature and it need not require heating or waiting time. The absorbance values of ruthenium(III)-OMePT complex increases with heating time in boiling water bath up to 5 min and above it the values were constant up to 25.0 min. Further heating decreases

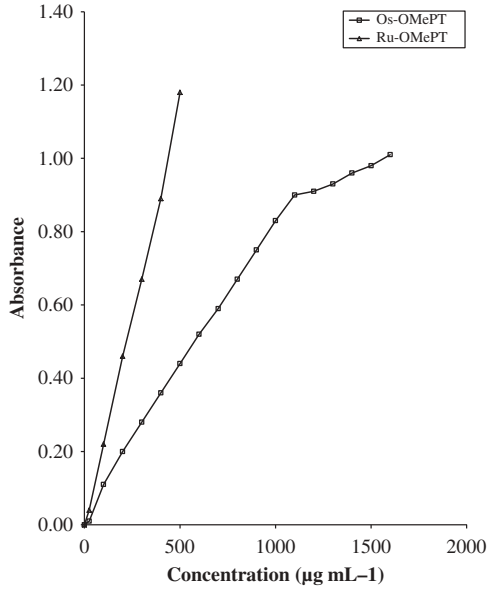


FIG. 4. Validity of Beer's law for Os(IV)-OMePT and Ru(III)-OMePT complex: OMePT: 2.0 mL, 0.009 mol L^{-1} and 0.012 mol L^{-1}; HCl concentration: 0.8mol L^{-1} and 3.4 mol sL^{-1}; λ_{max}: 518 nm. and 640 nm.

absorbance values slowly. Hence, minimum heating time of 5.0 min was fixed for study of ruthenium(III).

Choice of Extraction Solvent

The osmium(IV)-OMePT and ruthenium(III)-OMePT complex formation occurs in aqueous medium. Extractions of these complexes using organic solvent have no adverse effect on the absorbance values. The absorbance value was the same and constant in both aqueous and organic phase (chloroform). Various extraction solvents were studied for quantitative extraction of osmium(IV)-OMePT and ruthenium(III)-OMePT complex, viz. chloroform, isoamyl alcohol, methyl isobutyl ketone (MIBK), n-butyl acetate, toluene, xylene, and benzene. Amongst the extraction solvents studied, quantitative extraction with maximum absorbance values were obtained in chloroform (Table 2).

Effect of Equilibration Time

Osmium(IV)-OMePT and ruthenium (III)-OMePT complexes were extracted into chloroform quantitatively, immediately after addition of chloroform.

Color Stability of Complex

The stability of complexes was studied with measurement of the absorbance at regular time intervals of 1.0 h each. The Os(IV)-OMePT complex was stable for more than 8 days while Ru(III)-OMePT complex was stable for more than 48 h.

Analytical Figures of Merit

The osmium(IV)-OMePT and ruthenium(III)-OMePT complexes were obeys Beer's law over the concentration range up to 110.0 µg mL^{-1} and 50.0 µg mL^{-1}, respectively (Fig. 4). Ringbom's plot has the linearity range for the absorbance and concentration for osmium(IV) was 20.0 to 100.0 µg mL^{-1} and for ruthenium(III) it was 5.0 to 35.0 µg mL^{-1}. The slope values were 0.582, 0.580 for osmium(IV) and ruthenium(III) respectively (Fig. 5). For osmium(IV)-OMePT complex the ratio between the relative error in concentration and photometric error was 3.95, Sandell's sensitivity was 0.089 µg cm^{-2}, molar absorptivity was 2.12×10^3 L mol^{-1} cm^{-1}, and the correlation coefficient value was 0.99. The standard deviation and the relative standard deviation calculated from six determinations of a solution containing 150 µg osmium(IV) was 0.001 and 0.68%, respectively. For ruthenium(III)-OMePT complex the ratio between the relative error in concentration and photometric error was 3.95, Sandell's sensitivity was 0.043 µg cm^{-2}, molar absorptivity was 2.344×10^3 L mol^{-1} cm^{-1}, and the correlation coefficient value was 0.99. The standard deviation and the relative standard deviation calculated from six determinations of a solution containing 200 µg ruthenium(III) was 0.002 and 0.48%, respectively.

TABLE 2
Effect of solvent on extraction of osmium(IV)-OMePT and ruthenium(III)-OMePT complex

		Os(IV)-OMePT complex		Ru(III)-OMePT complex	
Solvent	∈	% E[a]	D	% E[a]	D
MIBK	13.1	43.7	1.94	67.38	5.16
n-Butyl acetate	5.0	49.95	2.49	60.86	3.88
n-Butanol	17.10	49.95	2.49	60.86	3.88
1,2 Dichloroethane	10.4	81.17	10.77	79.54	9.72
Isoamyl alcohol	13.9	87.41	17.35	19.56	0.61
Chloroform	4.4	99.9	2497.5	99.9	2497.5

[a]average of six determinations; ∈: Dielectric constant; % E: Percent Extraction;
D: Distribution ratio.

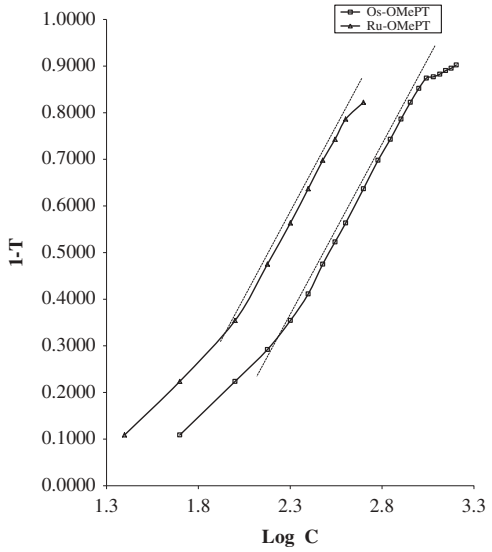


FIG. 5. Ringbom's plot for optimum concentration of Os(IV)-OMePT complex- OMePT: 2.0 mL; 0.009 mol L^{-1}; HCl concentration: 0.8 mol L^{-1}; λmax: 518 nm. Ru(III)-OMePT complex- OMePT: 2.0 mL; 0.012 mol L^{-1}; HCl concentration: 3.4 mol L^{-1}; heating time: 5.0 min; λ_{max}: 640 nm.

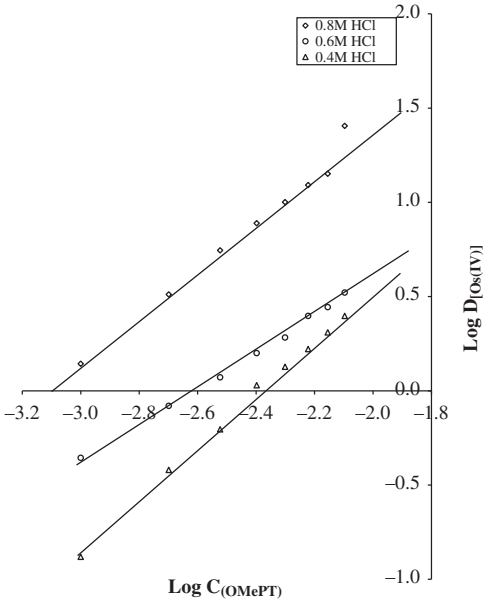


FIG. 6. Plot of log C $_{(OMePT)}$ vs. log D $_{[Os(IV)]}$: Os(IV): 15.0 μg mL^{-1}; OMePT: 2.0 mL, 0.001 mol L^{-1} to 0.008 mol L^{-1}; HCl concentration: 0.4 mol L^{-1}, 0.6 mol L^{-1}, 0.8 mol L^{-1}; λ_{max}: 518 nm.

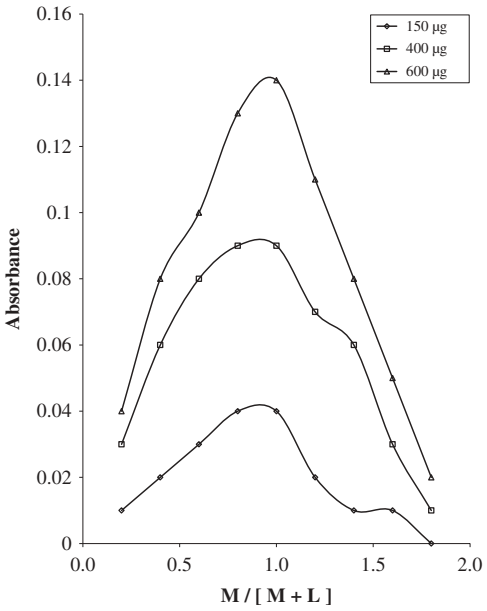


FIG. 7. Job's continuous variation method for Os(IV)-OMePT complex- Os(IV) = OMePT: 3.943 × 10^{-4} mol L^{-1}, 1.051 × 10^{-3} mol L^{-1} and 1.578 × 10^{-3} mol L^{-1}; HCl concentration: 3.4 mol L^{-1}; λ_{max}: 518 nm.

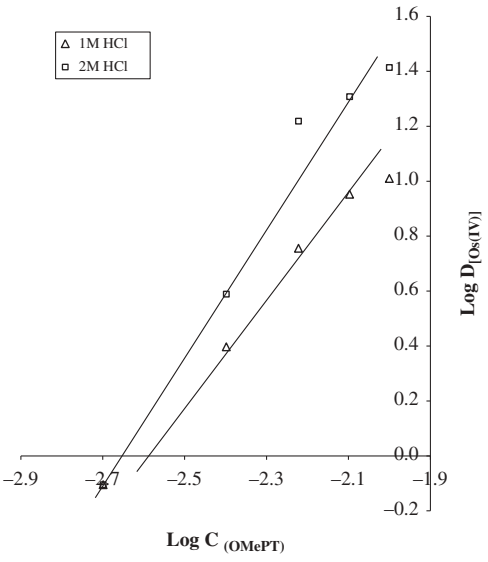


FIG. 8. Plot of log C $_{(OMePT)}$ vs. log D $_{[Ru(III)]}$: Ru(III): 20.0 μg mL^{-1}; OMePT: 2.0 mL, 0.002 mol L^{-1} to 0.01 mol L^{-1}; HCl concentration: 1.0 mol L^{-1}, 0.6 mol L^{-1} and 2.0 mol L^{-1}; heating time: 5.0 min; λmax: 640 nm.

The stoichiometry of complex was ascertained using slope ratio method and also confirmed by job's continuous variation method. For osmium(IV)-OMePT complex, the plot of log $D_{[Os(IV)]}$ against log $C_{(OMePT)}$ at 0.4 mol L^{-1}, 0.6 mol $L^{-1,}$ and 0.8 mol L^{-1} hydrochloric acid concentration gave the slope values as 1.28, 0.96, and 1.4, respectively (Fig. 6). Hence the probable composition of extracted species was calculated to be 1:1 [osmium(IV): OMePT]. The composition of complex was also confirmed as 1:1 by job's continuous variation method (Fig. 7). For ruthenium(III)-OMePT complex the plot of log $D_{[Ru(III)]}$ against log $C_{(OMePT)}$ at 1.0 mol L^{-1} and 2.0 mol L^{-1} hydrochloric acid concentration gave the slope values as 1.66 and 2.28, respectively (Fig. 8). Hence the probable composition of extracted species was calculated to be 1:2 [ruthenium(III): OMePT]. The composition of complex was also confirmed as 1:2 by job's continuous variation

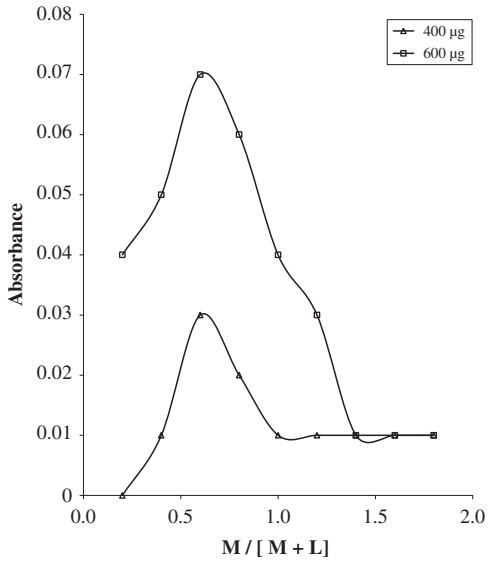


FIG. 9. Job's continuous variation method for Ru(III)-OMePT complex: Ru(III) = OMePT: 1.978 × 10^{-3} mol L^{-1} and 2.968 × 10^{-3} mol L^{-1}; HCl concentration: 3.4 mol L^{-1}; heating time: 5.0 min; λmax: 640 nm.

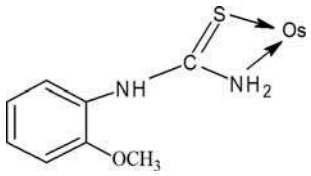


FIG. 10. Probable structure of Os(IV)-OMePT complex.

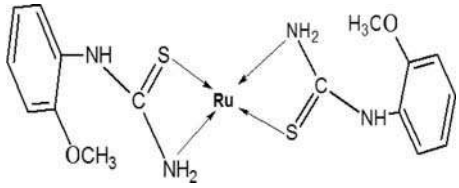


FIG. 11. Probable structure of Ru(III)-OMePT complex.

method (Fig. 9). Probable structures of Os(IV)-OMePT and Ru(III)-OMePT were given in Fig. 10 and 11.

Interference Study

The selectivity of method was checked by addition of foreign ions. The tolerance limit was fixed for the ions which do not cause deviation more than ± 2% in the absorbance value for both osmium(IV)-OMePT and ruthenium(III)-OMePT complex. The suitable masking agents are used to remove interference due to cations. Maximum limit of cations added was 50 mg and the maximum limit of anions added was 100 mg. Determination of osmium(IV) was precise and highly selective with the tolerance limit in the range of milligrams in presence

TABLE 3
Effect of foreign ions on determination of Os(IV) 150 µg and Ru(III) 200 µg

Foreign Ions	Added as	Tolerance limit (mg) Os(IV)	Ru(III)
Mn(II)[b]	$MnCl_2.6H_2o$	8.00	5.00
Cd(II)	$CdCl_2.2H_2o$	5.00	14.0
Fe(III)[b]	$(NH_4)Fe(SO_4)_2.12H_2O$	6.00	10.0
Hg(II)	$HgCl_2$	1.00	3.50
Bi(III)	$BiCl_3$	15.0	10.0
Ni(II)[b]	$NiCl_2.6H_2O$	20.0	5.00
Cu(II)[b]	$CuSO_4.5H_2O$	1.50	5.00
Al(III)	$AlCl_3.6H_2O$	5.00	10.0
La(III)	$LaCl_3.7H_2O$	2.50	3.80
Li(I)	LiCl	20.0	10.0
Ti(III)	$(Ti_2SO_4)_3$	2.50	5.00
Mg(II)	$MgCl_2.6H_2O$	25.0	22.0
Sn(II)	$SnCl_2.2H_2O$	3.50	1.00
Ga(III)	$GaCl_3$	0.20	2.00
Au(III)	$HAuClO_4.H_2O$	0.50	1.00
Mo(VI)	$(NH_4)_6MO_7O_{24}.2H_2O$	30.0	6.00
Sb(III)	Sb_2O_3	0.50	4.60
V(V)	V_2O_5	5.00	14.0
Ce(IV)	$Ce(SO_4)_2.4H_2O$	10.0	0.50
Pb(II)	$PbCl_2$	2.50	5.00
U(VI)	$UO_2(CH_3COO)_2.2H_2O$	50.0	50.0
Co(II)[b]	$CoCl_2.6H_2O$	5.00	5.00
Ba(II)	$BaCl_2.6H_2O$	50.0	25.0
Ca(II)	$CaCl_2.2H_2O$	50.0	20.0
Tl(III)	Tl_2O_3	1.00	2.40
In(III)	$InCl_3.4H_2O$	2.50	2.00
Rh(III)	$RhCl_3$	0.50	2.50
Pt(IV)	H_2PtCl_6	2.50	1.30
Os(IV)[c]	OsO_4	—	0.20
Ru(III)	$RuCl_3,3H_2O$	0.70	—
Pd (II)[d]	$PdCl_2$	—	0.18
Zr(IV)	$ZrOCl_2.8H_2O$	8.30	25.0
As (III)[b]	As_2O_3	—	4.50
W(VI)	$Na_2WO_4.2H_2O$	5.00	12.5
Fluoride	NaF	100	100
Phosphate	Na_3PO_4	100	100
Sulphate	K_2SO_4	100	100
Succinate	$(CH_3COONa)_2.6H_2O$	100	100
Citrate	$C_6H_8O_7.H_2O$	100	100
Malonate	$CH_2(COONa)_2$	100	100
Tartrate	$(CHOH:COOH)_2$	100	100
Acetate	$CH_3COONa.3H_2O$	100	100
Oxalate	$Na_2C_2O_4.2H_2O$	100	100
E.D.T.A	Na_2EDTA	100	100

*[b]masked with 100 mg EDTA; [c]prior extraction of osmium(IV); [d]prior extraction of palladium(II).

TABLE 4
Separation of osmium(IV) and ruthenium(III) from binary synthetic mixtures

Mixture	Amount taken (μg)	Recovery (%)[a]	RSD (%)	Chromogenic ligand	Ref
Os(IV)	150	99.13	0.59	OMePT	—
Ni(II)[b]	100	99.36	0.42	DMG	40.
Os(IV)	150	99.13	0.59	OMePT	—
Co(II)[b]	200	99.72	0.36	thiocynate	40.
Os(IV)	150	99.60	0.35	OMePT	—
Mo(VI)	40	99.41	0.42	Thiocynate-$SnCl_2$	40.
Os(IV)	150	99.44	0.30	OMePT	—
W(VI)	30	99.57	0.28	Thiocynate	40.
Os(IV)	150	99.45	0.58	OMePT	—
Mn(II)[b]	300	99.17	0.74	permanganate	40.
Os(IV)	150	99.29	0.71	OMePT	—
Mg(II)	30	99.09	0.54	Titan yellow	40.
Os(IV)	150	99.44	0.31	OMePT	—
Al(III)	50	99.40	0.86	8-Hydroxyquinoline	40.
Ru(III)	200	99.52	0.32	OMePT	—
Ni(II)[b]	100	99.48	0.30	DMG	40.
Ru(III)	200	99.68	0.18	OMePT	—
Co(II)[b]	200	99.98	0.93	thiocynate	40.
Ru(III)	200	99.68	0.18	OMePT	—
Mo(VI)	40	99.66	0.30	Thiocynate-$SnCl_2$	40.
Ru(III)	200	99.58	0.51	OMePT	—
W(VI)	30	99.29	0.84	Thiocynate	40.
Ru(III)	200	99.52	0.37	OMePT	—
Mn(II)[b]	300	99.01	0.78	permanganate	40.
Ru(III)	200	99.52	0.37	OMePT	—
Mg(II)	30	99.36	0.44	Titan yellow	40.
Ru(III)	200	99.42	0.48	OMePT	—
Al(III)	50	99.57	0.29	8-Hydroxyquinoline	40.

[a]Average of six determinations; [b]Masked with 100 mg EDTA.

of many added cations and anions except Fe(III), Ni(II), Cu(II), and Co(II). The interference due to these cations is removed by masking with EDTA. Palladium(II) and As(III) were interfered with in the method. Determination of ruthenium(III) using OMePT was highly selective with the tolerance limit in the range of milligrams for 200 μg ruthenium(III). The interference of Mn(II), Fe(III), Ni(II), Cu(II), Mo(VI), W(VI), and Co(II) was removed by masking these ions with EDTA, while interference of osmium(IV) and palladium(II) was removed by their prior extraction. For removal of osmium(IV), to a solution containing 200 μg ruthenium(III) and 200 μg osmium(IV), 2 mL of 0.009 mol L^{-1} OMePT in ethanol, and hydrochloric acid with respect to 0.8 mol L^{-1} are added. The pink colored Os(IV)-OMePT complex was extracted into 10 mL of chloroform. Palladium(II) is prior extracted as per reported method (31). Only Ir(III) interfered in the determination of both osmium(IV) and ruthenium(III) (Table 3).

APPLICATIONS

Separation and Determination of Osmium(IV) and Ruthenium(III) from Binary Synthetic Mixtures

The proposed method permits separation and determination of osmium(IV) and ruthenium(III) from associated metal ions containing Ni(II), Co(II), Mo(VI), W(IV), Mn(II), Mg(II), and Al(III). Osmium(IV) and ruthenium(III) were separated from Mo(VI), W(IV), Mg(II), and Al(III) as per recommended procedure. After quantitative extraction of osmium(IV) or ruthenium(III) from synthetic binary mixture, aqueous phase was evaporated to moist dryness followed by 3 mL concentrated hydrochloric acid. The residue obtained was cooled, dissolved in water, and then added metal ions were determined by reported methods (40).

To increase the selectivity of extraction of osmium(IV) and ruthenium(III) in the presence of Ni(II), Co(II), and Mn(II), these metal ions were masked with EDTA and the

TABLE 5
Separation of osmium(IV) and ruthenium(III) from ternary synthetic mixtures

Composition μg	Recovery[a] (%)	RSD (%)
Os(IV)150; Cu(II)[b]40; W(VI) 30	99.42	0.37
Os(IV)150; Mn(II) 100; Zr(IV) 50	99.38	0.44
Os(IV)150; Pb(II) 50; Mo(II) 50	99.36	0.46
Os(IV)150; Cu(II)[b]40; Co(II)[b] 50	99.31	0.94
Os(IV)150; Fe(III) 50;Co(II)[b] 50	99.29	0.47
Os(IV)150; Ni(II) [b]50; Mn(II) 100	99.26	0.46
Os(IV)150; W(VI) 30; Ni(II) [b]50	99.21	0.58
Os(IV)150; Fe(III) 50; Cr(IV) 30	99.18	0.64
Os(IV)150; Sb(III) 50; Co(II)[b] 50	99.14	0.52
Os(IV)150; Co(II)[b] 50; Cr(IV) 30	99.06	0.62
Ru(III) 200; Cu(II)[b] 30; W(VI) 75	99.59	0.25
Ru(III) 200; Cu(II)[b] 30; Mo(II) 50	99.62	0.27
Ru(III) 200; Mn(II) 100; Ni(II) 100	99.75	0.17
Ru(III) 200; As(III)[b] 25; Ni(II) 100	99.25	0.64
Ru(III) 200; Fe(III) 50; As(III)[b] 25	99.61	0.21
Ru(III) 200; Co(II)[b] 50; Cr(IV) 30	99.69	0.19
Ru(III) 200; Co(II)[b] 50; Fe(III) 50	99.46	0.43
Ru(III) 200; Fe(III) 50; Cr(IV) 30	99.51	0.34
Ru(III) 200; Co(II)[b] 50; Sb(III) 50	99.75	0.10
Ru(III) 200; Sb(III) 50; Ni(II) 100	99.74	0.22

[a]Average of six determinations; [b]Masked with 100 mg EDTA.

TABLE 6
Analysis of synthetic mixtures corresponding to platinum-osmium alloy

Metal ions added (μg)		Os(IV) Recovery	R.S.D
Os(IV)	Pt(II)	(%)	(%)
50	450	99.02	0.73
75	675	99.12	0.64
100	900	99.15	0.62

[a]average of six determinations.

recommended procedure was followed for quantitative extraction of Os(IV) and Ru(III) in 10 mL chloroform. Aqueous phase contains masked metal ions and were de-masked by treatment with 3.0 mL nitric acid then evaporated to moist dryness followed by 3.0 mL conc. hydrochloric acid. The residue was cooled, dissolved in water, and the added metal ions were determined by spectrophotometrically as per the reported method (40) (Table 4).

Separation and Determination of Osmium(IV) and Ruthenium(III) from Ternary Synthetic Mixtures

An aliquot of solution containing 150 μg osmium(IV) or 200 μg ruthenium(III) was taken and known amount of different compositions of associated metal ions were added followed by a suitable masking agent and osmium(IV) and ruthenium(III) are separated and determined as per the recommended method (Table 5).

Analysis of Synthetic Mixtures Corresponding to Alloys

The validity of the method was verified by applying the proposed method for extraction of osmium(IV) and ruthenium(III) from synthetic mixtures corresponding to alloys. The compositions were prepared in laboratory for platinum-osmium alloy (Table 6) and fissium alloy (Table 7). The osmium(IV) from platinum-osmium alloy and ruthenium(III) from fissium alloy was determined as per the recommended method. The results obtained were in good agreement with the amount of osmium(IV) and ruthenium(III) added.

Sequential Separation of Osmium(IV), Ruthenium(III), and Platinum(IV)

The proposed method was applied for sequential separation and determination of osmium(IV), ruthenium(III) and platinum(IV) from synthetic mixtures. The separation of these metal ions was resolved by taking advantage of acid concentrations and temperature conditions using the same reagent (Scheme 1). Osmium(IV) was extracted in chloroform from

TABLE 7
Analysis of synthetic mixtures corresponding to fissium alloy

Metal ions added (μg)							
U(VI)	Zr(IV)	Pd(II)[d]	Rh(III)	Mo(VI)	Ru(III)	Recovery[a] (%)	R.S.D (%)
1900	1	1	1	50	40	99.12	0.76
3800	2	2	2	100	80	99.58	0.28
5700	3	3	3	150	120	99.53	0.26
7600	4	4	4	200	160	99.76	0.17
9500	5	5	5	250	200	99.77	0.11

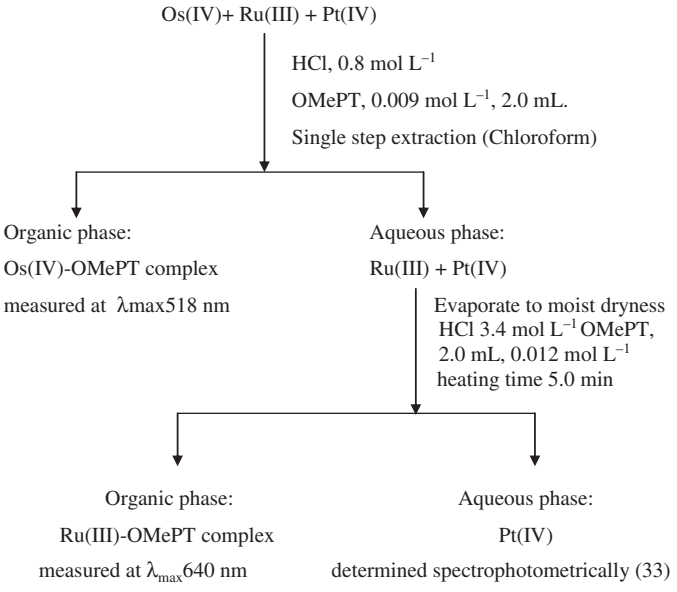
[a]average of six determinations; [d]prior extraction of palladium(II).

TABLE 8
Sequential separation of osmium(IV), ruthenium(III) and platinum(IV)

Mixture	Amount taken (μg)	Chromogenic ligand	Recovery[a] (%)	RSD (%)
Os(IV) + Ru(III) + Pt(IV)	Os (150)	OMePT	99.41	0.25
	Ru (150)	OMePT	99.42	0.12
	Pt (100)	OMPT	99.18	0.19
Os(IV) + Ru(III) + Pt(IV)	Os (150)	OMePT	99.41	0.18
	Ru (200)	OMePT	99.68	0.07
	Pt (100)	OMPT	99.22	0.36
Os(IV) + Ru(III) + Pt(IV)	Os (150)	OMePT	99.41	0.26
	Ru (250)	OMePT	99.54	0.12
	Pt (100)	OMPT	99.42	0.09

[a]Average of six determinations.

synthetic mixture using 2 mL, 0.009 mol L^{-1} OMePT in ethanol from 0.8 mol L^{-1} in hydrochloric acid media at room temperature. Aqueous solution containing ruthenium(III) and platinum(IV) was evaporated to moist dryness; the residue was dissolved in 10 mL water, in a solution 2 mL, 0.012 mol L^{-1} OMePT in ethanol and hydrochloric acid was added to make solution at 3.4 mol L^{-1} with respect to hydrochloric acid and heating in boiling water bath for 5 min. The Ru-OMePT complex was extracted in 10 mL chloroform. The aqueous solution containing platinum(IV) was evaporated to moist dryness, cooled, and dissolved in 10 mL distilled water. Platinum(IV) was determined spectrophotometrically (33) (Table 8).



SCHEME 1. Sequential separation of osmium(IV), ruthenium(III) and platinum(IV).

CONCLUSIONS

O-Methoxyphenyl Thiourea (OMePT) has been proved to be sensitive and selective spectrophotometric reagent for osmium(IV) and ruthenium(III). The proposed methods are simple, sensitive, selective, reproducible, and rapid with low reagent concentration. The quantitative extraction was carried out in a single step. The reported methods were suffer from interferences from cations and anions and were less sensitive. The proposed methods are free from interferences from a large number of cations and anions. Reported methods need a laborious lengthy procedure to be adopted, while in the proposed method for spectrophotometric determination of osmium(IV) is with instant complex formation at 0.8 mol L^{-1} hydrochloric acid. Minimum acidic condition merits the method for its

applications. The stability of osmium(IV)-OMePT complex was more than 8 days and for ruthenium(III)-OMePT was greater than 48 h, it confirms the applicability of the method for various sample matrices with even lapse in complexation and further its spectrophotometric determination. A precise scheme for sequential separation of osmium(IV), ruthenium(III), and platinum(IV) has been developed. The proposed method was successfully applied for determination of osmium(IV) and ruthenium(III) from synthetic mixtures corresponding to platinum-osmium alloy and fissium alloy, respectively.

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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.

KEYWORDS

Solvent extraction, spectrophotometric determination, o-methoxyphenyl thiourea, palladium.

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]

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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_2SO_4 5.0	0.02–0.4	2.01×10^4	Heating 10 min, Narrow Beer's range	16
2-Hydroxy-5-methylacetopheneoneisonicotinoylhydrazone	H_2SO_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-(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_2SO_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.

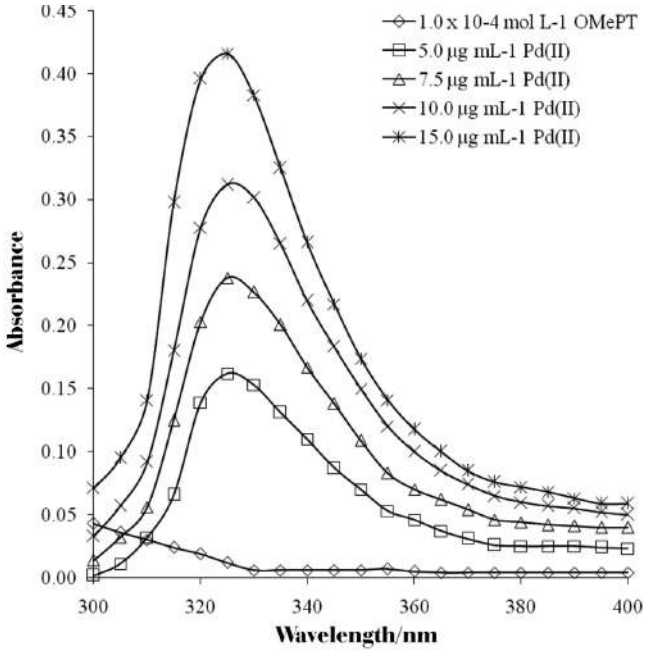

Figure 1 Absorbance spectra of Pd(II)-OMePT *vs*. OMePT reagent blank.

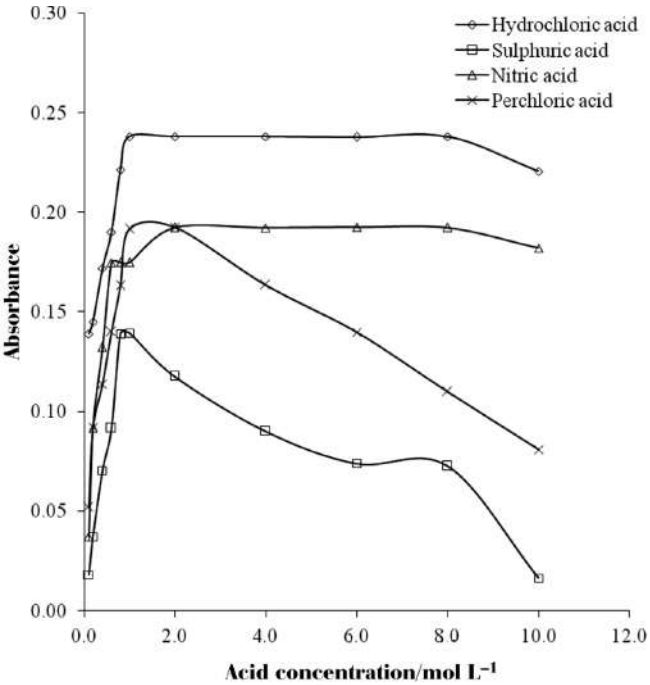

Figure 2 Effect of acid type and concentration on Pd(II)-OMePT complex formation.

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

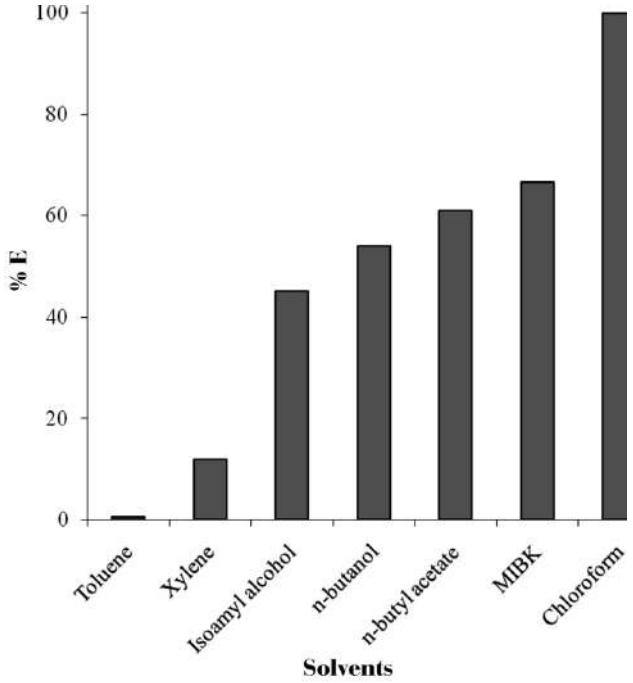

Figure 3 Effect of extraction solvent on Pd(II)-OMePT complex.

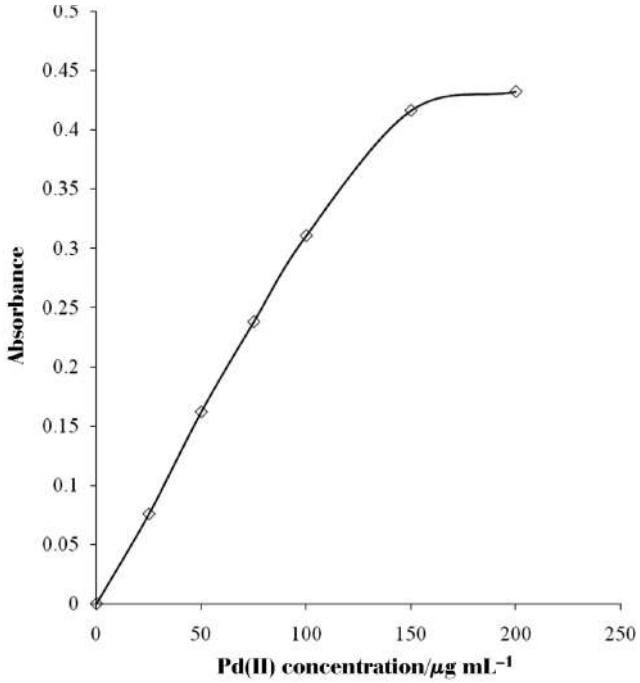

Figure 5 Applicability of Beer's law to Pd(II)-OMePT complex.

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

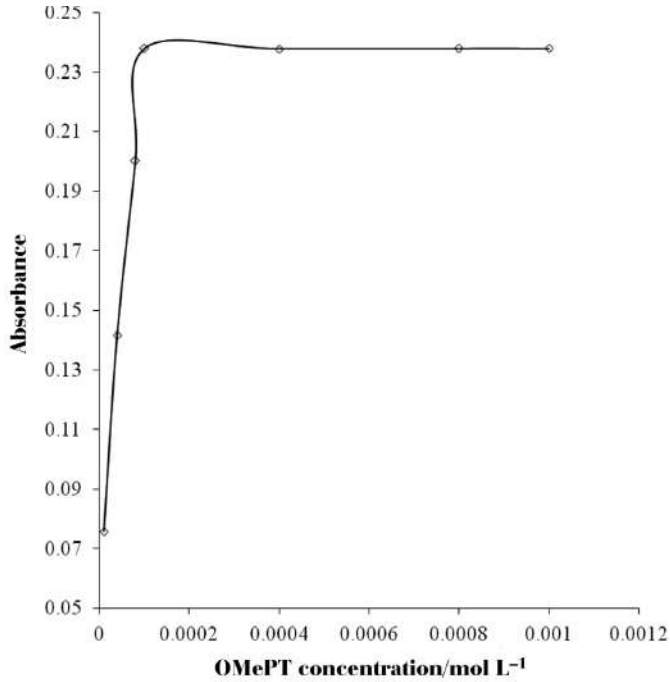

Figure 4 Effect of reagent concentration on Pd(II)-OMePT complex.

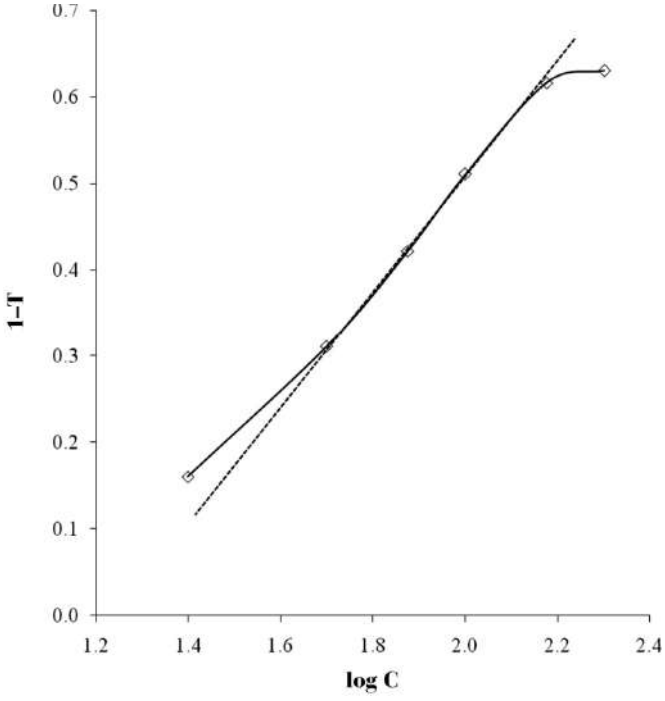

Figure 6 Ringbom's plot for Pd(II)-OMePT complex.

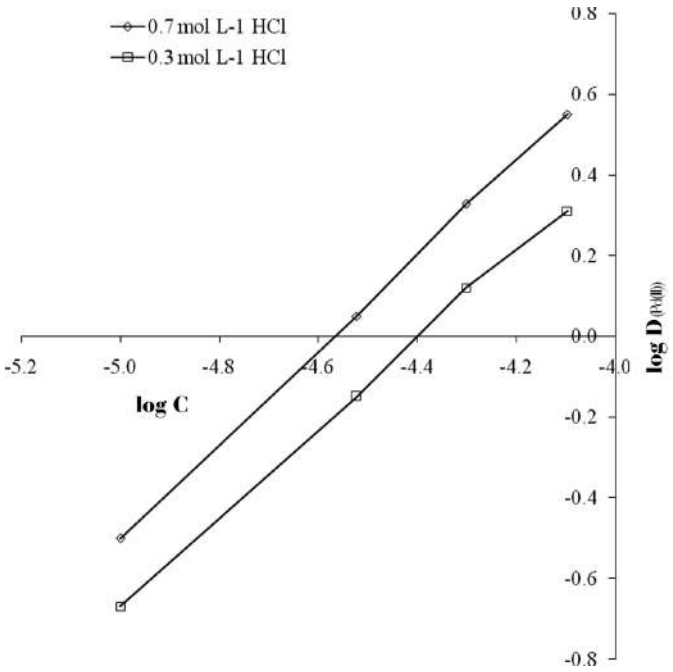

Figure 7 Plot of log $D_{Pd(II)}$ *vs.* log $C_{(OMePT)}$.

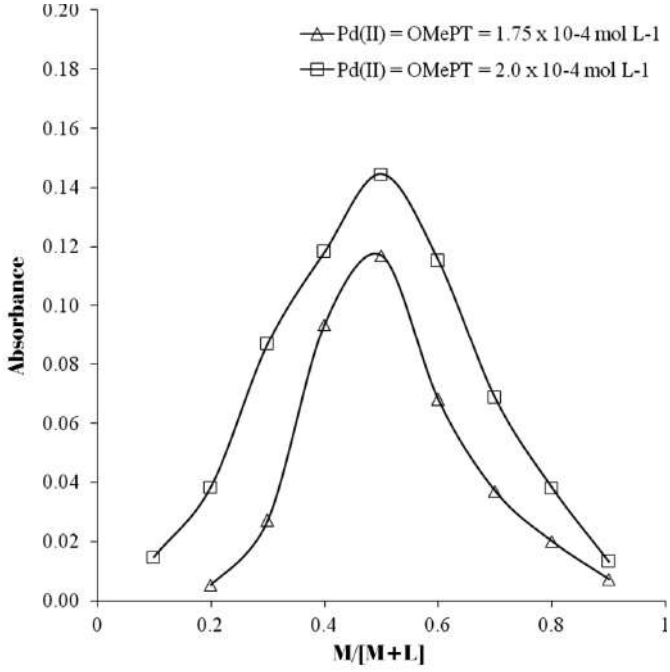

Figure 9 Job's continuous variation method for Pd(II)-OMePT complex.

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).

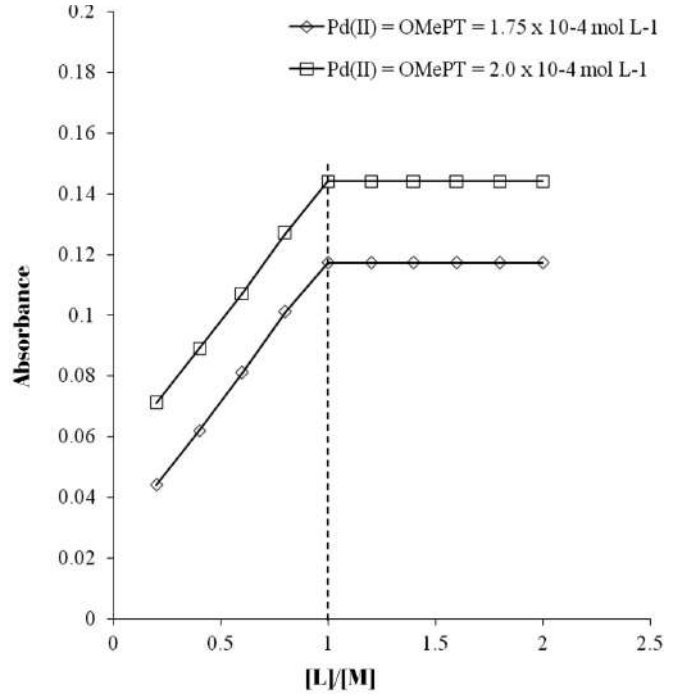

Figure 8 Mole ratio method for Pd(II)-OMPT complex.

4.1. Interference Study

Various amounts of foreign ions were added to a fixed amountof 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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BIOSYNTHESIS OF SILVER NANOPARTICLES USING *NICOTIANA TOBACCUM* LEAF EXTRACT

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ABSTRACT

Plant extract from tobacco leaf was used for the synthesis of silver nanoparticles (AgNps) using the silver nitrate solution. AgNps were characterized by UV-Vis spectrophotometer, X-ray diffractometer (XRD), Scanning electron microscope (SEM) and Energy dispersive spectroscopy (EDX). The formation and stability of the reduced silver nanoparticles in the colloidal solution were monitored by UV-Vis. Spectrophotometer analysis. The mean particle diameter of silver nanoparticles was calculated from the XRD pattern according to the line width of the plane, refraction peak using the scherrers equation. SEM determination of the brown colour stable sample showed the formation of silver nanoparticles and well dispersed nanoparticles could be seen in the samples treated with silver nitrate. EDX analysis gives elemental status that may be involved in the formation of nanoparticles. In the research, article we present a simple and eco- friendly bio-synthesis of silver nanoparticles using tobacco leaf extract as reducing agent.

KEYWORDS: Biosynthesis, Tobacco leaf extract, Silver nanoparticles.

INTRODUCTION

The field of nanotechnology is one of the most active areas of research in modern material science. Nanotechnology is emerging and a rapidly growing field with its application in science and technology for the purpose of manufacturing new material at the nanoscale level. (Albercht et. al 2006). New applications of nanoparticles and nonmaterial's fields are

emerging rapidly (Jahn 1999, Naiwa 2000 ; Murphy 2008). Nanocrystaline silver particles have found tremendous applications in the field of high sensitivity bimolecular detection and diagnosis (Schultz et. al.,2000), Antimicrobials and therapeutics (Rai et al., 2009, Elechiguerra et al., 2005), catalysis(Crooks et al.,2001) and micro-electronics (Gittins et al., 2000). Different types of nanomaterials like copper, zinc, titanium (Renchkiman- Schabes ety al., 2006), magnesium, gold (Gu. Et al.,2000) and silver have come up but silver nanoparticles have proved to be most effective as it has good antimicrobial efficacy against bacteria, viruses and other eukaryotic micro-organisms (Gong. et., al..2000). These silver nanoparticles are playing a major role in the field of nanotechnology and nanomedicine. A number of approaches are available for the synthesis of silver nanoparticles viz, reduction in solutions (Goia and Matijevic, 1998) chemical and photo chemical reactions in reverse micelles (Taleb.et.al.,1997), thermal decomposition of silver compounds (Esumi et. al., 1990), electrochemical (Rodriguez-Sanchez et. al.,2000) and recently via green chemistry route (Begum et al., 2009, Bar et al., 2009,Song and Kim, 2009). Green synthesis provides advancement over chemical and physical method as it is cost effective, environment friendly, easily scaled up for large scale synthesis and further there is no need to use high pressure, energy, temperature and toxic chemicals. Using plants for nanoparticles synthesis can be advantageous over other biological process because it eliminates the elaborate process of maintain cell-cultures and can also be suitably scaled up for large scale synthesis of nanoparticles under non aseptic environment. Silver nanoparticles play a profound role in the field of biology and medicine due to their attractive physico-chemical properties. Silver nanoparticles are reported to possess anti-fungal (Wiley et al., 2006; Ramirez et al., 2009), anti-inflammatory (Panacek et. al., 2009), anti-viral (Nadworny et. al., 2008), anti-angiogenesis (Rogers et. al., 2008) and anti-platelet activity (Gurunathan et. al.,2009). Recently, green bio-reduction methods for the synthesis of silver nanoparticles were adapted by many researchers using plant extract. In present communication we report green synthesis of silver nanoparticles using aqueous extract of tobacco leaf and its characterization.

MATERIAL AND METHOD

2.1. Plant material and preparation of the extract

Freshly and healthy Tobacco Leaves (Fig.1.) were collected, rinsed with distilled water thrice followed by milli Q water to remove the dust and other contaminants then dried at room temperature for 2 hrs to remove the moisture. About 5 gm of green fresh leaves were

weighed and then sliced into small pieces. Then 100 ml of milli Q water was added and boiled for 25 min.After cooling the extract was filtered using Whatman No. 1 filter paper and stored at 40º for further use.

Fig. 1 A standing crop of Nicotiana tobaccum

2.2. Synthesis of silver nanoparticles

Aqueous solution (1 mM) of silver nitrate (AgN03) was prepared and used for the synthesis of silver nanoparticles. 5 ml of leaf extract was added to 100 ml of 1 mM silver nitrate solution for bioreduction process and observed for the change in color. Reduction of silver ions to silver nanoparticles was confirmed by the color change from colorless to dark brown (Fig.2).

Fig. 2 a) Solution of silver nitrate 1 mM before. b) Reddish brown colour formed due to reduction.

2.3. Chactererisation of Silver nanoparticles

The bioreduction of silver ions was monitored by measuring a spectrum of the reaction medium. The UV-Vis spectral analysis of the sample was done by using ELICO SL-159 UV –Vis spectrophotometer at room temperature operated at a resolution of 1 nm between 300

and 700 nm ranges. The leaf extract was used as reference blank. Further the morphology of synthesized silver nanoparticles was determined by using scanning electron microscopy, (Hitachi S -3000N. Japan). 25µL of sample was sputter coated on copper stub and then observed the image of nanoparticles. To check phase formation and purity, XRD patterns were recorded using powder X –ray diffractometer operating at 40 kV and running a current of 30 mA with Cukα radiation in a 2θ configuration.

RESULTS AND DISCUSSION

The detailed study on biosynthesis of silver nanoparticles by natural plant extract as tobacco was employed and is reported in this work. It is well known that silver nanoparticles exhibit yellowish brown color in aqueous solution due to excitation of surface Plasmon vibrations in silver nanoparticles (Krishnaraj et. al., 2010). As the Tobacco leaf extract was mixed with aqueous solution of silver nitrate, it started to change the color from colorless to yellowish brown due to reduction of silver ions; which indicated the formation of silver nanoparticles. The formation and stability of the reduced silver nanoparticles in the colloidal solution was monitored by UV-Vis spectrophotometer analysis. It is generally recognized that UV-Vis spectroscopy could be used to examine size and shape controlled nanoparticles in aqueous suspensions (Shrivasatava and Dash, 2009). Absorption spectra of silver nanoparticles formed in the reaction media has absorbance peak at 450 nm and broadening of peak indicated that the particles are polydispersed(fig. 3). It is reported earlier that absorbance at around 450 nm for silver is a characteristic of these nobel metal particles (Nestor et. al.,2008).

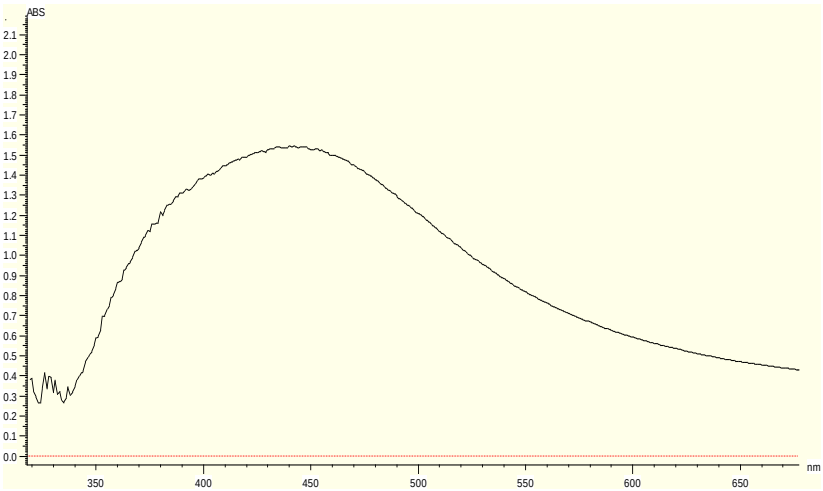

Fig. 3 UV-Vis absorption spectra of silver nanoparticles synthesized from tobacco leaf extract at 1mM silver nitrate.

To determine the morphology of synthesized silver nanoparticles the sample was analyzed with scanning electron microscope (fig. 4). The SEM analysis revealed that a synthesized nanoparticle was in the range of 5 to 6 nm.

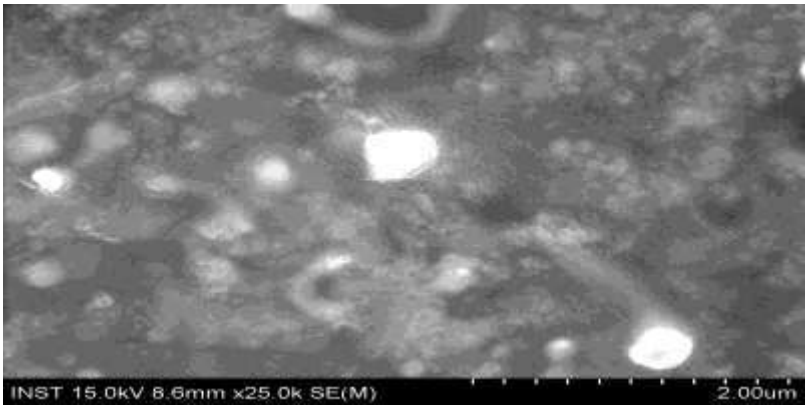

Fig. 4 SEM image of silver nanoparticles synthesized from tobacco leaf extract.

Further studies were carried out using X-ray diffraction to confirm the crystalline nature of the particles and the XRD pattern obtained was shown in Fig. 5. It shows the XRD pattern for silver nanoparticles synthesized using natural plant extract. The mean particle diameter of silver nanoparticles was calculated from the XRD pattern according to the line width of the plane refraction peak using the following Scherer's equation (Balaji et. al.,). $D = K\lambda / \beta \cos \theta$. The equation uses the reference peak width at angle θ, where λ is the X-ray wavelength (1.541Å). $\beta^{1/2}$ is the width of XRD peak at half height and K is a shape factor. A comparison of our XRD spectrum with the standard has been confirmed that the silver particles formed in our experiments were in the form of nanocrystals as evidenced by the peaks at 2θvalues of such peaks 26.4º, 31.3º, 38.1º and 46º Planes for silver respectively. By using Debye Scherer's equation the average particle size of the silver was found to be 6 nm.

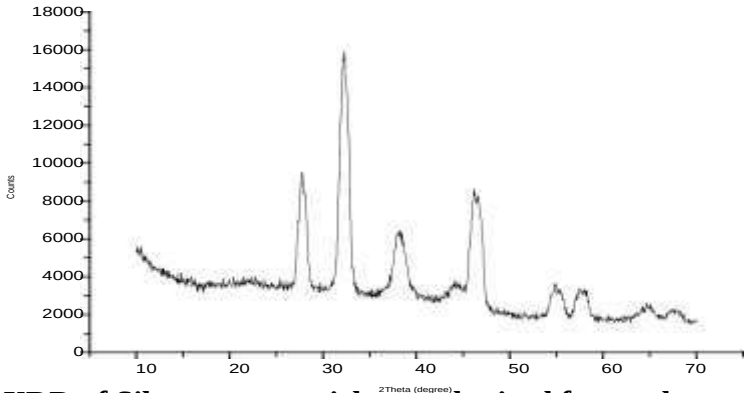

Fig. 5 XRD of Silver nanoparticles synthesized from tobacco leaf extract.

EDX analysis gives quantitative as well as qualitative status of elements that may be involved in the formation of nanoparticles. The analysis revealed highest proportion of silver in the nanoparticle followed by carbon, oxygen, silicon etc. (Fig.6).

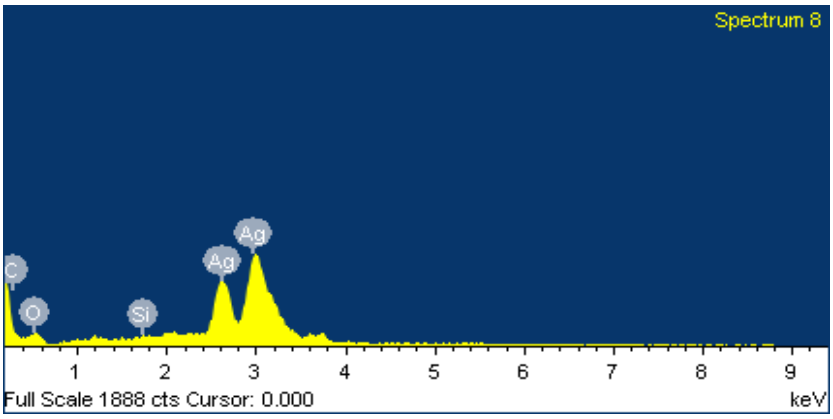

Fig. 6 EDX spectra of silver nanoparticles synthesized from tobacco leaf extract.

CONCLUSION

Green synthesis of silver nanoparticles using tobacco leaf extract showed an absorption peak at 450 nm in the UV-Vis spectra and the size of the biosynthesized nanoparticles was found to be crystalline in nature. The present study showed a simple, rapid and economical route to synthesis silver nanoparticles.

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Research Article

EXTRACTION CHROMATOGRAPHIC STUDIES OF THALLIUM(III) WITH N-n-OCTYLANILINE

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Abstract

A selective method has been developed for extraction, chromatographic separation of thallium(III) with N-n-octylaniline (a liquid anion exchanger) as a stationary phase on silica gel. Quantitative extraction of thallium(III) has been achieved in 1.0 mol L^{-1} hydrochloric acid media from 0.0315 mol L^{-1} (0.7%) N-n-octylaniline. The extracted metal has been eluted with 25.0 ml distilled water and estimated spectrophotometrically. The effects of acid concentrations, reagent concentration and diverse ions have been studied. Thallium(III) has been separated from its associated elements and synthetic mixtures corresponding. The probable extracted species were ascertained from log C - log D plots.

Keywords: Extraction chromatography, N-n-Octylaniline, Thallium(III)

Introduction

Thallium has low abundance in the earth's crust, but wide uses. A low melting glass of thallium, sulpher, arsenic and selenium is used as an encapsulating material for semiconductors, capacitors and other electrical devices. Due to various applications of thallium it is necessary to develop a selective separation method from associated metals. Liquid anion exchangers have been used for solvent extraction of many metals[1,2] Thallium(III) has been extracted with 2-propanol/water phase using sodium chloride[3]. Extraction separation of thallium(III) from thallium(I) has been reported by using n-Octylaniline from salicylate medium[4]. N-octylaniline has been also used extensively for the solvent extraction, separation of various elements[5-10]. N-n-Octylaniline has been used for reversed phase paper chromatographic separation of zinc, cadmium and mercury[11]. Recently N-n-octylaniline was applied for extraction chromatographic separation of platinum[12], palladium[13], ruthenium[14], iridium[15], gold[16], copper[17], molybdenum[18], manganese[19] and lead(II)[20]. In the present communication, reversed phase extraction behavior of thallium (III) towards N-n-octylaniline as a function of hydrochloric acid has been studied. A simple, rapid method for separation of thallium (III) from its associated elements has been proposed.

Experimental

Instrumentation

Elico make (model SL-191) double beam UV-visible spectrophotometer with matching 10 mm quartz cells was used for absorbance measurements. An electronic balance (Contech make, 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.

Reagents

All the reagents used were of analytical reagent grade unless otherwise stated. A standard stock solution of thallium (III) has been prepared by dissolving 2.0 gm of thallous nitrate ($TlNO_3$ dried at 110°c) into distilled water containing 2.0 mL of concentrated nitric acid and diluted this solution to 250 mL with distilled water. Thallium (I) was oxidized to thallium (III) by adding few drops of saturated bromine water and warming to remove excess bromine. The solution was standardized by complexometrically[21]. A working standard solution of thallium (III) 100 µg mL^{-1} was prepared by diluting the standard stock solution with distilled water. Other standard solutions of different metal ions used to study the effect of foreign ions were prepared by dissolving their respective salts in water or dilute hydrochloric acid and diluted suitably. The N-n-octylaniline was prepared using the method reported by Gardlund[22]. Chloroform is used for further dilutions of N-n-octylaniline. Double distilled water was used throughout the work.

Recommended procedure

In a 25 mL volumetric flask, an aliquot of 100 µg Tl (III) was taken and sufficient amount of hydrochloric acid was added to make solution 1.0 mol L^{-1} after dilution with water to the mark. The solution was passed through 0.7% (V/V) N-n-octylaniline coated silica gel (pre-saturated with 1.0 mol L^{-1} hydrochloric acid) column at a rate of 1.0 mL min^{-1}. The Tl(III) found completely extracted on the column. The Tl (III) was eluted by 40 mL of distilled water. Collected fraction was analyzed for Tl(III) spectrophotometrically by iodide-starch method[23].

Results and discussion

Effect of hydrochloric acid concentration on extraction of Tl(III)

Thallium(III) 100 µg in final volume 25 mL of 0.01 to 4.0 mol L^{-1} hydrochloric acid media was studied for effect of acid concentration on extraction of Tl(III) as per the recommended procedure. It was observed that the extraction of thallium(III) increases with increase in concentration of hydrochloric acid. It was found that there is quantitative extraction at 1.0 mol L^{-1} hydrochloric acid. Hence all the extractions were carried out at the concentration 1.0 mol L^{-1} of hydrochloric acid (Figure 1).

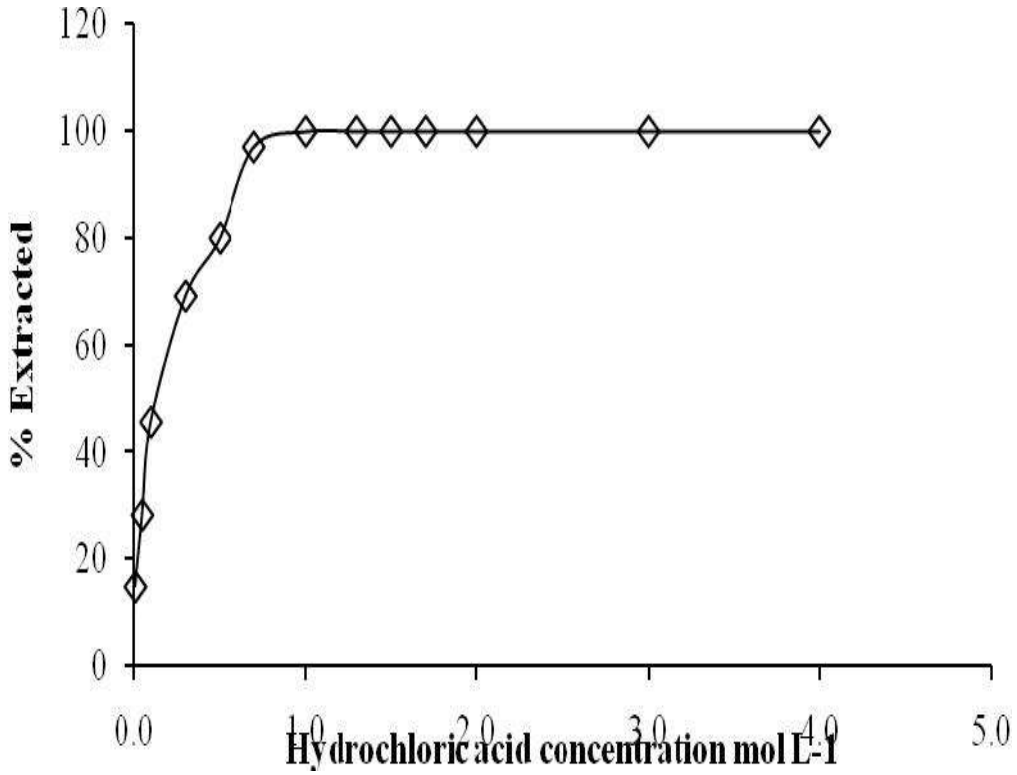

Figure 1. Effect of hydrochloric acid concentration on extraction of Tl(III).

Effect of N-n-octylaniline concentration

The concentration of N-n-octylaniline on a silica support was varied from 0.1% (v/v) to 1.0% (v/v). It was observed that 0.7% (v/v) N-n-octylaniline was sufficient for quantitative extraction of Tl(III) from 1.0 mol L^{-1} hydrochloric acid media. There is an increase in the extraction of Tl(III) with increasing concentration of N-n-octylaniline. The plot of log D Vs log C for 0.1 and 0.5 mol L^{-1} hydrochloric acid gave a slope of 1.17 and 1.09 respectively (Figure 2). The probable composition of extracting species was calculated as 1:1 (metal to amine ratio).

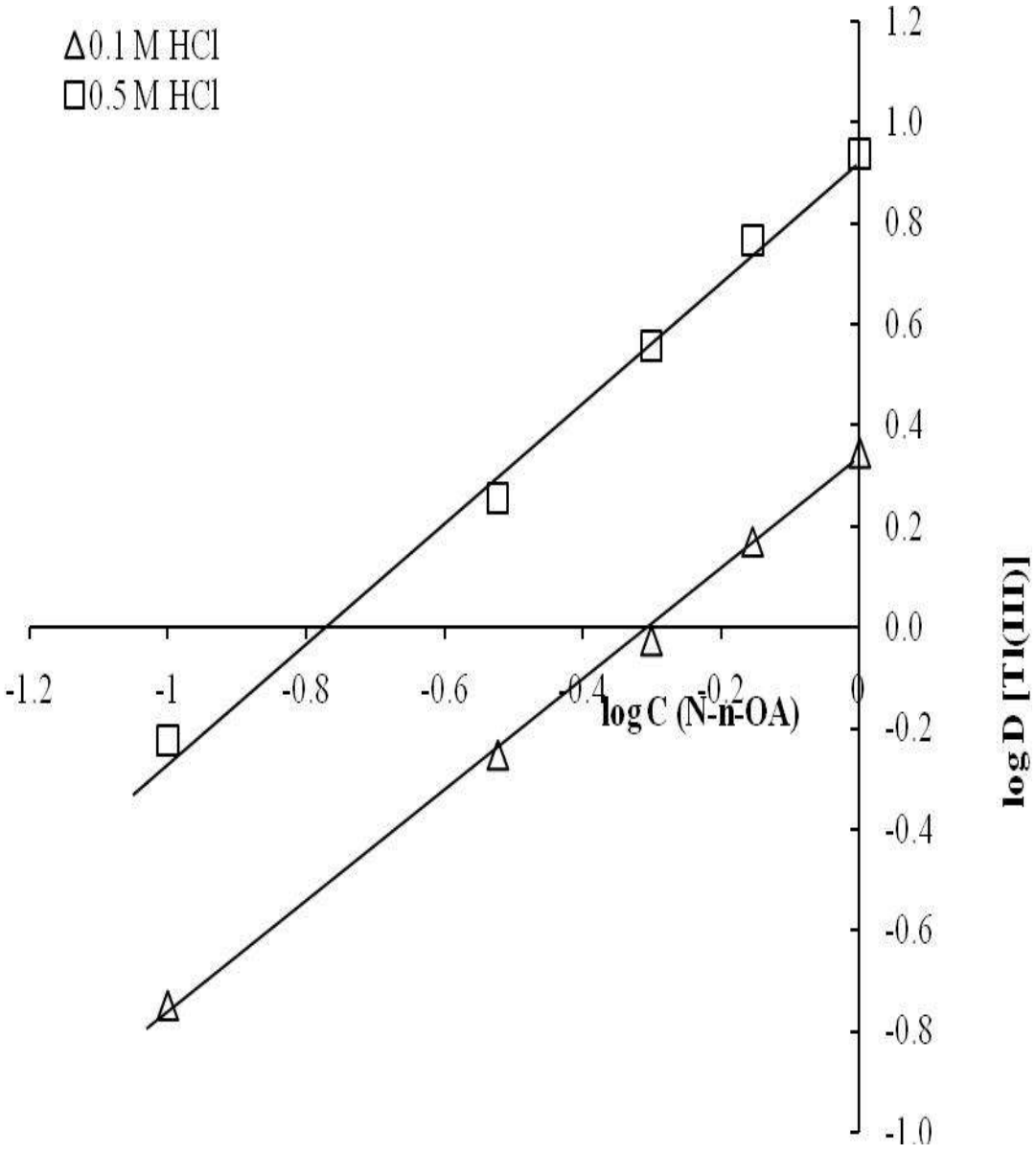

Figure 2. Plot of log $C_{(N\text{-}n\text{-}OA)}$ vs. log $D_{[Tl(III)]}$: Tl(III): 100.0 µg; N-n-OA: 0.1% to 1%; HCl concentration: 0.1 mol L^{-1}, 0.5 mol L^{-1}, λ_{max}: 590 nm.

Extraction mechanism

$[RR'NH]_{org.} + [H^+]_{aq.} \rightleftharpoons [RR'NH_2^+]_{org.}$

$[Tl^{3+}]_{aq} + [Cl^-]_{aq.} \rightleftharpoons [TlCl_4^-]_{aq}$

$[RR'NH_2^+]_{org} + [TlCl_4^-]_{aq} \rightleftharpoons [RR'NH_2^+ .TlCl_4^-]_{org}$

Where R= $-C_6H_5$ R'= $-CH_2(CH_2)_6CH_3$

Effect of foreign ions

Various amounts of foreign ions were added to a fixed amount of thallium(III) to investigate the interference of these ions and to find their tolerance limit in the extraction of Tl(III). Thallium(III), 100 µg, was extracted in the presence of a large number of foreign ions. An error of ± 2% in the absorbance values was considered to be tolerable. It was observed that the proposed method is free from interference of the large number of alkaline earth metals, toxic metals, transition metals and anions (Table 1).

Table 1. Effect of foreign ions

Foreign Ions	Added as	Tolerance limit µg	Foreign Ions	Added as	Tolerance limit µg
Mn(II)	$MnCl_2.6H_2O$	100	W(VI)	$Na_2WO_4.2H_2O$	50
Cd(II)	$CdCl_2.2H_2O$	150	Pb(II)	$PbCl_2$	150
Fe(III)	$(NH_4)Fe(SO_4)_2.12H_2O$	50	Zn(II)	$ZnSO_4.7H_2O$	50
Hg(II)	$HgCl_2$	75	Ti(IV)	TiO_2	200
Bi(III)	$BiCl_3$	75	Mg(II)	$MgCl_2.6H_2O$	100
Ni(II)	$NiCl_2.6H_2O$	50	Fluoride	NaF	500
Al(III)	$AlCl_3.6H_2O$	50	Sulphate	K_2SO_4	500
Fe(II)	$FeSO_4.7H_2O$	25	Citrate	$C_6H_8O_7.H_2O$	500
Sn(II)	$SnCl_2.2H_2O$	50	Malonate	$CH_2(COONa)_2$	500
Mo(VI)	$(NH_4)_6MO_7O_{24}.2H_2O$	100	Acetate	$CH_3COONa.3H_2O$	500
V(V)	V_2O_5	100	Oxalate	$Na_2C_2O_4.2H_2O$	200
U(VI)	$UO_2(CH_3COO)_2.2H_2O$	50	E.D.T.A	Na_2EDTA	500
Co(II)	$CoCl_2.6H_2O$	200	H_2O_2	H_2O_2	0.3 mL

Applications

Separation of thallium(III) from multi-component mixtures

The proposed method was successfully applied for extraction of thallium(III) from multi-component mixtures. The study shows that the separation of thallium (III) is possible in the presence of mercury(II), manganese(II), zinc(II), tin(II), cadmium(II) and aluminum(III) using the proposed method (Table 2).

Table 2. Separation of thallium(III) from multi-component mixtures

Composition µg	Thallium(III) found µg	% RSD
Tl(III) 100; Mn(II) 50; Cd(II) 100; Hg(II) 50	98.36	0.53
Tl(III) 100; Mn(II) 50; Cd(II) 100; Hg(II) 50; Al(III) 25	97.95	0.31
Tl(III) 100; Al(III) 25; Sn(II) 50	99.59	0.58
Tl(III) 100; Cd(II) 100; Hg(II) 50; Zn(II) 50	99.18	0.76
Tl(III) 100; Cd(II) 100; Sn(II) 50; Al(III) 25	98.36	0.93
Tl(III) 100; Cd(II) 100; Sn(II) 50; Al(III) 25; Mn(II) 50	98.77	0.89

Conclusion

The proposed method is simple, selective, reproducible and rapid. It is free from interferences from a large number of foreign ions which are associated with thallium(III). Low N-n-octylaniline and hydrochloric acid concentrations required for quantitative extraction of thallium(III) using the proposed method. It is successfully applied for separation of thallium(III) from multi-component mixtures.

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Synthesis and antimicrobial evaluations of some novel fluorinated chromones and pyrazoles

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2-Hydroxy acetophenone on treatment with 4-chloro-2,5-difluorobenzoic acid in $POCl_3$ as condensing agent gives ester. The ester on reaction with KOH undergoes Baker-Venkatraman rearrangement and gives ketoenols. The ketoenols on reaction with conc. HCl gives 2-substituted chromones which on further reaction with hydrazine hydrate gives 2-[5-(4-chloro-2,5-difluorophenyl)-1*H*-pyrazol-3-yl]phenol. The structures of all newly synthesized compounds have been confirmed on the basis of IR, ^{1}H NMR and mass spectral techniques. Some of the synthesized compounds exhibit good antimicrobial activity against the tested strains.

Keywords: Fluorinated**,** pyrazole, chromone, antibacterial activity, antifungal activity

Microorganisms resistant to multiple anti-infective agents have increased around the world[1]. The resistance towards wide spectrum antibacterial and antifungal agents has initiated discovery and modification of new antibacterial and antifungal drugs[2]. The introduction of fluorine in organic molecules may lead to significant influence on the biological and physical properties of compounds due to increase in membrane permeability, hydrophobic binding and stability against metabolic oxidation[3]. It is known that fluorinated compounds exhibit broad spectrum of biological activities such as anti-inflammatory, antiviral, anti-HIV, antibacterial, anticancer, antimalarial, antidepressants, antipsychotics, anaesthetics and steroids[4].

Pyrazole and their derivatives are key substructures in a large variety of compounds with important biological and pharmacological properties[5]. They are known to possess wide spectrum of activities such as antibacterial[6], antifungal[7], antidiabetic[8], herbicidal[9], antitumor[10], anti-anxiety[11], and found as active pharmacophore in celecoxib *i.e.* COX-2 inhibitors[12] and slidenafil citrate *i.e.* cGMP specific phosphodiesterase type 5 inhibitors[13]. The pyrazole nucleus is found as an active pharmacophore in well known drugs (**Figure 1**).

Chromones are naturally occurring oxygen heterocycles which show interesting biological activities with low toxicity[14]. They exhibit biological activities such as antiviral[15], anticancer[16], anti-inflammatory[17] and antioxidant[18] properties. The aromatic 1,3-diketones are used as ultraviolet adsorbents[19] and are well known intermediates for synthesis of 1*H*-pyrazoles[20]. There are report found in the literature for synthesis of fluorinated pyrazoles[21,22].

In view of the biological activities associated with fluorinated compounds, chromones and pyrazoles and as a part of ongoing research, herein is reported the synthesis of some novel fluorinated chromones, pyrazoles and evaluation of their antibacterial and antifungal activities.

Result and Discussion

Chemistry

The synthesis of fluorinated pyrazole derivatives is a sequence of four steps as outlined in **Scheme I**. The structures of all newly synthesized compounds have been confirmed on the basis of spectral techniques.

The substituted 2-hydroxy acetophenones **1a-h** on reaction with 4-chloro-2,5-difluorobenzoic acid **2** in pyridine using $POCl_3$ gave 2-acetylphenyl-4-chloro-2,5-difluorobenzoate **3a-h**. ^{1}H NMR spectrum of **3a** shows a singlet at δ 2.55 for ketonic methyl group protons while the aromatic proton appeared in the range δ 7.23-7.94. The IR spectrum of compound **3a** showed characteristic stretching frequency bands at 1755 and 1685 cm^{-1} due to ester and ketonic C=O

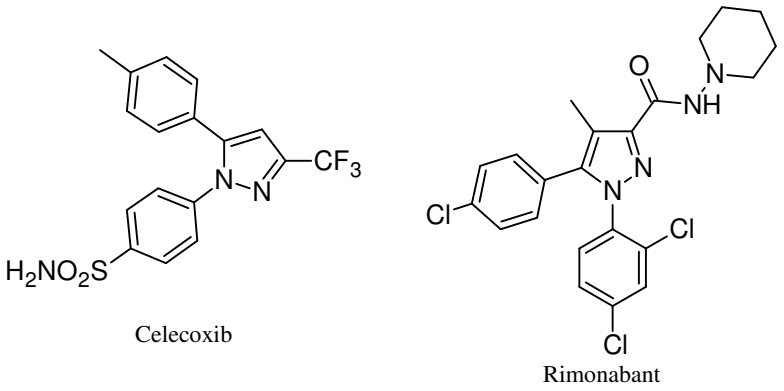
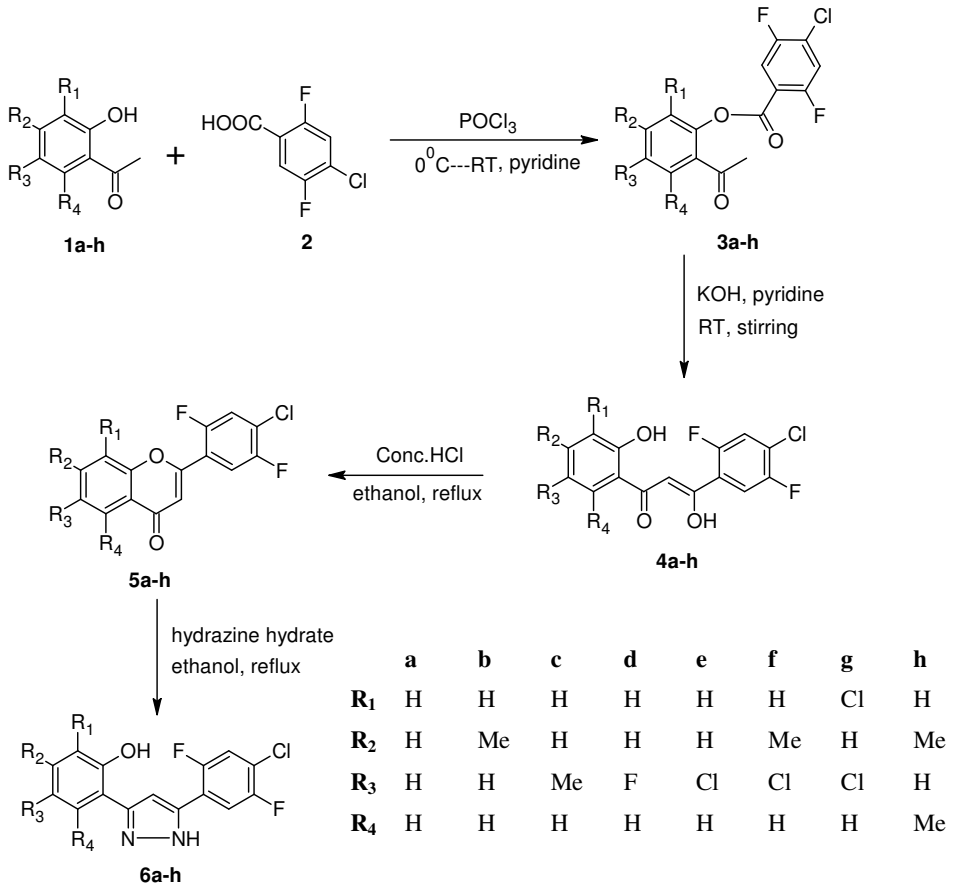


Figure 1 — Pyrazole containing drugs



	a	b	c	d	e	f	g	h
R_1	H	H	H	H	H	H	Cl	H
R_2	H	Me	H	H	H	Me	H	Me
R_3	H	H	Me	F	Cl	Cl	Cl	H
R_4	H	H	H	H	H	H	H	Me

Scheme I — General route for synthesis of fluorinated chromones and pyrazoles

functions respectively. The compound showed molecular ion peak at *m/z* 310 (M^+) which confirms its structure.

The compound **3** on reaction with KOH in pyridine undergoes a Baker-Venkatraman rearrangement to give (2Z)-3-(4-chloro-2,5-difluorophenyl)-3-hydroxy-1-(2-hydroxyphenyl)prop-2-en-1-one **4a-h**. This involves abstraction of methyl ketone proton by KOH to generate a carbanion which attacks the ester carbonyl to give compound **4**. ^{1}H NMR spectrum of **4b** exhibited a characteristic peak at δ 11.92 and 15.38 as broad singlets due to phenolic and enolic OH group proton respectively. The singlet at δ 2.36 is due to Ar-CH_3 group protons. In its IR spectrum, the ester carbonyl stretching frequency peak did not appear and new characteristic stretching frequency peaks were obtained at 3410 and 1739 cm^{-1} due to phenolic O-H and C=O

functions respectively. In its mass spectrum a molecular ion peak at *m/z* 324 (M^+) was obtained, which confirms the structure.

The compound **4** on reaction under acidic condition using conc. HCl in ethanol under reflux undergoes cyclodehydration reaction to give 2-(4-chloro-2,5-difluorophenyl)-4*H*-chromen-4-one **5a-h**. ^{1}H NMR spectrum of **5b** resonates a singlet at δ 6.92 due to C_3 proton of chromone ring while the aromatic proton peaks appeared in the range δ 7.25-8.09. In its IR spectrum, the O-H stretching frequency disappeared and a peak at 1685 cm^{-1} was obtained due to chromone C=O stretching. In its mass spectrum, a molecular ion peak was obtained at *m/z* 306 (M^+) corresponding to its molecular weight thus confirming the structure.

The compound **5** on reaction with hydrazine hydrate in ethanol under reflux undergoes opening of chromone ring to give the target compound 2-[5-(4-chloro-2,5-difluorophenyl)-1*H*-pyrazol-3-yl]phenol **6a-h**. ^{1}H NMR spectrum of **6e** exhibited characteristic peaks at δ 10.58 and 13.50 as broad singlets due to phenolic O-H and pyrazole N-H protons respectively. The proton of pyrazole nucleus appeared as a singlet at δ 7.69. In its IR spectrum the new stretching frequency peaks at 3361 and 3335 cm^{-1} are due to O-H and N-H functions respectively. In its mass spectrum, a molecular ion peak was obtained at *m/z* 341 (M^+) corresponding to the molecular weight thus confirming the structure. All newly synthesized compounds showed satisfactory elemental analysis.

Antimicrobial activity

The synthesized compounds were tested for their *in vitro* antimicrobial activity against Gram positive (*Staphylococcus aureus* MTCC 96 and *Streptococcus pyogenes* MTCC 443) and Gram negative (*Escherichia coli* MTCC 442 and *Pseudomonas aeruginosa* MTCC 441) bacteria using ampicillin as standard. The biological activity results of the tested compounds are given in **Table I**. The combined activity data reveals that the synthesized compounds **5a-h** and **6a-h** possess moderate to good activity profile.

The investigation of antibacterial screening data revealed that most of the synthesized compounds *i.e.* **5b**, **5c**, **5d**, **5e**, **5f**, **5h**, **6a**, **6b**, **6d**, **6e**, **6f**, **6g** and **6h** possessed good activity against *Staphylococcus aureus*. Among them **5e** and **6f** possessed the highest activity. *i.e.* 62.5 µg/mL. Compounds **5c** and **6e** exhibited good activity against *Streptococcus pyogenes* while compounds **5a**, **5e**, **5f**, **5h** and **6b** show good activity against *Escherichia coli*. Among the synthesized compounds **5a** and **6c** possessed good activity against *Pseudomonas aeruginosa*.

Antifungal activity was screened against three fungal species (*Candida albicans* MTCC 227, *Aspergillus niger* MTCC 282 and *Aspergillus clavatus* MTCC 1323) where griseofulvin was used as standard. Reviewing antifungal activity data it was observed that among the synthesized compounds **5a**, **5b**, **5d**, **5g**, **5h**, **6b**, **6e** and **6f** exhibited good activity against *Candida albicans*. Among them **5b** and **6b** possessed the highest activity.

Table I — Inhibitory antibacterial and antifungal activity of **5a-h** and **6a-h** expressed as minimum inhibitory concentration (MIC) in µg/mL

Compd	Gram positive bacteria		Gram negative bacteria		Fungi		
	S. aureus	*S. pyogenes*	*E. coli*	*P. aeruginosa*	*C. albicans*	*A. niger*	*A. clavatus*
5a	500	250	100	100	500	1000	>1000
5b	125	125	200	125	250	500	500
5c	100	100	125	200	1000	>1000	>1000
5d	200	200	250	250	500	>1000	>1000
5e	62.5	250	62.5	125	1000	>1000	>1000
5f	200	200	100	200	1000	>1000	>1000
5g	500	500	125	250	500	1000	1000
5h	250	200	62.5	200	500	500	1000
6a	200	200	200	125	1000	>1000	>1000
6b	200	250	100	125	250	>1000	>1000
6c	250	200	125	62.5	1000	>1000	>1000
6d	200	200	200	250	1000	1000	1000
6e	100	100	500	500	500	500	1000
6f	62.5	200	500	500	500	1000	1000
6g	125	200	250	250	1000	1000	1000
6h	100	250	200	200	1000	>1000	>1000
Ampicillin	250	100	100	100	-	-	-
Griseofulvin	-	-	-	-	500	100	100

The synthesized compounds possessed moderate activity against *Aspergillus niger* and *Aspergillus clavatus*. In general, it was observed that most of the synthesized compounds were found to be active against *S. aureus* bacterial strain and *C. albicans* fungal strain.

Experimental Section

All the chemicals used were of analytical grade. Melting points were taken in open capillaries and are uncorrected. The IR spectra were recorded in KBr on a Shimadzu FTIR 8400 spectrophotometer and only characteristic peaks are reported in cm^{-1}. The ^1H NMR spectra were recorded in $CDCl_3$ or DMSO-d_6 on a Bruker Avance spectrometer using TMS as an internal standard at 400 MHz and chemical shifts are reported in parts per million (ppm). Mass spectra were scanned on a Finnigan mass spectrometer. Thin-layer chromatography (TLC, on aluminium plates coated with silica gel 60F254, 0.25 mm thickness, Merck) was used for monitoring the progress of reactions and homogeneity of the synthesized compounds.

General procedure for synthesis of 2-acetylphenyl 4-chloro-2,5-difluorobenzoate, 3a-h

Equimolar amount (0.01 mol) of 2-hydroxy acetophenone **1a-h** and 4-chloro-2,5-difluorobenzoic acid **2** were dissolved in dry pyridine (10 mL) at 0°C in an ice bath. To this reaction mixture phosphorous oxychloride (0.015 mol) was added dropwise by maintaining the temperature below 5°C. After complete addition of phosphorous oxychloride the reaction mixture was stirred overnight. Then it was poured into crushed ice and acidified using conc. HCl. The solid product obtained was filtered and washed with cold 1% NaOH solution followed by washing with water. The product obtained was purified by recrystallization from ethanol to get yellow crystalline solid products **3a-h**.

2-Acetylphenyl 4-chloro-2,5-difluorobenzoate, 3a: Yield 65%; m.p. 82-83°C; IR (KBr): 1755 (C=O ester), 1685 (C=O ketonic), 1600 (C=C), 1151 cm^{-1} (Ar-F); ^1H NMR (400MHz, $CDCl_3$): δ 2.55 (s, 3H, O=C-CH_3), 7.23-7.25 (m, 1H, Ar-H), 7.29-7.33 (m, 1H, Ar-H), 7.37-7.41 (m, 1H, Ar-H), 7.57-7.62 (m, 1H, Ar-H), 7.87-7.94 (m, 2H, Ar-H); MS: *m/z* 310 (M^+).

2-Acetyl-5-methylphenyl 4-chloro-2,5-difluorobenzoate, 3b: Yield 63%; m.p. 95-96°C; IR (KBr): 1749 (C=O ester), 1680 (C=O ketonic), 1596 (C=C), 1166 cm^{-1} (Ar-F); ^1H NMR (400MHz, $CDCl_3$): δ 2.42 (s, 3H, Ar-CH_3), 2.52 (s, 3H, O=C-CH_3), 7.03 (s, 1H, Ar-H), 7.17-7.19 (m, 1H, Ar-H), 7.28-7.32 (m, 1H, Ar-H), 7.78 (d, 1H, Ar-H, *J* = 8 Hz), 7.91-7.94 (m, 1H, Ar-H); MS: *m/z* 324 (M^+).

2-Acetyl-4-methylphenyl 4-chloro-2,5-difluorobenzoate, 3c: Yield 60%; m.p. 85-86°C; IR (KBr): 1759 (C=O ester), 1683 (C=O ketonic), 1601 (C=C), 1171 cm^{-1} (Ar-F); ^1H NMR (400MHz, $CDCl_3$): δ 2.43 (s, 3H, Ar-CH_3), 2.54 (s, 3H, O=C-CH_3), 7.09 (d, 1H, Ar-H, *J* = 8 Hz), 7.29-7.33 (m, 1H, Ar-H), 7.38-7.40 (m, 1H, Ar-H), 7.66 (s, 1H, Ar-H), 7.90-7.94 (m, 1H, Ar-H); MS: *m/z* 324 (M^+).

2-Acetyl-4-fluorophenyl 4-chloro-2,5-difluorobenzoate, 3d: Yield 67%; m.p. 107-108°C; IR (KBr): 1763 (C=O ester), 1686 (C=O ketonic), 1599 (C=C), 1163 cm^{-1} (Ar-F); ^1H NMR (400MHz, $CDCl_3$): δ 2.54 (s, 3H, O=C-CH_3), 7.19-7.23 (m, 1H, Ar-H), 7.27-7.34 (m, 2H, Ar-H), 7.54-7.57 (m, 1H, Ar-H), 7.89-7.92 (m, 1H, Ar-H); MS: *m/z* 328 (M^+).

2-Acetyl-4-chlorophenyl 4-chloro-2,5-difluorobenzoate, 3e: Yield 68%; m.p. 112-13°C; IR (KBr): 1745 (C=O ester), 1681 (C=O ketonic), 1605 (C=C), 1157 cm^{-1} (Ar-F); ^1H NMR (400MHz, $CDCl_3$): δ 2.54 (s, 3H, O=C-CH_3), 7.17 (d, 1H, Ar-H, *J* = 8 Hz), 7.30-7.34 (m, 2H, Ar-H), 7.55-7.57 (m, 1H, Ar-H), 7.82 (d, 1H, Ar-H, *J* = 4 Hz); MS: *m/z* 345 (M^+).

2-Acetyl-4-chloro-5-methylphenyl 4-chloro-2,5-difluorobenzoate, 3f: Yield 59%; m.p. 91-92°C; IR (KBr): 1766 (C=O ester), 1677 (C=O ketonic), 1590 (C=C), 1169 cm^{-1} (Ar-F); ^1H NMR (400MHz, $CDCl_3$): δ 2.44 (s, 3H, Ar-CH_3), 2.52 (s, 3H, O=C-CH_3), 7.11 (s, 1H, Ar-H), 7.30-7.33 (m, 1H, Ar-H), 7.85 (s, 1H, Ar-H), 7.89-7.92 (m, 1H, Ar-H); MS: *m/z* 359 (M^+).

2-Acetyl-4,6-dichlorophenyl 4-chloro-2,5-difluorobenzoate, 3g: Yield 55%; m.p. 68-69°C; IR (KBr): 1757 (C=O ester), 1689 (C=O ketonic), 1593 (C=C), 1174 cm^{-1} (Ar-F); ^1H NMR (400MHz, $CDCl_3$): δ 2.54 (s, 3H, O=C-CH_3), 7.32-7.36 (m, 1H, Ar-H), 7.66 (d, 1H, Ar-H, *J* = 4 Hz), 7.72 (d, 1H, Ar-H, *J* = 4 Hz), 7.91-7.94 (m, 1H, Ar-H); MS: *m/z* 379 (M^+).

2-Acetyl-3,5-dimethylphenyl 4-chloro-2,5-difluorobenzoate, 3h: Yield 62%; m.p. 106-107°C; IR (KBr): 1758 (C=O ester), 1691 (C=O ketonic), 1589 (C=C), 1158 cm^{-1} (Ar-F); ^1H NMR (400MHz, $CDCl_3$): δ 2.32 (s, 6H, Ar-CH_3), 2.52 (s, 3H, O=C-CH_3), 6.99 (s, 1H, Ar-H), 7.28-7.32 (m, 1H, Ar-H), 7.65 (s, 1H, Ar-H), 7.91-7.94 (m, 1H, Ar-H); MS: *m/z* 338 (M^+).

General procedure for synthesis of (2Z)-3-(4-chloro-2, 5-difluorophenyl)-3-hydroxy-1-(2-hydroxyphenyl)-prop-2-en-1-one, 4a-h

Ester (0.01mol) was dissolved in dry pyridine (15 mL) and to this reaction mixture excess of powdered potassium hydroxide (2 g) was added with constant stirring. The reaction mixture was stirred at RT for 3 h.

After completion of reaction, the contents were poured into crushed ice and acidified with conc. HCl. The product obtained was filtered and purified by recrystallization from ethanol to get yellow crystalline solid products **4a-h**.

(2Z)-3-(4-Chloro-2, 5-difluorophenyl)-3-hydroxy-1-(2-hydroxyphenyl)prop-2-en-1-one, 4a: Yield 60%; m.p. 172-73°C; IR (KBr): 3421 (O-H stretching), 1735 (C=O), 1612 (C=C olefinic), 1566 (C=C aromatic), 1172 cm^{-1} (Ar-F); ^1H NMR (400MHz, $CDCl_3$): δ 6.93 (s, 1H, olefinic proton), 7.00-7.03 (m, 2H, Ar-H), 7.27-7.31 (m, 1H, Ar-H), 7.49-7.52 (m, 1H, Ar-H), 7.72 (d, 1H, Ar-H, *J* = 8 Hz), 7.79-7.83 (m, 1H, Ar-H), 11.89 (s, 1H, phenolic O-H proton), 15.35 (s, 1H, enolic O-H proton); MS: *m/z* 310 (M^+).

(2Z)-3-(4-Chloro-2, 5-difluorophenyl)-3-hydroxy-1-(2-hydroxy-4-methylphenyl)prop-2-en-1-one, 4b: Yield 58%; m.p. 137-38°C; IR (KBr): 3410 (O-H stretching), 1739 (C=O), 1615 (C=C olefinic), 1570 (C=C aromatic), 1160 cm^{-1} (Ar-F); ^1H NMR (400 MHz, $CDCl_3$): δ 2.36 (s, 3H, Ar-CH_3), 6.72 (s, 1H, olefinic proton), 7.18 (d, 1H, Ar-H, *J* = 8 Hz), 7.27-7.33 (m, 2H, Ar-H), 7.77-7.81 (m, 2H, Ar-H), 11.92 (s, 1H, phenolic O-H proton), 15.38 (s, 1H, enolic O-H proton); MS: *m/z* 324 (M^+).

(2Z)-3-(4-Chloro-2, 5-difluorophenyl)-3-hydroxy-1-(2-hydroxy-5-methylphenyl) prop-2-en-1-one, 4c: Yield 61%; m.p. 145-46°C; IR (KBr): 3425 (O-H stretching), 1733 (C=O), 1607 (C=C olefinic), 1550 (C=C aromatic), 1152 cm^{-1} (Ar-F); ^1H NMR (400 MHz, $CDCl_3$): δ 2.32 (s, 3H, Ar-CH_3), 6.89 (s, 1H, olefinic proton), 6.99 (s, 1H, Ar-H), 7.25-7.31 (m, 2H, Ar-H), 7.46-7.48 (m, 1H, Ar-H), 7.76-7.80 (m, 1H, Ar-H), 11.70 (s, 1H, phenolic O-H proton), 15.47 (s, 1H, enolic O-H proton); MS: *m/z* 324 (M^+).

(2Z)-3-(4-Chloro-2,5-difluorophenyl)-1-(5-fluoro-2-hydroxyphenyl)-3-hydroxy prop-2-en-1-one, 4d: Yield 62%; m.p. 147-48°C; IR (KBr): 3397 (O-H stretching), 1728 (C=O), 1621 (C=C olefinic), 1552 (C=C aromatic), 1160 cm^{-1} (Ar-F); ^1H NMR (400MHz, $CDCl_3$): δ 6.92 (s, 1H, olefinic proton), 6.96-6.99 (m, 1H, Ar-H), 7.20-7.23 (m, 1H, Ar-H), 7.27-7.32 (m, 1H, Ar-H), 7.36-7.37 (m, 1H, Ar-H), 7.78-7.82 (m, 1H, Ar-H), 11.64 (s, 1H, phenolic O-H proton), 15.37 (s, 1H, enolic O-H proton); MS: *m/z* 328 (M^+).

(2Z)-3-(4-Chloro-2,5-difluorophenyl)-1-(5-chloro-2-hydroxyphenyl)-3-hydroxy prop-2-en-1-one, 4e: Yield 60%; m.p. 132-33°C; IR (KBr): 3402 (O-H stretching), 1729 (C=O), 1611(C=C olefinic), 1547 (C=C aromatic), 1145 cm^{-1} (Ar-F); ^1H NMR (400MHz, $CDCl_3$): δ 6.94 (s, 1H, olefinic proton), 6.96 (d, 1H, Ar-H, *J* = 8 Hz), 7.29-7.33 (m, 1H, Ar-H), 7.41-7.44 (m, 1H, Ar-H), 7.65 (d, 1H, Ar-H, *J* = 4 Hz), 7.78-7.82 (m, 1H, Ar-H), 11.82 (s, 1H, phenolic O-H proton), 15.34 (s, 1H, enolic O-H proton); MS: *m/z* 345 (M^+).

(2Z)-3-(4-Chloro-2,5-difluorophenyl)-1-(5-chloro-2-hydroxy-4-methylphenyl)-3-hydroxy prop-2-en-1-one, 4f: Yield 58%; m.p. 133-34°C; IR (KBr): 3407 (O-H stretching), 1720 (C=O), 1603 (C=C olefinic), 1559 (C=C aromatic), 1164 cm^{-1} (Ar-F); ^1H NMR (400 MHz, $CDCl_3$): δ 2.38 (s, 3H, Ar-CH_3), 6.90-6.91 (m, 2H, one olefinic proton and one Ar-H), 7.28-7.32 (m, 1H, Ar-H), 7.64 (s, 1H, Ar-H), 7.77-7.81 (m, 1H, Ar-H), 11.78 (s, 1H, phenolic O-H proton), 15.33 (s, 1H, enolic O-H proton); MS: *m/z* 359 (M^+).

(2Z)-3-(4-Chloro-2,5-difluorophenyl)-1-(3, 5-dichloro-2-hydroxyphenyl)-3-hydroxy prop-2-en-1-one, 4g: Yield 57%; m.p. 154-55°C; IR (KBr): 3409 (O-H stretching), 1725 (C=O), 1620 (C=C olefinic), 1543 (C=C aromatic), 1140 cm^{-1} (Ar-F); ^1H NMR (400 MHz, $CDCl_3$): δ 6.95 (s, 1H, olefinic proton), 7.28-7.36 (m, 1H, Ar-H), 7.66 (d, 1H, Ar-H, *J* = 4 Hz), 7.72 (d, 1H, Ar-H, *J* = 4 Hz), 7.91-7.94 (m, 1H, Ar-H), 12.71 (s, 1H, phenolic O-H proton), 15.19 (s, 1H, enolic O-H proton); MS: *m/z* 379 (M^+).

(2Z)-3-(4-Chloro-2, 5-difluorophenyl)-3-hydroxy-1-(2-hydroxy-4,6-dimethylphenyl) prop-2-en-1-one, 4h: Yield 60%; m.p. 147-48°C; IR (KBr): 3430 (O-H stretching), 1727 (C=O), 1599 (C=C olefinic), 1548 (C=C aromatic), 1145 cm^{-1} (Ar-F); ^1H NMR (400 MHz, $CDCl_3$): δ 2.22 (s, 3H, Ar-CH_3), 2.27 (s, 3H, Ar-CH_3), 6.80 (s, 1H, olefinic proton), 6.97 (s, 1H, Ar-H), 7.27-7.30 (m, 1H, Ar-H), 7.41(s, 1H, Ar-H), 7.77-7.81 (m, 1H, Ar-H), 11.73 (s, 1H, phenolic O-H proton), 15.48 (s, 1H, enolic O-H proton); MS: *m/z* 338 (M^+).

General procedure for synthesis of 2-(4-chloro-2,5-difluorophenyl)-4*H*-chromen-4-one, 5a-h

The compound **4a-h** (0.001mol) was dissolved in ethanol (10 mL) and to this reaction mixture conc. HCl (1 mL) was added. The reaction mixture was heated under reflux for 2 hr. After completion of reaction, the contents were allowed to attain RT and then poured into crushed ice. The product obtained was filtered and purified by recrystallization from ethanol to get yellow crystalline solid products **5a-h**.

2-(4-Chloro-2, 5-difluorophenyl)-4*H*-chromen-4-one, 5a: Yield 55%; m.p. 157-58°C; IR (KBr): 1670 (C=O chromone ring), 1615 (C=C chromone ring), 1590 (C=C aromatic), 1160 cm^{-1} (Ar-F); ^1H NMR (400 MHz, $CDCl_3$): δ 6.96 (s, 1H, C_3 proton of chromone ring),

7.32-7.36 (m, 2H, Ar-H), 7.43-7.47 (m, 1H, Ar-H), 7.54-7.56 (m, 1H, Ar-H), 7.71-7.79 (m, 1H, Ar-H), 8.21-8.24 (m, 1H, Ar-H); MS: *m/z* 292 (M^+).

2-(4-Chloro-2, 5-difluorophenyl)-7-methyl-4*H*-chromen-4-one, 5b: Yield 56%; m.p. 180-81°C; IR (KBr): 1685 (C=O chromone ring), 1618 (C=C chromone ring), 1580 (C=C aromatic), 1150 cm^{-1} (Ar-F); ^{1}H NMR (400MHz, $CDCl_3$): δ 2.51 (s, 3H, Ar-CH_3), 6.92 (s, 1H, C_3 proton of chromone ring), 7.25-7.27 (m, 1H, Ar-H), 7.31-7.33 (m, 1H, Ar-H), 7.35 (s, 1H, Ar-H), 7.73-7.77 (m, 1H, Ar-H), 8.09 (d, 1H, Ar-H, *J* = 8 Hz); MS: *m/z* 306 (M^+).

2-(4-Chloro-2, 5-difluorophenyl)-6-methyl-4*H*-chromen-4-one, 5c: Yield 59%; m.p. 175-76°C; IR (KBr): 1679 (C=O chromone ring), 1620 (C=C chromone ring), 1591 (C=C aromatic), 1168 cm^{-1} (Ar-F); ^{1}H NMR (400MHz, $CDCl_3$): δ 2.47 (s, 3H, Ar-CH_3), 6.93 (s, 1H, C_3 proton of chromone ring), 7.30-7.34 (m, 1H, Ar-H), 7.43 (d, 1H, Ar-H, *J* = 8 Hz), 7.52-7.54 (m, 1H, Ar-H), 7.73-7.74 (m, 1H, Ar-H), 8.00-8.02 (m, 1H, Ar-H); MS: *m/z* 306 (M^+).

2-(4-Chloro-2, 5-difluorophenyl)-6-fluoro-4*H*-chromen-4-one, 5d: Yield 55%; m.p. 189-90°C; IR (KBr): 1675 (C=O chromone ring), 1628 (C=C chromone ring), 1566 (C=C aromatic), 1157 cm^{-1} (Ar-F); ^{1}H NMR (400MHz, $CDCl_3$): δ 6.94 (s, 1H, C_3 proton of chromone ring), 7.33-7.37 (m, 1H, Ar-H), 7.43-7.47 (m, 1H, Ar-H), 7.55-7.58 (m, 1H, Ar-H), 7.73-7.77 (m, 1H, Ar-H), 7.85-7.88 (m, 1H, Ar-H); MS: *m/z* 310 (M^+).

6-Chloro-2-(4-chloro-2,5-difluorophenyl)-4*H*-chromen-4-one, 5e: Yield 58%; m.p. 212-13°C; IR (KBr): 1681 (C=O chromone ring), 1618 (C=C chromone ring), 1597 (C=C aromatic), 1160 cm^{-1} (Ar-F); ^{1}H NMR (400MHz, $CDCl_3$): δ 6.87 (s, 1H, C_3 proton of chromone ring), 7.75-7.85 (m, 2H, Ar-H), 8.00 (s, 1H, Ar-H), 8.08-8.12 (m, 1H, Ar-H), 8.17-8.19 (m, 1H, Ar-H); MS: *m/z* 327 (M^+).

6-Chloro-2-(4-chloro-2, 5-difluorophenyl)-7-methyl-4*H*-chromen-4-one, 5f: Yield 53%; m.p. 217-18°C; IR (KBr): 1670 (C=O chromone ring), 1625 (C=C chromone ring), 1583 (C=C aromatic), 1166 cm^{-1} (Ar-F); ^{1}H NMR (400MHz, $CDCl_3$): δ 2.52 (s, 3H, Ar-CH_3), 6.92 (s, 1H, C_3 proton of chromone ring), 7.31-7.35 (m, 1H, Ar-H), 7.44 (s, 1H, Ar-H), 7.71-7.75 (m, 1H, Ar-H), 8.16 (s, 1H, Ar-H); MS: *m/z* 341 (M^+).

6,8-Dichloro-2-(4-chloro-2, 5-difluorophenyl)-4*H*-chromen-4-one, 5g: Yield 56%; m.p. 164-65°C; IR (KBr): 1677 (C=O chromone ring), 1622 (C=C chromone ring), 1571 (C=C aromatic), 1160 cm^{-1} (Ar-F); ^{1}H NMR (400 MHz, $CDCl_3$): δ 6.95 (s, 1H, C_3 proton of chromone ring), 7.29-7.36 (m, 1H, Ar-H), 7.63 (d, 1H, Ar-H, *J* = 4 Hz), 7.66 (d, 1H, Ar-H, *J* = 4 Hz), 7.91-7.94 (m, 1H, Ar-H); MS: *m/z* 361 (M^+).

2-(4-Chloro-2, 5-difluorophenyl)-5,7-dimethyl-4*H*-chromen-4-one, 5h: Yield 58%; m.p. 133-34°C; IR (KBr): 1688 (C=O chromone ring), 1620 (C=C chromone ring), 1569 (C=C aromatic), 1150 cm^{-1} (Ar-F); ^{1}H NMR (400MHz, $CDCl_3$): δ 2.37 (s, 3H, Ar-CH_3), 2.41 (s, 3H, Ar-CH_3), 6.91 (s, 1H, C_3 proton of chromone ring), 7.14-7.20 (m, 1H, Ar-H), 7.57-7.60 (m, 1H, Ar-H), 7.70-7.76 (m, 1H, Ar-H), 7.93 (s, 1H, Ar-H); MS: *m/z* 320 (M^+).

General procedure for synthesis of 2-[5-(4-chloro-2,5-difluorophenyl)-1*H*-pyrazol-3-yl]phenol, 6a-h

Chromone **5a-h** (0.001 mol) was taken in ethanol (10 mL) and to this reaction mixture hydrazine hydrate (0.002 mol) was added. The reaction mixture was heated under reflux for 3 h. After completion of reaction, the contents were allowed to attain RT, then poured into crushed ice and acidified with acetic acid. The product obtained was filtered and purified by recrystallization from ethanol to get yellow crystalline solid products **6a-h**.

2-[5-(4-Chloro-2,5-difluorophenyl)-1*H*-pyrazol-3-yl]phenol, 6a: Yield 59%; m.p. 236-37°C; IR (KBr): 3363 (O-H stretching), 3335 (N-H stretching), 1631 (C=N), 1516 (C=C aromatic), 1172 cm^{-1} (Ar-F); ^{1}H NMR (400MHz, DMSO-d_6): δ 6.87-6.91 (m, 1H, Ar-H), 6.95-6.98 (m, 1H, Ar-H), 7.12-7.18 (m, 2H, one pyrazole proton & one Ar-H), 7.40-7.45 (m, 1H, Ar-H), 7.65-7.67 (m, 1H, Ar-H), 7.87-7.91 (m, 1H, Ar-H), 10.39 (bs, 1H, phenolic O-H proton), 13.15 (bs, 1H, N-H proton); MS: *m/z* 306 (M^+).

2-[5-(4-Chloro-2,5-difluorophenyl)-1*H*-pyrazol-3-yl]-5-methylphenol, 6b: Yield 60%; m.p. 238-39°C; IR (KBr): 3370 (O-H stretching), 3343 (N-H stretching), 1620 (C=N), 1520 (C=C aromatic), 1165 cm^{-1} (Ar-F); ^{1}H NMR (400MHz, DMSO-d_6): δ 2.30 (s, 3H, Ar-CH_3), 6.70 (d, 1H, Ar-H, *J* = 8 Hz), 6.78 (s, 1H, pyrazole proton), 7.06-7.07 (m, 1H, Ar-H), 7.37-7.41 (m, 1H, Ar-H), 7.51-7.53 (m, 1H, Ar-H), 7.85-7.89 (m, 1H, Ar-H), 10.31 (bs, 1H, phenolic O-H proton), 13.21 (bs, 1H, N-H proton); MS: *m/z* 320 (M^+).

2-[5-(4-Chloro-2,5-difluorophenyl)-1*H*-pyrazol-3-yl]-4-methylphenol, 6c: Yield 57%; m.p. 256-57°C; IR (KBr): 3380 (O-H stretching), 3330 (N-H stretching), 1615 (C=N), 1530 (C=C aromatic), 1156 cm^{-1} (Ar-F); ^{1}H NMR (400MHz, DMSO-d_6): δ 2.29 (s, 3H, Ar-CH_3), 6.84-6.86 (m, 1H, Ar-H), 6.95(d, 1H, Ar-H, *J* = 8 Hz), 7.13 (s, 1H, pyrazole proton), 7.48-7.52 (m,

2H, Ar-H), 7.89-7.93 (m, 1H, Ar-H), 10.05 (bs, 1H, phenolic O-H proton), 13.09 (bs, 1H, N-H proton); MS: *m/z* 320 (M^+).

2-[5-(4-Chloro-2,5-difluorophenyl)-1*H*-pyrazol-3-yl]-4-fluorophenol, 6d: Yield 61%; m.p. 250-51°C; IR (KBr): 3359 (O-H stretching), 3325 (N-H stretching), 1631 (C=N), 1511 (C=C aromatic), 1159 cm^{-1} (Ar-F); ^{1}H NMR (400MHz, DMSO-d_6): δ 6.86-6.95 (m, 2H, Ar-H), 7.16 (d, 1H, Ar-H, *J* = 4 Hz), 7.37-7.44 (m, 2H, one pyrazole proton & one Ar-H), 7.85-7.89 (m, 1H, Ar-H), 10.35 (bs, 1H, phenolic O-H proton), 13.15 (bs, 1H, N-H proton); MS: *m/z* 324 (M^+).

4-Chloro-2-[5-(4-chloro-2,5-difluorophenyl)-1*H*-pyrazol-3-yl]phenol, 6e: Yield 63%; m.p. 260-61°C; IR (KBr): 3361 (O-H stretching), 3335 (N-H stretching), 1603 (C=N), 1510 (C=C aromatic), 1163 cm^{-1} (Ar-F); ^{1}H NMR (400MHz, DMSO-d_6): δ 6.94 (d, 1H, Ar-H, *J* = 8 Hz), 7.11-7.13 (m, 1H, Ar-H), 7.19 (d, 1H, Ar-H, *J* = 4 Hz), 7.39-7.43 (m, 1H, Ar-H), 7.69 (s, 1H, pyrazole proton), 7.86-7.90 (m, 1H, Ar-H), 10.58 (bs, 1H, phenolic O-H proton), 13.50 (bs, 1H, N-H proton); MS: *m/z* 341 (M^+).

4-Chloro-2-[5-(4-chloro-2,5-difluorophenyl)-1*H*-pyrazol-3-yl]-5-methylphenol, 6f: Yield 59%; m.p. 313-14°C; IR (KBr): 3390 (O-H stretching), 3349 (N-H stretching), 1621 (C=N), 1519 (C=C aromatic), 1185 cm^{-1} (Ar-F); ^{1}H NMR (400MHz, DMSO-d_6): δ 2.30 (s, 3H, Ar-CH_3), 6.88 (s, 1H, Ar-H), 7.15-7.16 (m, 1H, Ar-H), 7.41-7.45 (m, 1H, Ar-H), 7.67 (s, 1H, Ar-H, pyrazole proton), 7.86-7.90 (m, 1H, Ar-H), 10.43 (bs, 1H, phenolic O-H proton), 13.19 (bs, 1H, N-H proton); MS: *m/z* 355 (M^+).

2,4-Dichloro-6-[5-(4-chloro-2, 5-difluorophenyl)-1*H*-pyrazol-3-yl]phenol, 6g: Yield 55%; m.p. 240-41°C; IR (KBr): 3381 (O-H stretching), 3340 (N-H stretching), 1629 (C=N), 1529 (C=C aromatic), 1153 cm^{-1} (Ar-F); ^{1}H NMR (400MHz, DMSO-d_6): δ 7.32-7.38 (m, 1H, Ar-H), 7.41 (d, 1H, Ar-H, *J* = 4 Hz), 7.45 (d, 1H, Ar-H, *J* = 4 Hz), 7.51-7.55 (m, 1H, Ar-H), 7.59 (s, 1H, pyrazole proton), 10.11 (bs, 1H, phenolic O-H proton), 13.30 (bs, 1H, N-H proton); MS: *m/z* 375 (M^+).

2-[5-(4-Chloro-2, 5-difluorophenyl)-1*H*-pyrazol-3-yl]-3,5-dimethylphenol, 6h: Yield 54%; m.p. 257-58°C; IR (KBr): 3395 (O-H stretching), 3329 (N-H stretching), 1635 (C=N), 1525 (C=C aromatic), 1167 cm^{-1} (Ar-F); ^{1}H NMR (400MHz, DMSO-d_6): δ 2.21 (s, 3H, Ar-CH_3), 2.25 (s, 3H, Ar-CH_3), 6.57-6.75 (m, 3H, Ar-H), 7.41 (s, 1H, Ar-H, pyrazole proton), 8.04-8.06 (m, 1H, Ar-H), 10.02 (bs, 1H, phenolic O-H proton), 13.12 (bs, 1H, N-H proton); MS: *m/z* 334 (M^+).

Antimicrobial activity

All newly synthesized compounds were evaluated for their antimicrobial activity by broth microdilution method according to National Committee for Clinical Laboratory Standards[23]. The results were determined using minimum inhibitory concentration (MIC) values in µg/mL. Antibacterial activity was screened against two Gram positive (*Staphylococcus aureus* MTCC 96 and *Streptococcus pyogenes* MTCC 443) and two Gram negative (*Escherichia coli* MTCC 442 and *Pseudomonas aeruginosa* MTCC 441) bacteria using ampicillin as a standard. Antifungal activity was screened against three fungal species (*Candida albicans* MTCC 227, *Aspergillus niger* MTCC 282 and *Aspergillus clavatus* MTCC 1323) where griseofulvin was used as standard. All MTCC cultures were collected from Institute of Microbial Technology, Chandigarh and tested against above mentioned known drugs.

All tests were performed in Mueller Hinton broth for bacterial strains and Sabouraud's dextrose broth for fungal strains. Overnight broth cultures of each strain were prepared, and the final inoculum concentration in each well was adjusted to 2×10^6 CFU mL^{-1} for the bacterial strains and 2×10^7 CFU mL^{-1} for fungal strains. Stock solutions of all compounds at 2000 µg/mL were prepared by dissolving them in DMSO. Serial dilutions were prepared by primary and secondary screening. In primary screening 1000, 500, 250 and 200 µg/mL concentrations of the synthesized compounds were taken. The compounds found active in primary screening were further tested in a second set of dilutions of 100, 62.5, 50 and 25 µg/mL concentration against all microorganisms. The microbial growth was determined after 24 h incubation at 37°C for the bacteria and at 25°C after 48 h for the fungi. The MIC is defined as the lowest concentration of a compound at which the microorganism does not demonstrate visible growth. All determinations were performed in duplicate to check the accuracy of results. The antimicrobial activity results (MIC) are presented in **Table I**.

Conclusion

In the present investigation a series of novel fluorinated chromones and pyrazoles have been synthesized and screened for their antimicrobial activity. Antimicrobial activity result reveals that synthesized compounds possess moderate to good activity profile. The insights gained in this study will be useful for development of new anti-infective agents.

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Comparative Study of Feeding Soyachakali and Soyaflakes to Malnourished Preschool Children and its Impact on their Biochemical Analysis

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Abstract

More than five million children die each year as a result of under nutrition. Furthermore, billions of people suffer from vitamin and mineral deficiencies, especially of iron, iodine, vitamin A and zinc. Good nutrition is also constrained by inadequate safe drinking water and sanitation. To treat malnutrition among the preschool children the formulation of locally based protein rich product is must hence attempt was made to formulate soyabased food products such as soyachakali and Soyaflakes Chiwada. Soya products were formulated and prepared by standard methods. Organoleptically selected soya products were analyzed for its chemical composition such as protein, fat, vitamins, minerals, and anti nutritional factors. These products were supplemented to preschool malnourished children @ 40 gm/head/day for six months. Preschool malnourished children were graded according to grade of malnutrition. Their biochemical parameter such as serum iron (µg/dl) serum proteins (gl/dl), serum vitamin A (IU/dl), serum zinc (µg ml), blood glucose mg/dl and Haemoglobin g/dl had done monthly for six months. It had shown highly significant changes in blood glucose level, haemoglobin, serum protein, serum vitamin A, serum iron and serum zinc of preschool children after supplementation of soyaproducts.

Keywords: Soyaflakes Chiwada, Soyachakali, and supplementary feeding.

Introduction

Soyabean is higher in protein than other legumes and many animal products. The protein derived near by 40 per cent by Soyabean. Soyabean is a complete plant protein. Due to its high biological value and content good numbers of essential amino acids it can be use to prevent protein calorie malnutrition among vulnerable groups in the community. Hence, by keeping in view the feasibility in the preparation of formulated foods and due to nutritional significance of soya bean, its low cost, locally available and high amino acid profile it is planned to use the Soyabean after proper processing techniques in the preparation of soya by products with its effect on the treatment of malnourished preschool children to overcome the problem Messina and Barne 1994[1]

Material and Methods

Formulation: Formulation and preparation of soyachakali and soyaflakes chiwada was done by using standard method by Phillips and Thangana 1971[2]

Sensory Evaluation: Soya products were prepared and evaluated organoleptically by "Hedonic scale" Amerine et al. 1965[3].

Nutritional Evaluation: Nutritional quality analysis. Moisture content, total ash, major nutrient like crude protein, fat, carbohydrates, B complex vitamins including vitamin B_1,B_2 and B_3 , minerals such as iron, calcium, zinc and crude fiber were analyzed by use of methods described in AOAC 1984 and Rghunramula 1983[4]

Statistical analysis: The analysis significant at $p < 0.05$ level, S. E. and CD. at 5 per cent level by the procedure given by Gomez and Gomez 1984[5].

Biochemical Analysis: The nutritional status of the preschool children before and after the experimental period was evaluated through biochemical analysis method. The parameters such as haemoglobin g/dl, serum protein g/dl, blood glucose level mg/dl, serum vitamin A µ/dl, serum iron µg/dl and serum zinc µg/dl were analyzed by using methods given by Raghuramalu et.al. 1983[6].

Results and Discussion

Biochemical analysis of Experimental Groups of preschool children: This utilization of food depends on the conversion of food into functional nutrients after its absorption. This relevance is essential to study the facts and significance of food after consumption. Biochemical analysis is one of best and very relevant scientific method for assessment of nutritional status of the community. In this method biochemical parameters like blood, serum, plasma etc are used for the study.

The constituents in the blood such as blood glucose level, hemoglobin content serum protein, serum vitamin A, serum iron and serum zinc were analyzed in the experimental groups of children before and after supplementation.

The data of average in biochemical analysis of experimental group was given in table-1 It explained that, group I children found more average values of blood glucose i.e. 65.7mg/dl, haemoglobin 8.6±1.1 g/dl, serum protein 5.8 g/dl, serum vitamin A 112.3 IU/dl and zinc 1.05 µg/m respectively.

There was no major difference noticed in the average values of blood glucose level, serum protein, serum vitamin A, serum iron and serum zinc of group I and II children after supplementation. Haemoglobin level group I children noticed as 8.6 g/dl, i.e. 68.8 per cent. Where as it was reported as 9.8 g/dl i.e.78.2 per cent in group II.

Serum vitamin A observed in group I children as 112.3 IU/dl i.e 74.7 per cent. Where as it was recorded as 87.0 IU/dl i.e.58.0 per cent in group II children. All the average values of biochemical parameters were noted below the standard level in control group of children. Serum vitamin A (36.0 IU/dl) and zinc (0.54 µg/ml) level found drastically poor in this group of children.

The biochemical parameters which analyzed after supplementation were compared with their previous i.e. before supplementation values. The relevant data was presented in table 2 and 3. There was no major difference noticed in the average values of blood glucose level, serum protein, serum vitamin A, serum iron and serum zinc of group I and II children after supplementation. Blood glucose in group I was raised from 60.4 percent to 72.9 percent and in group II it was reported that it was ranges from 63.5 to 78.2 percent. The significant change was seen in blood glucose level in group I and II after supplementation. Haemoglobin level I group children noticed as 8.6 g/dl, i.e. 68.8 per cent. Where as it was reported as 10.0 g/dl i.e.78.2 per cent in group II children. The table-3 revealed average values of serum, protein vitamin A, iron and zinc. Serum vitamin A observed in group I children as 112.3 IU/dl i.e 74.7 per cent. Where as it was recorded as 87.0 IU/dl i.e.58.0 per cent in group II children. All the average values of biochemical parameters were noted below the standard level in control group of children. Serum vitamin A (36.5 IU/dl) and zinc (0.54 µg/ml) level found drastically poor in this group of children.

Serum iron in group I raised from 47.7 to 66.5 percent and in group II it raised from 48.3 to 65.5. The Significant change have seen after supplementation of soya product in supplemented group. No change have seen in control group.

Similarly serum protein values reported in group I it raised from 62.7 to 86.5percent significant changes have seen in group I and II. No change in values of serum protein in control group.

Serum vit A in group I significantly changed from 24.0 percent to 81.9 percent. Where as in group II serum vit A significantly changed but in group I significant range was more serum zinc value in group I and II were 11.65 µg/ml to 14.8 µg/ml and 8.8 µg/ml to 14.8 µg/ml respectively. No change is seen in control group.

Conclusion

On the whole, it can be concluded that, the supplementary feeding through soya byproducts found positive impact on improving the biochemical parameters of preschool malnourished children. The soya byproducts supplementation shown a highly significant effects on increasing blood glucose level, blood haemoglobin, serum protein, serum vitamin A, serum iron and serum zinc status of preschool children. All the analyzed biochemical parameters noted increased moderate to normal standard level. It indicated that soya byproducts have effectively worked. These products have capacity in improving the nutritional status of malnourished preschool children.

Table-1
Average in Biochemical Analysis of Experimental Groups

Biochemical analysis	Group I Mean ± S.D.	Group II Mean ± S.D.	Group III Mean ± S.D.
Blood glucose (mg/dL)	65.7 ± 2.9 (72.9)	68.7± 3.3 (76.3)	66.0 ± 9.0 (73.3)
Haemoglobin (g/dl)	8.6 ± 1.1 (68.8)	9.8 ± 1.3 (78.2)	7.6 ± 1.02 (60.7)
Serum protein(g/dl)	5.8 ± 0.8 (86.6)	6.0 ± 0.8 (89.7)	4.3±0.7 (65.5)
Serum Vitamin A (IU/dl)	112.3±2.9 (74.7)	87.0 ± 2.3 (58.0)	36.0±1.1 (24.0)
Serum Iron (µg/dl)	69.7±9.5 (66.4)	128.5±9.3 (65.2)	105.4±6.8 (48.2)
Serum Zinc (µg/ml)	1.05±2.0 (75.0)	1.02±2.0 (72.9)	0.54±0.9 (24.0)

Group I- Experimental group with supplementation of soyachakali.
Group II - Experimental group with supplementation of soyaflakes chiwada .
Group III - No supplementation i.e. control group.
Figures in paran theses indicate percentage.

Table-2
Average of Blood Glucose and Haemoglobin level of Experimental groups before and after supplementation

Biochemical analysis	Group I Mean ± S.D.			Group II Mean ± S.D.			Group III Mean ± S.D.		
I	**BS**	**AS**	**'t' value**	**BS**	**AS**	**'t' value**	**BS**	**AS**	**'t' value**
Blood glucose (mg/dl)	60.4± 2.2 (60.4)	65.7± 2.9 (72.9)	3.2*	63.7± 2.7 (63.0)	68.7±2.3 (73.6)	3.1*	60.9± 1.9 (65.9)	66.0± 1.8 (72.4)	1.5NS
Hemoglobin (g/dl)	8.1± 1.1 (64.4)	8.6± 1.2 (68.8)	1.4 NS	6.6± 0.9 (65.2)	10.0± 1.3 (78.2)	2.1*	7.6± 1.0 (60.0)	7.8± 1.1 (61.3)	-0.90 NS

Group I - Experimental group with supplementation of soyachakali.
Group II - Experimental group with supplementation of soyaflakes chiwada .
Group III - No supplementation i.e. control group.
Figures in Paran theses indicate percentage.
* significant at 5 per cent level ** significant at 1 per cent level
NS Non Significant BS – Before supplementation AS – After supplementation

Table-3
Average of Serum Protein, Vitamin A, Iron and Zinc Status Of Experimental Groups Before And After Supplementation

Biochemical analysis	Group I Mean ± S.D.			Group II Mean ± S.D.			Group III Mean ± S.D.		
II	**BS**	**AS**	**'t' value**	**BS**	**AS**	**'t' value**	**BS**	**AS**	**'t' value**
Serum Iron (µg/dl)	50.06±6.8 (47.7)	69.7± 9.5 (66.3)	2.50*	50.8± 6.9 (48.3)	68.5± 9.3 (65.2)	2.74*	50.5± 6.8 (48.2)	52.5± 6.8 (50.2)	0.47 NS
Serum protein (gl/dl)	4.2 ± 0.6 (62.7)	5.8± 0.8 (86.5)	2.7*	4.5 ± 0.6 (67.1)	6.0 ± 0.8 (89.7)	3.41**	4.4 ± 0.7 (67.7)	4.9 ± 0.5 (69.7)	1.24 NS
Serum Vitamin A (IU/dl)	8.28± 1.1 (24.0)	28.4 ± 3.9 (81.9)	3.71**	9.23 ± 1.3 (26.8)	20.0 ± 2.3 (58.7)	2.88*	8.21± 1.1 (23.7)	8.4± 1.4 (25.7)	0.71 NS
Serum Zinc (µg/ml)	11.65± 1.6 (61.3)	14.8 ±2.0 (76.7)	3.18**	8.8 ± 1.2 (46.3)	14.8 ± 2.0 (76.7)	3.06**	7.27± 1.0 (38.2)	7.8± 1.8 (40.2)	0.64 NS

Group I - Experimental group with supplementation of soyachakali.
Group II - Experimental group with supplementation of soyaflakes chiwada.
Group III - No supplementation i.e. control group.
Figures in Paran theses indicate percentage.
*significant at 5 per cent level ** significant at 1 per cent level
NS Non Significant BS – Before supplementation AS – After supplementation

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Research Paper

Study on impact of feeding soyaladoo and soyaflakes chiwada to malnourished pre-school children and their biochemical analysis

■ N.S. GHATGE

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■ **ABSTRACT :** To prevent malnutrition among children in the country in a sustainable manner are a critical component in this endeavor. This would require a multipronged effected in the form of capacity building for nutritional research, programme intervention development and evaluation. To treat malnutrition among the preschool children the formulation of locally based protein rich product is done. Hence attempt was made to formulate soyabased food products such as soyaladoo and soyaflakes chiwada. Soya products were formulated and prepared by standard methods. Organoleptically selected soya products were analyzed for its chemical composition such as protein, fat, vitamins, minerals, and ant nutritional factors. These products were supplemented to pre-school malnourished children @ 40 g/head/day for six months. Pre-school malnourished children were graded according to grade of malnutrition. Their biochemical parameter such as serum iron (µg/dl) serum proteins (gl/dl), serum vitamin A (IO/dl), serum zinc (µg ml), blood glucose mg/dl and Haemoglobin g/dl had done monthly for six months. It had shown highly significant changes on blood glucose level, haemoglobin, serum protein serum vitamin A, serum iron and serum zinc states of pre-school children after supplementation of soyaproducts.

■ **KEY WORDS:** Soyladoo, Soyaflakes chiwada, Supplementary feeding

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Soybean belongs to family leguminace and sub family papilionidae. It is a legume as well as an oil crop. It is one of the natures wonder and nutritional gift for the human nutrition. Therefore many researchers have recommended soybean supplementations in different forms of by products for the malnutrition treatment. Soyabean is very much popular food crop in most of the countries of the world whereas large number of people is found of soya products are prepared from soya seeds. Several recent scientific studies (Messina and Barne Presky, 1994) have shown that regular intake of traditional soya foods may help to prevent breast cancer, postrate cancer, color cancer and menopausal problems of women (Kaushik and Jaiswal, 2010). Due to presence of isoflavones and phytoesrogen in soyabean, it helps to prevents cancer

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...parative study of feeding soyladoo and soychakali ...alnourished pre-school children and its impact on their biochemical analysis

N.S. GHATGE

...rition is a worldwide health issue. It imposes a toll on child mortality, 53 per cent of deaths in children under 5 ...n age are nutrition related in worldwide. It may be due to the role of nutrients in disease and immunity. To treat ...rition among the preschool children the formulation of locally based protein rich product is must hence attempt ...de to formulate soybased food products such as soyladoo and soychakali. These soyabased food products formulated ...repared by standard methods. Organoleptically selected soya products were analyzed for its chemical composition ...as protein, fat, vitamins, minerals, and ant nutritional factors. These products were supplemented to pre-school ...ourished children @ 40 g/head/day for six months. Pre-school malnourished children were graded according to ...de of malnutrition. Their biochemical parameter such as serum iron (µg/dl) serum proteins (gl/dl), serum vitamin A ...g/dl), serum zinc (µg ml), blood glucose mg/dl and Haemoglobin g/dl had done monthly for six months. It had shown ...ghly significant changes on blood glucose level, haemoglobin, serum protein, serum vitamin A, serum iron and serum ...nc states of pre-school children after supplementation of soyaproducts.

Key Words : Soyladoo, Soychakali, Supplementary feeding

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INTRODUCTION

Soybean is very much popular food crop in most of the countries of the world whereas large number of people is found of soya products are prepared from soya seeds. Soybean is now getting wide acceptance in India. The soybean have the potentially to become industrial raw material in dairy products and agricultural stuff. Soybean is higher in protein than other legumes and many animal products. The protein derived near by 40 per cent by soybean. However, the quality of soya protein that is most remarkable health care professionals across the global recognizes. The superiority in quality of soya protein considers equivalent to that of the other high quality protein sources. It has been also significant that the amino acids of the protein of soybean are much similar to those of cow milk protein Carrington (2008).

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METHODOLOGY

Formulation:

Formulation and preparation of soyladoo, soychakali and soyflakes chiwada was done by using standard method by Thangamms (1971).

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Study of cereal and legume intake by 24 hrs diet recall method of pre-school malnourished children after supplementation of soya products

N.S. GHAIGE

Malnutrition among pre-school children is global problem to cope with this problem formulation of locally available protein and cereal base traditional products is done. The products are affordable and rich in nutrient content. The infant and pre-school children are extremely vulnerable. Hence, it is very essential to supply energy protein rich food products for better health and good nutritional status of the children. Hence, soya based food products are prepared such as soyaladoo, soyachakali and soyaflakes chiwada. These products were evaluated for its minor, major nutrients and antinutrients. The cereal and legume intake recorded by 24 hrs diet recall method. The intake of cereal and legume significantly increased after supplementation of soya products to pre-school malnourished children for six months. These products were given to at @40 g product/day /child. It provides energy, protein and fat as per ICMR recommendation. The malnourished pre-school children were classified as grade II and III. The intake of cereal and legume significantly increased after supplementation.

Key Words : Soyladoo, Soyachakali, Soyaflakes chiwada, Supplementary feeding

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INTRODUCTION

Soybean is higher in protein than other legumes and many animal products. The protein derived near by 40 per cent by soybean. However, the quality of soya protein that is most remarkable health care professionals across the global recognizes. The superiority in quality of soya protein considers equivalent to that of the other high quality protein sources. It has been also significant that the amino acids of the protein of soybean are much similar to those of cow milk protein (Carrington,2008). Soybean has high quality of amino acid, better protein digestibility. It also contents a better lipoxidase activity, lecithin and lipid profile. Due to these qualities in soybean and soya products are used in the dietary treatment of various deficiencies diseases.

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METHODOLOGY

Formulation :

Formulation and preparation of soyaladoo, soyachakali and soyaflakes chiwada was done by using standard method (Thangana, 1971).

Sensory evaluation :

Soya products were prepared and evaluated organoleptically with the help of trained panel of judges on a nine point "Hedonic scale" (Amerine *et al.*, 1965).

RESEARCH ARTICLE

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Neonatal care practices regarding traditional beliefs and customs adopted by slum families in Parbhani district

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ABSTRACT

Background: A human infant from time of Birth up to 28th day of life is called a newborn or neonate. Nearly 27 million babies are born in India each year. Every year 4 million babies die in first month of life in the world and quarter of these takes place in India. Child birth and neonatal period are culturally important times during which there is strong adhere to traditional practices. The objective of this study is to identify the neonatal care practices regarding traditional beliefs and customs adopted by slum families in Parbhani town of Maharashtra.

Materials and Methods: A descriptive research design was adopted for this study. Purposive sampling method was used to select 120 samples from selected slums in Parbhani town. A close ended questionnaire was used to collect the data from the subject.

Results: The data collected from 120 families were analysed using descriptive statistics. Almost all of the mothers (98%) have followed oil massage for baby before bath. Majority (65%) of the mothers have provided home remedies for treating their neonates during illness. Majority of families irrespective of SES and gender had various beliefs for not feeding colostrums, for oiling sensory organs, not to feed the baby in presence of others, adding and deleting food items from mother's diet , feeding pre lacteal feeds and using ornaments and cosmetics to their neonates for many reasons.

Conclusion: Findings of the study revealed 5that there is Strong relationship between SES and cultural practices and beliefs on neonatal care among mothers. Awareness programs regarding do's and don'ts of neonatal care should be conducted in slum area which will minimize the unhealthy traditional practices.

INTRODUCTION

Globally, there has been a considerable decline in under five and infant mortality during last four decades. However, neonatal mortality rates remain unchanged especially in developing countries (Tinker *et al.*, 2005; Arulam Palam and Bhalotra, 2006). The newborn health challenge faced by India is more formidable thing that experienced by any other country in the world. It is estimated that out of 3.9 million neonatal deaths that occur worldwide, almost 30 per cent occur in India (Black *et al.*, 2003). Global under – five mortality rates have declined over the past four decades, but the neonatal mortality rates (NMR) still remains high (Lawn *et al.*, 2005). Irrespective of urban- rural differences in NMR, neonatal deaths are a bare of poorest. A study done by

Baqui *et al.* (2007) in Rural Uttar Pradesh showed that out of 618 neonatal deaths, 32 per cent deaths were on the day of birth, 50 per cent occurred during first 3 days of life and 71 per cent were during the first week (Baqui *et al.*, 2007). Despite a plethora of health institutions, over 50 per cent births amongst the urban poor continue to occur in home settings under the supervision of untrained birth attendants (Agarwal *et al.*, 2007).

Care practices immediately after delivery play a major role in causing neonatal morbidities and mortalities. Cultural and traditional practices, values and beliefs play in attention seeking behaviour of past partum mothers as well as in new born babies during postnatal period (Dorlands, 2007). A family which mirrors values, traditions, customs and beliefs *i.e.*, culture of a society to which it belongs, plays a important role in psychological, social development and health in children (Datta, 2007).

Some of the traditional practices applying cow dung on umbilical stump, oil installation into nose, pre lacteal feeds also contribute to new born's risk of morbidity and mortality. The purpose of this study is to explore the traditional beliefs and practices of neonatal care by slum families.

MATERIAL AND METHODS

The present study was conducted in slum area of Parbhani town which is considered as a backward district of Maharashtra. A stratified random sample of 120 families having a neonate of full three weeks age was identified from 10 slum colonies of Parbhani town. Out of 120 slum families, 60 were from low SES and remaining 60 were from middle SES group. The data collection tool or questionnaire consists of two parts. First part has information related to socio-economic status, maternal, birth and delivery related factors. Second section has information of traditional new born practices followed after delivery. During data collection, interviews were conducted in Marathi using local vocabulary. The collected data were pooled, tabulated and statistically analyzed.

OBSERVATIONS AND ANALYSIS

The results obtained from the present investigation as well as relevant discussion have been summarized under following heads :

Description of background of neonates :

Socio demographic variables of mothers revealed that onto 120 mothers. Majority mothers were below 25 years of age (49 %), from low SES and 49 per cent from 26 to 30 years of age, majorly belonging to nuclear family *i.e.*, 53 and 57 per cent from low and middle SES, respectively, from middle sized family, having no formal education to 42 per cent mothers from low SES and middle school level education 48 per cent of middle SES mothers, 67 per cent were having first child and 80 per cent from middle SES were housewives while 68 per cent were unskilled labours doing work on daily wages.

Table 1 : Demographic characteristics / background of neonates

Sr. No.	Demographic variable	Socio-economic status	
		Low (60)(%)	Middle (60)(%)
Age in years of mother			
1.	Less than 25 Years	49	42
2.	26 – 30 Years	38	49
3.	Above 30 Years	13	09
Type of family			
1.	Nuclear	53	57
2.	Joint	42	43
3.	Extended	05	–
Size of family			
1.	Small(1 to 4)	28	33
2.	Middle(4 to 6)	45	39
3.	Large (more than 6)	27	28
Education of mothers			
1.	No formal Education	42	20
2.	Primary	20	17
3.	Middle School	33	48
4.	Higher School	04	13
5.	Graduation	–	2
Occupation			
1.	House Wife	32	30
2.	Daily wages/ Unskilled Labour	68	20
3.	Govt./Private Employee	–	–
Ordinal position			
1.	First	67	67
2.	Later	33	33

Traditional beliefs and customs observed for Neonatal care :

It is evident from the Table 2 that all the slum families in low and middle SES groups had the custom of using ornaments including silk and/or cotton thread tied to th

waist, wrist and neck of their neonates from 5th day onwards and the anklets made of silver or copper and white/black plastic bangles etc. put on neonate for various causes like to safeguard neonates from evil eyes, for protection of neonates health. Majority of the slum families in both SES groups had the habit of applying *kajal* prepared at home/purchased from market to safeguard neonate from evil eye and better eye sight and beautification.

Massaging neonates was adopted by almost all the slum families from both SES groups with sweet oil, castor oil, coconut oil as it was a customary and good for health of neonates. Oiling sensory organs of neonates was done by large per cent of families in low and middle SES groups for cleaning purpose of those organs.

Household remedies included application of *Kumkum* and sweet oil paste on umbilical stump for quick healing purpose, feeding the paste made out of *Hirda Sheng* to decrease fever, blowing air on neonate's stomach after grinding azwan inside the mother's mouth etc. were practiced by 65-47 per cent families in low and middle SES groups. Feeding the pre lacteal foods to neonates was followed by 93 and 75 per cent families in both SES groups and not breast-feeding neonates in the presence of others. (22- 28.33 %) due to fear of evil eye casting.

't' values indicated that significantly more percentage of low SES groups mothers discarded colostrums and had given pre lacteal foods to their neonates while in middle SES group higher percentage of mothers had special diet as compared to their counterparts in low SES groups.

In this study majority of mothers (98 – 100 %) applied *kajal* on the baby's face to prevent evil eye. According to the descriptive study conducted in Chandigarh revealed that out of 226 mothers who had children below 3 months practice of applying *kajal* was prevalent in 94.7 per cent in slums and 28.3 per cent in urban areas.

Majority of mothers (98- 100%) massaged the baby with oil before bath. According to the study conducted in Rawalpindi District, Pakistan, out of 100 mothers who were having baby of 6 months age, it was found that oil massage was a frequent practice in 61 per cent of babies.

In this study 93 per cent of mothers gave pre lacteal feeds soon after birth. According to the descriptive study conducted in Civil Hospital, Ahmedabad, among 435 mothers, it was found that about 66.2 per cent of mothers offered boiled water as a first feed. And according to the qualitative study conducted in 6 urban slum areas of Dhaka, Bangladesh, among 18 recently delivered mothers it was found that 40 per cent of women gave honey while 16 per cent of women gave sugar water soon after birth. Many studies from India and other South Asian countries have indicated that women commonly wait for several days after birth to begin breast feeding, avoid giving colostrums or supplement breast feeding with other liquids

Table 2 : Traditional beliefs and customs observed for neonatal care in slum families

Sr. No.	Traditional beliefs	Socio-economic status		't' value
		Low (60)	Middle (60)	
1.	Discarding colostrum	80	40	4.70**
2.	Commencement of breast feeding			
	On the 1st Day	22	40	00.8NS
	From 2nd Day	40	27	1.65NS
	From 3rd Day	27	23	0.39NS
	From 4th Day	11	10	0.18NS
3.	Oiling sensory organs	98		
4.	Massaging the body with oil before bath	100	98	1.11NS
5.	Giving pre lacteal Feeds	93	75	2.76NS
6.	Tying black thread in the neck	67	63	0.46NS
7.	Applying *Kajal*	100	98	1.11NS
8.	Using ornaments	100	100	–
9.	House hold remedies for treating stump	66	48	1.65NS
10.	Deleting food items from mother's diet	88	88	–
11.	Having special diet	48	87	4.8**
12.	No breast feeding in presence of others	22	28	0.89NS

NS=Non-significant

** indicate significance of value at P=0.01

(Sharma, 2010; Huffman *et al.,* 2001).

Delayed breast feeding especially up to three days was common and non-feeding of colostrums was recorded in all home births. This is a negative factor because if neonates are not breast fed, within the first one hour of birth then it puts these neonates at an increased risk for deaths (Edmond *et al.,* 2006).

In this study, majority of mothers oiling sensory organs of their neonates for cleaning purpose. Mohamed *et al.* (2010) found 36 per cent mothers were of opinion that oil instillation in the nostrils is good for babies, it protects their babies from cough and cold by clearing the nose and throat and also suggested as a measure to reduce body heat.

Conclusion :

This study indicates that awareness and attitude of mothers towards neonatal care has lots of lacunae especially in those who belong to the lower SES. There is scope for improvement by providing awareness programs and health education for pregnant mothers at primary care level itself.

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Effect of Aqua Exercises on the Sit Ups Test of School Going Girls

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Abstract: ***In India school, in academic curriculum physical education is involved as a compulsory subject. After independence Kothari commission (1964-1966), Mudaliar Commission (1952-53) had given suggestion and emphasis in the compulsory program for them and also National policy on education (1986 and 1996) they have given importance regarding physical education program in school going children still is not been executed properly at school level, number of physical activities involved in curriculum of the school level, like sports & games, Gymnastics, formal and informal activities as well. Exercise enthusiasts, athletes, elderly and the physically challenged are discovering aquatic exercise programme that suit their fitness desires. Sit ups are the most popular, convenient and perhaps an ideal mode of aerobic exercise since it involves the maximum number of the body's muscle and abdominal.***

Keywords: Aqua exercises, Sit ups.

1. Introduction

In India school, in academic curriculum physical education is involved as a compulsory subject. After independence Kothari commission (1964-1966), Mudaliar Commission (1952-53) had given suggestion and emphasis in the compulsory program for them and also National policy on education (1986 and 1996) they have given importance regarding physical education program in school going children still is not been executed properly at school level, number of physical activities involved in curriculum of the school level, like sports & games, Gymnastics, formal and informal activities as well. In school program some training method going to adopt but results are not revealed proper. In the school program the different training program should be used.

"Aqua exercises are the exercises that are performed in deep or shallow water."

Water exercise is rapidly growing in popularity. Exercise enthusiasts, athletes, elderly and the physically challenged are discovering aquatic exercise programme that suit their fitness desires. An advantage of aquatic exercise is that it can involve the upper and lower extremities through optimal ranges of motion while minimizing joint stress. The aquatic medium is eight hundred times as dense as air.

Sportsmen are trained scientifically with the latest training method and sophisticated instruments for improvement in their performance in different sphere of sports. Sport science have enabled sportsman to develop physical capacities beyond anything imagined. Sports have become highly competitive and records are being broken at a greater speed.

The physical capacities of strength, power and speed are important qualities for many sports. Maximum strength and/or power can clearly discriminate athletes of different performance levels in certain sports such as Basketball, Volleyball Swimming and sprint running. As such any sport involving jumping, throwing and striking depends much on the power of musculature. Consequently, the quest for the optimal power training method has led to the development of various training modes.

Sit ups are the most popular, convenient and perhaps an ideal mode of aerobic exercise since it involves the maximum number of the body's muscle and abdominal. Another mode of aerobic exercise is resistance work for maintaining bodily strength in order to gain and retain leg & abdominal muscle mass and have mass.

Due to changed perception of the forces acting on the body, movement in water is something special. On the one hand, each movement require greater exertion because of the need to overcome water resistance , the movements are more difficult than on land (as you will quickly see if you try to jog through thigh deep water). On the other hand the buoyancy (lift) in water makes it possible for everyone, including heavy people to float or glide peacefully almost without effort.

The benefits of exercising in water have been well known since Greek and Roman times. Examples are:

1) Exercising in water is easier: it supports body weight (up to 85% in water up to chest level).
2) Water acts as a shock absorb, reducing stress on joints.
3) Water allows a full range of movement without excessive strain. Less coordinated individuals can carry out movements in water without the embarrassment they may feel with exposed land-based classes.
4) The massaging effect of water increases circulation and promotes relaxation.
5) Aqua fitness is a novel and enjoyable way to become and stay fit.
6) For these reasons aquatic exercises is one of the most useful and recommendable form of training.

Objective of the Study

To determine the effect of aqua exercise on Bent Knee Sit ups test performance of a school going girls.

Assumptions

1) It is assumed that aqua exercise would help to improve physical fitness of school going girls.

2) It is assumed that the school girls will take part actively and enthusiastically in whole programme.
3) Further it will assume that the effect of aqua exercises may be of immense use for improving physical fitness of school girls.
4) It is assumed that trainees were not familiar with aqua exercises.

Though scientific method of research is used, it is assumed that the effect of dependent variable after experiment will be because of independent variable

HYPOTHESIS

Non-Directional Research Hypothesis

H_1: There would be significant change in Bent Knee Sit ups test performance of school girls due to aqua exercise.

$H_1 : M_1 \neq M_2$

2. Materials and Methods

The methodology of this study consisted of one experiment using one experimental and one control group for testing the effects of selected aqua exercises on the AAHPER physical fitness test. The purpose of the present study to gather scientific evidence in connection with the utility of aqua exercises in the promotion of Physical Fitness.

For the study experimental method was used. All the 50 subjects were divided randomly into two equal groups viz group I is experimental and group II is control consisted of 25 subjects each. Training intervention was delimitated to aqua exercises. The group I receives training of aqua exercises for a total period of 24 weeks, whereas group II (i.e. control group) did not participate in any training program. However, all the subjects participated in their regular school activities as per daily timetable of the school.

The design of the experiment was **pre test post test random group design** and has been planned in three phases:

Phase I: Pre test

Phase II: Aqua training program

Phase III: Post Test

3. Analysis and Interpretation of Results

After the data collection was over, the data were analyzed by using **Independent 't' Test** the results have been narrated, interpreted and discussed logically with scientific reasoning to arrive to conclusion.

Table 1: Sit ups Group Statistics

Group	N	Mean	Std. Deviation	Std. Error Mean
Experimental	25	3.24	4.14	.8292
Control	25	0.2	3.61	.7234

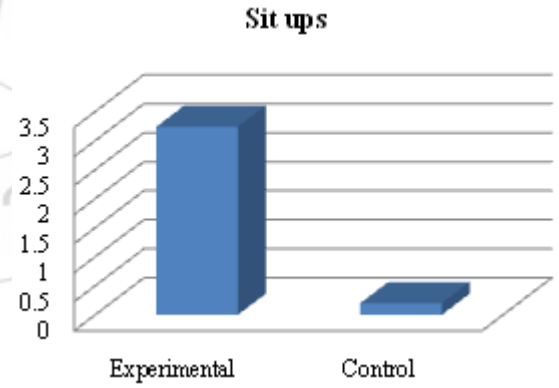
Table 2: Sit ups Independent Samples Test

	Leven's Test for Equality of Variance		t-test for Equality of Means				
	F	**Sig.**	**t**	**df**	**Sig. (2-tailed)**	**Mean Diff.**	**Std. Error of Diff.**
Equal variances assumed	.021	0.88	2.76	48	0.008	3.04	1.1
Equal variances not assumed			2.76	47.13	0.008	3.04	1.1

Sit ups Group Statistics:

Change in sit ups performance of experimental group was 3.24 and standard deviation 4.14 and that for control group it was 0.02 and standard deviation 3.61. Change of performance was compare with independent sample 't' test. Equality of variances was tested by Levenes's test for equality of variances 'F' value .021 which was not found statistically significant at 0.05 significance level. (p=0.88) This indicates that Variances was equal mean difference between change sit ups score of experimental and control group was 3.04.

The mean difference between control and experimental was tested by Independent sample 't' test where 't' value was 2.76 (df=48) which was statistically significant at 0.05 significance level(p=0.008). This indicates that Experimental group has shown significant growth in Sit ups performance than control group.



Graphical representation Mean Difference of Sit ups

4. Conclusion

The observation of the experimental data, within limitations, help to conclude that –

There was significant improvement in Bent knee Sit ups performance of school going girls age between 14 to 16 years who underwent the Aqua training programme.

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Effect of Aqua Exercises on the Shuttle Run Test of School Going Girls

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Abstract: *In the modern scientific age in every field of human Endeavour systematic objectives and scientific procedures are followed in accordance with the principals based on experiences, understanding and application of knowledge of science. The main factor responsible for this improvement is the development of new training methods based on scientific principles derived from exercise physiology, which are incorporated in basic physical education and advanced sports training at the same time development of improved technique and tactics, new equipment and improved facilities. The study proved that the girl students can actively participate in physical as wel as aquatic activities without fear and aqua exercise training can help them to achieve physical fitness*

Key words- Aqua exercises, Shuttle run.

1. Introduction

In the modern scientific age in every field of human Endeavour systematic objectives and scientific procedures are followed in accordance with the principals based on experiences, understanding and application of knowledge of science. The field of games and sports is also no exception to this. Advanced countries like U.S.A., Germany, Russia, Australia, Britain and other have made rapid progression in games and sports like Athletics, Soccer, Hockey, Basketball etc. this progress and the international achievements have been possible due to the research experimentation and application of scientific knowledge.

The performance level of sportsman in various games and sports is showing considerable improvement day by day. The main factor responsible for this improvement is the development of new training methods based on scientific principles derived from exercise physiology, which are incorporated in basic physical education and advanced sports training at the same time development of improved technique and tactics, new equipment and improved facilities, scientific understanding rendered by the sport scientist also responsible for improved performance.

Leg Strength is an important component of physical fitness which effects the performances in all activities in some form or the other. Development of strength is essential for power and speed. It has been proved that wise use of weights not only increases an athlete's strength and ability but also aids speed of reaction. Since strength base is an advantageous in Aqua exercises training program has been designed to complement the development of leg power and speed.

Mackenzie stated that, "Exercise comprises of movements designed to act on the muscles; the blood vessel, nervous system, skin and abdominal organs. Active exercises are done by person of average health and require definite exertion of the will power, while passive exercises are restored for the cure and treatment of certain diseases that do not require any exertion of will power."

Exercise is physical activity that is planned, structured, and repetitive bodily movement done to improve or maintain one or more of the components of health related fitness.

Exercise improves the efficiency of the body, refreshes the brain, enhances overall vitality of various organs of the body, increases longevity, and significantly improves the quality of life.

There are many authorities who say that swimming is the best all around exercise, whereas others feel jogging is the best. There are still others who feel that progressive weight training is the best because you can exercise every part of the body and gradually increase the resistance along with strength and stamina.

Water exercise is rapidly growing in popularity. Exercise enthusiasts, athletes, elderly and the physically challenged are discovering aquatic exercise programme that suit their fitness desires. An advantage of aquatic exercise is that it can involve the upper and lower extremities through optimal ranges of motion while minimizing joint stress. The aquatic medium is eight hundred times as dense as air.

The benefits of exercising in water have been well known since Greek and Roman times. Examples are:

1) Aqua fitness is a novel and enjoyable way to become and stay fit.
2) There is little post-exercise stiffness. This is due, possibly, to the lack of eccentric muscular contractions when using water as a mode of resistance.
3) Water provides resistance to motion through resistive drag. The intensity of the exercise can be easily controlled by varying the degree of resistance (drag). By moving faster, or in deeper water where the resistance is greater, the intensity is increased. By moving more slowly or in shallower water the intensity is decreased.
4) Buoyancy properties of water assist in supporting the body (up to 90%), often making exercise feel easier.
5) Up to 85% of jarring is eliminated as the water absorbs impact when jogging or jumping
6) Water acts as a shock absorb, reducing stress on joints.
7) Water acts a coolant to prevent overheating.

8) For these reasons aquatic exercises is one of the most useful and recommendable form of training.

It was considered appropriate by the research scholar to investigate effectiveness of aqua exercise training on the physical fitness. The purpose of the study is to see the effect of a set of aqua exercises on physical fitness; which might be used to decide desirability of aqua exercises for improving and maintaining the physical fitness if possible. To achieve this purpose, the following programme was selected. "*Effect of aqua exercises on the Shuttle Run Test of School Going Girls*"

2. Objectives of the Study

To determine the effect of aqua exercise on Shuttle Run test performance of a school going girls.

3. Assumptions

1) It is assumed that aqua exercise would help to improve physical fitness of school going girls.
2) It is assumed that the school girls will take part actively and enthusiastically in whole programme.
3) Further it will assume that the effect of aqua exercises may be of immense use for improving physical fitness of school girls.
4) It is assumed that trainees were not familiar with aqua exercises.
5) Though scientific method of research is used, it is assumed that the effect of dependent variable after experiment will be because of independent variable.

Hypothesis

H_1: There would be significant change in Shuttle Run test performance of school girls due to aqua exercise.

$H_1 : M_1 \neq M_2$

4. Materials and Methods

The methodology of this study consisted of one experiment using one experimental and one control group for testing the effects of selected aqua exercises on the **Shuttle Run test.** The purpose of the present study to gather scientific evidence in connection with the utility of aqua exercises in the promotion of Physical Fitness.

For the study experimental method was used. All the 50 subjects were divided randomly into two equal groups via group I is experimental and group II is control consisted of 25 subjects each. Training intervention was delimitated to aqua exercises. The group I receives training of aqua exercises for a total period of 24 weeks, whereas group II (i.e. control group) did not participate in any training program. However, all the subjects participated in their regular school activities as per daily timetable of the school.

The design of the experiment was **pre test post test random group design** and has been planned in three phases:
Phase I: Pre test
Phase II: Aqua training program
Phase III: Post Test

Shuttle Run (4 x10 Meter):-
Objective: To measure Agility
Equipment: Stopwatch and two blocks of wood (2"x2"x4"), wooden clapper.
Procedure: Marking of two parallel lines 3 meter in length were drawn 10 meters apart, considering one as starting point. The subject stood at starting point, with the two wooden blocks placed on the edge of the other line. On the starting signal with clapper, the subject ran to the wooden block, and lifted one block and return to the starting line and place the block behind the line. He then returns to the second block, lifted it and then sprinted across the starting line on the way back.
Scoring: The score was elapsed time recorded in seconds

5. Analysis And Interpretation Of Results

In the previous chapter the methodology in details has been presented. After the data collection was over, the data were analyzed by using **Independent 't' Test** the results have been narrated, interpreted and discussed logically with scientific reasoning to arrive to conclusion.

Shuttle Run Group Statistics

Group	N	Mean	Std. Deviation	Std. Error Mean
Experimental	25	-0.32	0.59	0.11
Control	25	-0.64	2.74	0.54

Table: Shuttle Run Independent Samples Test

	Leven's Test for Equality of Variances		t-test for Equality of Means				
	F	Sig.	T	df	Sig. (2-tailed)	Mean Diff.	Std. Error of Diff.
Equal variances assumed	4.54	0.038	0.57	48	0.57	0.32	0.56
Equal variances not assumed			0.57	26.22	0.57	0.32	0.56

Shuttle Run Group Statistics

Change in Shuttle run performance of experimental group was -0.32 and standard deviation 0.59 and that for control group it was -0.64 and standard deviation 2.74. (Table) Change of performance was compare with independent sample 't' test. Equality of variances was tested by Levenes's test for equality of variances 'F' value 4.54 which was found statistically significant at 0.05 significance level. (p=0.038) This indicates that variances was equal mean difference between change Shuttle run score of experimental and control group was 0.32 (Table).

The mean difference between control and experimental was tested by Independent samples 't' test where 't' value was 0.57 (df=48) which was statistically not significant at 0.05 significance level(p=0.57). This indicates that Experimental group has shown significant growth in Shuttle run performance than control group.

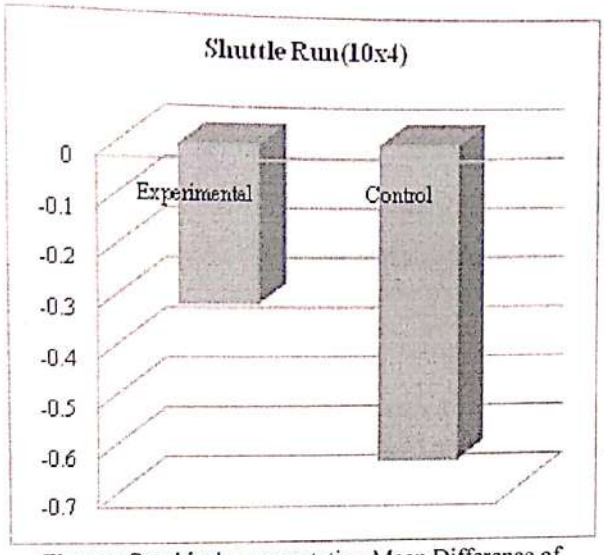

Figure: Graphical representation Mean Difference of Shuttle Run (10x4)

6. Conclusion

The observation of the experimental data, within limitations, help to conclude that, there was significant improvement in Shuttle run performance of school going girls underwent the Aqua training programme.

Contribution to the Knowledge

- This study contributed one scientific as well as innovative schedule of aqua exercises that are found useful for the high school girls.
- Since majority of the school girls does not participate in physical activity, the result of the present study may be a motivating factor.
- This study proved that the girl students can actively participate in physical as wel as aquatic activities without fear and aqua exercise training can help them to achieve physical fitness.

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Pravara Rural Education Society's

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3.2.1 *Number of papers published per teacher in the Journals notified on UGC website during the last five years*

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Original article

Microbial growth, biomass, community structure and nutrient limitation in high pH and salinity soils from Pravaranagar (India)

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ABSTRACT

pH, salinity and nutrient conditions are major determinants of microbial biomass, activity and community composition; all being hypothesized to favour bacterial over fungal activity. Soils from Pravaranagar (India), having high nutrient content and high pH (pH_w 7.4–8.8), with sometimes increased salinity, were thus expected to have high bacterial/fungal ratios. Twelve soils were characterized for microbial growth, biomass, community structure and nutrient limitation. The phospholipid fatty acid (PLFA) pattern was typical for high pH soils, with relative high amounts of several unsaturated PLFAs, like 18:ω7, and relatively low in e.g. cy19:0. The adaptation to high pH was also seen in the bacterial community tolerance to pH, with optimum pH for growth around pH 7.5. The high pH had resulted in soils with high bacterial but low fungal growth. However, adding substrate conducive for fungal growth, like straw, could induce fungal growth. Some soils had high electric conductivity, indicating salinization. The bacterial community had developed increased tolerance to NaCl in these soils. These soils also differed in the PLFA pattern, suggesting that saline soils had more fungal biomass. In all soils bacterial growth was limited by lack of carbon, but secondary limitation due to nitrogen was also found, while phosphorus addition did not affect growth. The high nutrient condition was evident in more than 5-fold increases in bacterial growth in some soils when adding only C. We could thus show that in these soils, high pH, salinity and nutrient conditions all had affected soil microbial activity and community structure. Although the high pH favoured bacteria, this was, however, not found for high salinity soils.

1. Introduction

Modern agricultural practices can drastically alter soil physicochemical conditions and thus the environment for the soil microorganisms. This is not only due to the use of monocrops or different mechanical practices like ploughing and tilling, shaping the physical soil environment. Fertilization practices have also altered nutrient conditions, and application of lime has increased pH. These changes are all made in order to improve plant productivity, but other changes can in the long time perspective have negative consequences. This includes salinization of soils due to artificial watering [1]. Worldwide more than 900 million hectares of the total agriculture land are affected by salt; this account to more than 6% of the world's total area [2]. Part of the salinity problem is due to agricultural practices.

In the present study soils from Pravaranagar, India, was investigated. The Pravaranagar area has a well developed agriculture sector. An intensive agriculture has been practiced since the sugar industry established in 1953. Part of the agriculture practices includes the use of spent wash from the sugarcane production as a liquid fertilizer; an organic fertilizer rich in both nutrients and organic matter [3]. Farmers also frequently use chemical and organic fertilizers. All the nutrients from these fertilizers are not taken up by the plants; hence they remain in the soil. This has led not only to saturation of certain nutrients in the soil, but also in some cases to increased salinity. This, together with the initially high soil pH (pH_w up to >8.5), has led to soils with rather extreme physicochemical characteristics.

Soil pH has been shown to be one of the most determining environmental factors for microbial community composition [4,5],

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1164-5563/

with the bacterial community pH tolerance closely tracking the soil pH [6,7]. Soil pH will also drive the balance of bacterial and fungal growth in soil, low pH favouring the latter and high pH the former [8]. So far this has hardly been studied on soils with pH > 8, but one would expect such high pH conditions being even more conducive for bacterial growth than at lower pH.

Decreasing soil osmotic potential due to high salinity will also affect soil microbial composition and function, with decreasing microbial biomass and activity [9–11], and a shift towards lower fungal/bacterial biomass ratios commonly being reported [9,12]. High N content in the soil due to fertilization has also been connected to a decrease in fungi, both regarding biomass [13,14] and growth [15]. Thus high pH, high salinity and high fertility all have been connected with increasing importance of bacterial function in soil. Thus we hypothesized that the Pravanagar soils would result in bacteria being relatively more important than fungi, both in biomass and activity (growth), with a bacterial community being well adapted to the pH and osmotic potential conditions. We also expected the bacterial community to be mainly carbon limited in this situation of high fertility, although the secondary limiting nutrient for bacterial growth would be either N or P.

We initially characterized the soil microbial community of 12 soils from the Pravaranagar area (district Ahmednagar), estimating biomass, growth and community composition (using phospholipid fatty acids, PLFAs, as a proxy). We also determined the main and secondary nutrient limiting bacterial growth, the bacterial community response to pH, and salt tolerance of the bacterial community. Finally, since these high pH soils were expected to have low fungal activity, we studied if more extensive fungal growth could be induced by adding different plant-derived substrates.

2. Materials and methods

2.1. Soils and chemical analyses

12 soils from Pravaranagar (India), located between latitude 19°30′ to 19°34′ N and longitude 74° 20′ to 74°25′ E, were studied. All soils were clayish, classified as Vertisols. The regional name is regur (black cotton soils). All were agricultural soils, most of them recently being cropped by sugarcane. Three soil samples were collected from each sampling site at 0–15 cm depth using a shovel. They were mixed into one bulk sample per soil, sieved using 2 mm mesh size, packed into polythene bags, brought to the laboratory and analysed for chemical and biological parameters. Thus, each soil was considered one replicate in further calculations. Soil pH was determined using a glass electrode both in distilled water (pH_w; soil:water 1:5 w:w) and in 0.1 M KCl (pH_{KCl}; 1:1 w:w). Water content was determined gravimetrically after heating at 105 °C over night. Organic matter content was determined using loss on ignition (600 °C for 4 h), and soil C was assumed to be 45% of organic matter. Electric conductivity (EC) was measured in 1:5 soil:water extracts ($EC_{1:5}$).

2.2. Microbial characterization

Bacterial growth was estimated using the leucine (Leu) incorporation technique [16,17]. Briefly, 1 g of soil was mixed with 20 ml distilled water, vortexed for 3 min, and then centrifuged for 10 min at 3000 rpm to obtain a bacterial suspension (the supernatant). From the bacterial suspension, 1.5 ml was transferred into 2 ml micro-centrifugation tubes. Radiolabeled Leu (2 μl L-4, 5-^{3}H-Leucine, 37 MBq ml^{-1}, 1.48–2.22 TBq mmol^{-1}, Perkin Elmer, USA) was added together with non-radioactive Leu (final concentration 275 nM). After a 2-h incubation period at 22 °C, growth was terminated by adding 75 μl 100% trichloroacetic acid (TCA). Washing and subsequent measurement of radioactivity of the bacteria were performed according to [17]. Leu incorporation per h into bacteria extracted from soil, expressed as pmol Leu h^{-1} g^{-1} soil C, was used as a proxy of bacterial growth.

Fungal growth was estimated by acetate incorporation into ergosterol (Ac-in-erg) [18–20]. 0.5 g of soil was put into 10 ml test tubes with 1.5 ml water, 20 μl [1-^{14}C] acetic acid (sodium salt; 7.4 MBq ml^{-1}, 2.04 GBq mmol^{-1}, Perkin Elmer, USA), and 480 μl unlabelled sodium acetate, resulting in a final acetate concentration of 220 μM. The test tubes containing the soil slurry was then incubated at 22 °C for 4 h. One ml of 5% formalin was used to terminate the incorporation of acetate, after which the tubes were centrifuged and the supernatant discarded. Ergosterol in the soil was then extracted in 5 ml 10% KOH in methanol, separated and quantified using HPLC with a UV detector (282 nm) according to [20]. The ergosterol peak was collected and the amount of incorporated radioactivity was determined using a scintillator counter. The amount of ergosterol was used as a proxy of fungal biomass in soil. Acetate incorporation into ergosterol, expressed as pmol Ac h^{-1} g^{-1} soil C, was used as a proxy of fungal growth.

Respiration was measured by transferring 1 g of soil to a 20 ml glass vial. The vial was sealed with a crimp cap and incubated for 24 h at 22 °C, after which the CO_2 concentration was determined using a GC. We did not apply any correction factor to avoid underestimation of respiration due to the high pH in the soils [21]. Instead we normalized respiration to that in the non-amended control soil, assuming similar correction factor for all treatments.

The phospholipid fatty acid (PLFA) pattern was determined according to [22] using duplicate samples from each soil bulk sample. Briefly, 0.25 g of soil were extracted for 2 h in a one phase mixture of chloroform, methanol and citrate buffer (1:2:0.8, v:v:v). After splitting the extract into two phases by adding chloroform and buffer, the lipid-containing lower phase was collected and evaporated under N_2. The lipid material was fractionated on columns containing silicic acid into neutral, glycolipids and polar lipids. The polar fractions containing phospholipids was collected for further analysis. Methyl nonadecanoate (19:0) was then added as an internal standard. The phospholipids were methylated by mild alkaline methylation before being analysed on a GC. 28 different PLFAs were detected. The sum of these (totPLFA) were used as indicator of microbial biomass, the PLFA 18:2ω6,9 was used as an indicator of fungal biomass and the ratio of 18:2ω6,9 to the sum of bacterial PLFAs [23] was used as an index for fungal: bacterial biomass ratio. The PLFA 18:1ω9, although not only emanating from fungi, was used as additional evidence for changes in fungal biomass [24]. A principal component (PCA) analysis was performed on mol% of the PLFAs after standardizing to unit variance.

2.3. Nutrient limitation of bacterial growth

In order to study nutrient limitation, carbon (C as glucose), nitrogen (N) and phosphorus (P) was added to soil in a full factorial design and bacterial growth was then measured using Leu incorporation [25,26]. The optimal amounts of nutrients were initially tested to find suitable concentrations of glucose, NH_4NO_3 and K_2HPO_4 that together gave a strong bacterial growth response. We choose 5 mg g^{-1} glucose (equivalent to 2 mg g^{-1} glucose-C), 0.142 mg g^{-1} NH_4NO_3 (equivalent to 0.05 mg g^{-1} NH_4NO_3–N) and 0.112 mg g^{-1} K_2HPO_4 (equivalent to 0.02 mg g^{-1} K_2HPO_4–P), which gave a growth response in all soils except no. 6 and 8, which became anaerobic. These soils were thus not used. For soil no. 5 we used the double amounts of glucose in order to achieve a growth response. In the final test, 1 g of soil was placed in 50 ml centrifuge tubes, and the different combinations of C, N and P were added in 100 μl of water. The tubes were sealed with lids to avoid drying. The

soils were incubated for 72 h at 22 °C and then bacterial growth was estimated by the Leu incorporation technique (see 2.2.).

2.4. Bacterial community growth response to pH and tolerance to NaCl

The response of the bacterial community to pH was determined according to [6]. Briefly, a soil suspension was prepared (see 2.2.) and aliquots (1.35 ml) of this suspension were transferred into 2 ml micro-centrifugation tubes. Then 0.15 ml of different pH buffers, or deionized water as a control, were added. Buffers with pH values between 4.0 and 9.0 were used. Three types of buffers were used to cover a large range of pH: citrate–phosphate (pH: 4–7; citrate 10.3–3.2 mM), phosphate buffer (pH: 6–8; 66.6 mM) and borate–HCl buffer (pH: 9; 2.1 mM). Bacterial growth was then determined by the Leu incorporation technique (see 2.2.). Leu incorporation was standardized to one in the sample with deionized water (having pH of the soil). Then two models were applied. We used a second degree equation as a simple symmetrical, unimodal model [6]. The nonsymmetrical, unimodal cardinal pH model (CPM) for pure culture bacterial growth at different pH was also used [27]. The models were fitted by nonlinear regression using Kaleidagraph 4.0 (Synergy Software).

Bacterial community tolerance to NaCl was estimated after exposing the bacterial community to different concentrations of NaCl according to [17], as modified by Ref. [28]. Briefly, a soil suspension was prepared (see 2.2.) and aliquots (1.35 ml) of this suspension were transferred to 2 ml micro-centrifugation tubes. Then 0.15 ml of different concentrations of NaCl, or deionized water as a control, was added to the bacterial suspension (final concentrations 1.5–800 mM NaCl). Bacterial growth was then determined by the Leu incorporation technique (see 2.2.). Leu incorporation was standardized to one in the control with deionized water. A logistic equation [28] was then fitted to the data and IC_{50}-values (inhibition concentration of NaCl giving 50% of Leu incorporation in the control) were calculated.

2.5. Effect of substrate addition

Due to lack of soil material, soils No. 3, 7, 10 and 11, all having high pH_w (>8), were combined in order to study if fungal growth could be induced by substrate addition in these high pH soils. Soluble starch (Merck), straw (milled, using the fraction <250 μm) and alfalfa (also milled using the fraction <250 μm) were added into soil (10 mg g^{-1} soil) in duplicate together with a no amendment control. The eight jars containing 30 g of soil were then incubated at 22 °C and the soils were sampled after 1, 2, 4, 7, 14 and 28 days. Bacterial growth, fungal growth and biomass, and respiration were measured (see 2.2.).

2.6. Statistics

ANOVA were used to analyse data of nutrient and substrate addition. Data were log transformed to stabilize the variance. Tukeys post-hoc test ($p < 0.05$) was used to differentiate between treatments.

3. Results

3.1. Soil chemistry

Soil pH_w ranged between 7.4 and 8.8 and pH_{KCl} between 7.0 and 7.9 (Table 1). The highest value was observed in soil 8, and the lowest was in soil 12. $EC_{1:5}$ values were fairly low (9–29 mS m^{-1}) in most soils, but high (89, 154 and 229 mS m^{-1}) in soils 12, 5 and 6.

Table 1
Chemical data and optimum pH (pH_{opt}) for bacterial growth of the 12 soils from Pravaranagar (India). Optimum pH for bacterial growth calculated by 2nd degree polynomial and CPM model (see Fig. 5).

Soil no.	Organic matter (%)	pH_W	pH_{KCl}	$EC_{(1:5)}$ (mS m^{-1})	pH_{opt} (CPM)	pH_{opt} (2nd degree)
1	12.8	7.5	7.4	29	7.5	7.5
2	10.9	7.9	7.5	16	6.9	7.0
3	10.8	8.6	7.4	13	7.2	7.2
4	3.7	8.0	7.3	9	7.8	7.7
5	5.9	7.6	7.0	154	7.6	7.3
6	8.9	8.7	7.9	229	7.5	7.5
7	5.4	8.1	7.4	14	7.7	7.4
8	10.6	8.8	7.5	22	8.0	7.8
9	11.1	7.6	7.2	11	7.4	7.3
10	8.4	8.3	7.4	11	7.7	7.6
11	7.6	8.4	7.3	12	7.6	7.4
12	8.3	7.4	7.3	89	7.5	7.3

Organic matter content varied between 3.7 and 12.8%, with highest values in soil 1 and lowest in soil 4 (Table 1).

3.2. Microbial biomass and activity

TotPLFA in the 12 soils had a mean of 1.35 μmol g^{-1} soil organic C, with a low fungal/bacterial PLFA index of 0.11 (ranging between 0.05 and 0.18). Relative bacterial growth varied between 960 and 12600 pmol Leu h^{-1} g^{-1} soil C in extracted bacteria, while fungal growth varied between 96 and 769 pmol Ac incorporated into ergosterol h^{-1} g^{-1} soil C (mean 280). This resulted in a low fungal/bacterial growth ratio index, ranging from 0.035 to 0.315, with a mean of 0.124.

3.3. Community composition (PLFA)

There was a good reproducibility between replicate soil samples. The first principal component (PC1, explaining 26.0% of the variation) partly reflected salinity ($EC_{1:5}$), with two of the saline soils, 6 and 12, having the most negative values for PC1 (Fig. 1A). There was also a significant correlation between PC1 and log $EC_{1:5}$ ($r = 0.58$, $p < 0.05$). Saline soils, especially soil 6, were high in fungi, suggested by high relative values of the fungal PLFAs 18:2ω6,9 and 18:1ω9 (Fig. 1B). PC2, explaining 18.8% of the variation, was positively correlated with pH_W ($r = 0.69$, $p < 0.05$).

3.4. Effect of substrate addition

The respiration rate following alfalfa application increased around 100 times compared to the control after 2 days, after which it decreased rapidly (Fig. 2A). It was still 2 times higher than the control after 28 days. The respiration rate after straw addition reached a maximum about 50 times compared to the control after 2 days, eventually converging with the control value after 28 days. Starch addition resulted in 10–15 time higher respiration rate than in the control during the first 14 days and then decreased to 4 times the control after 28 days. The cumulative respiration was 35, 19 and 11 times higher following alfalfa, straw and starch addition compared with the control ($p < 0.001$ in all cases, Fig. 3).

Alfalfa addition resulted in more than 10 times higher bacterial growth rate than the control during the first days, while an increase of around 3 times was found after straw and starch addition (Fig. 2B). Maximum growth rate was reached later for straw then for alfalfa and starch addition. Cumulative bacterial growth was about 10 times higher than that of the control sample after alfalfa addition (Fig. 3), with straw addition increasing bacterial growth 3

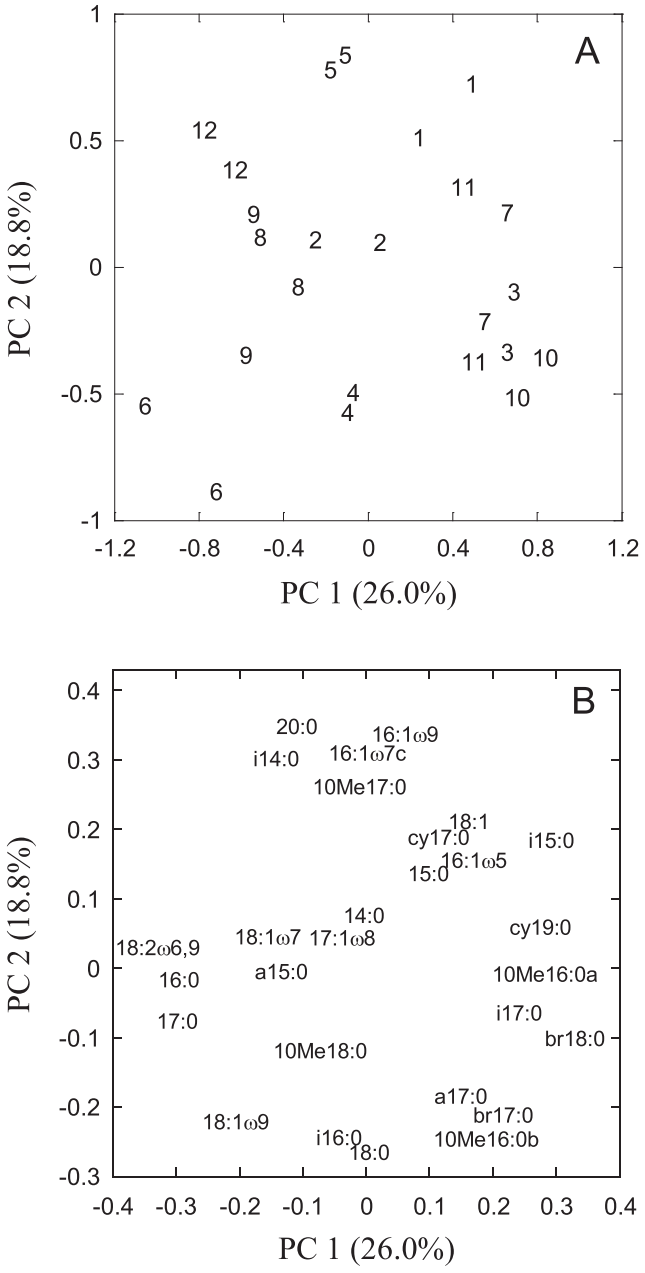

Fig. 1. Principal component analysis of mol% of the phospholipid fatty acid (PLFA) pattern of the 12 soils from Pravaranagar (India). A) Scores of replicate soil samples (numbers indicate soils in Table 1), B) loadings of the individual PLFAs.

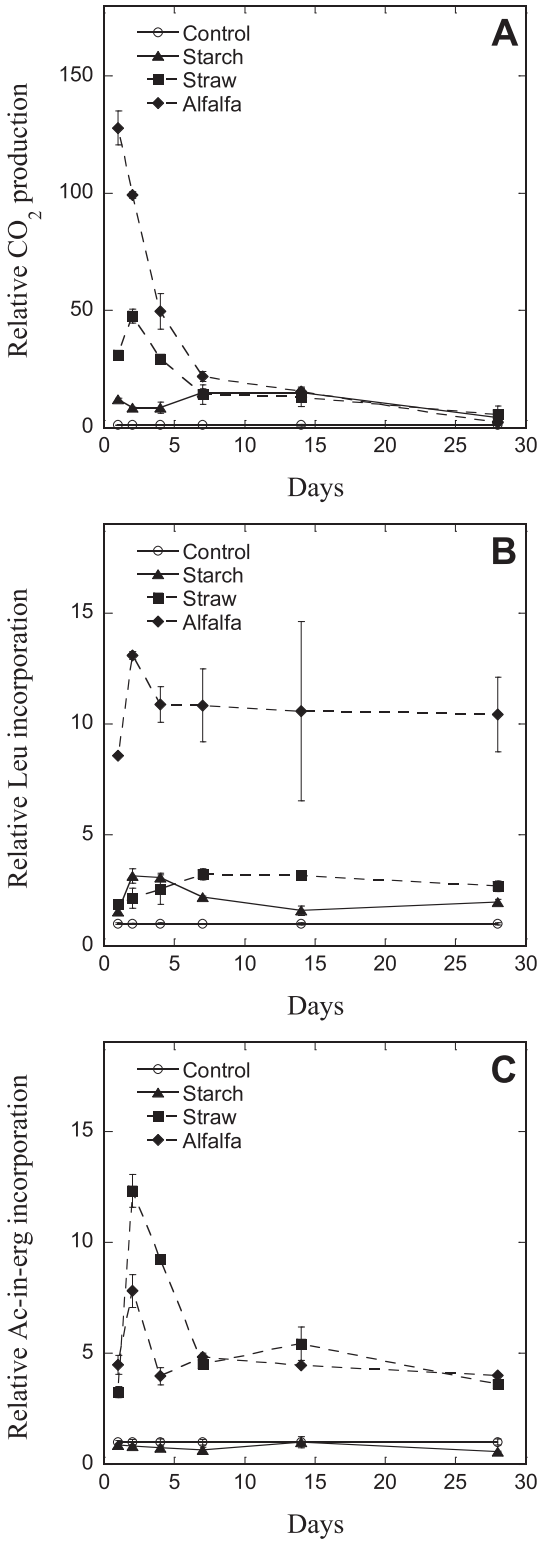

Fig. 2. The effect of substrate amendments (control = no addition, starch, alfalfa and straw amendment) on A) relative respiration rate, B) relative bacterial growth as leucine (Leu) incorporation and C) relative fungal growth as acetate in ergosterol (Ac-in-erg) incorporation. Data were standardized to that in the control with no addition.

and starch addition 2 times that of the control (in all cases $p < 0.001$).

Straw addition increased fungal growth 12 times at day 2, decreasing to about 5 times at day 28 compared to the control (Fig. 2C). Alfalfa addition increased fungal growth around 5 times during the entire experiment. Starch addition did not affect fungal growth. Cumulative fungal growth was 5 times higher than the control following straw and alfalfa addition ($p < 0.001$ for both, Fig. 3).

Fungal biomass (ergosterol content) increased by all three substrates (Fig. 3). After 28 days, ergosterol content was around 4 times the control for starch and around 5 to 6 times the control for straw and alfalfa addition ($p < 0.001$ for all). Fungal biomass started to increase immediately following straw and alfalfa addition, reaching maximum values after 7 days, while after starch addition fungal biomass only started to increase after around one week, having highest values at the end of the incubation period (data not shown).

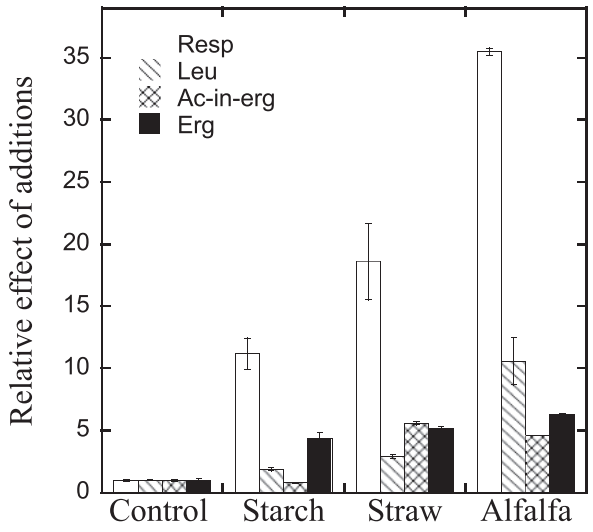

Fig. 3. The effect of substrate amendments (control = no addition, starch, alfalfa and straw amendment) on cumulative (28 days) respiration rate, cumulative bacterial growth as leucine (Leu) incorporation, cumulative fungal growth as acetate in ergosterol (Ac-in-erg) incorporation and relative fungal biomass as ergosterol (measured after 28 days). Data were standardized to that in the control with no addition.

3.5. Limiting nutrients for bacterial growth

P addition had no effect on bacterial growth as compared to the similar treatment without P addition in any of the soils. The mean P/No addition ratios for the 10 soils tested were 1.04 ± 0.03, for the NP/P ratio 0.95 ± 0.04 and for the CP/C ratio 0.95 ± 0.04. Thus, the ANOVA was made using the P treatments as replicates, and only having a full factorial C and N treatment design (Fig. 4).

All soils were primarily limited by C, while the addition of only N had no effect (the mean N/No addition ratio over all soils was 1.00 ± 0.05). Soil 1, 5, and 12 was only limited by C ($p < 0.001$ for the C effect in all cases, with no significant interaction). For the other soils a significant C × N interaction showed that adding N together with C resulted in additional bacterial growth, indicating that N was the secondary limiting nutrient (Fig. 4).

3.6. Bacterial community pH tolerance

Bacterial growth was strongly influenced by pH (Fig. 5), being close to zero at low pH values (pH 4), and having a maximum value around pH 7 to 8 in all soils. The data for bacterial growth were fitted both to a 2nd degree polynomial function (all $R^2 \geq 0.95$, $p < 0.001$) and the cardinal pH model (CPM; all $R^2 \geq 0.98$, $p < 0.001$) to calculate optimum pH (pH_{opt}) for the bacterial growth (Table 1, fitted lines to the CPM model in Fig. 5). The optimum pH for bacterial growth varied between 6.9 and 8.0 for the CPM model and between 7.0 and 7.8 for the 2nd degree polynomial function. This is similar to the soil pH measure with KCl, but slightly lower than that measured in water (Table 1). Mean value for all soils was 8.1 for pH_w and 7.4 for pH_{KCl}, while mean pH_{opt} for bacterial growth, calculated using the CPM model was 7.5 and calculated using a 2nd degree polynomial 7.4.

3.7. Bacterial community tolerance to NaCl

In all 12 soils NaCl inhibited bacterial growth at high concentrations, resulting in clear dose–response effects (Fig. 6). In case of soils 1–4 and 8–11, IC_{50} values (inhibition concentration giving 50% of growth without any salt addition) for salt tolerance were 1.8–1.9 log mM NaCl (Fig. 6A), while soil 5, 6 and 12 had the highest IC_{50} values, 3.5, 1.9 and 2.2 log mM NaCl (Fig. 6B). A significant positive linear regression was found between electrical conductivity and IC_{50} values ($r = 0.68$, $p < 0.05$) (Fig. 6C), indicating higher salt tolerance of the bacterial community in soils with high salt concentration.

4. Discussion

4.1. Microbial biomass and activity

Microbial biomass-C usually ranges between 1 and 2.5% of the soil organic C [29]. TotPLFA indicated a microbial biomass amounting to around 0.4% of soil organic C using a conversion factor of 1 mg biomass-C = 340 nmol tot PLFA [30] and around 1.1% using 1 mg biomass-C = 130 nmol tot PLFA [31]. There was no indication of a negative effect in the three high salinity soils (5, 6 and 12).

Since bacterial and fungal growth is measured using different units, one cannot directly compare these growth rates. However, the ratio fungal/bacterial growth can be used as a relative index to compare with other studies. Bacterial growth was fairly high and fungal growth fairly low compared to studies in other soils [7], making the fungal/bacterial growth ratio very low, around 0.1. This is similar to the ratio found earlier for soils with pH around 7 and above [7,8,32], indicating that the high pH in the studied soils was the reason for the relative dominance of bacterial growth over fungi.

4.2. Community composition (PLFA)

There was a tendency for relatively higher fungal biomass, estimated using the fungal indicator PLFA 18:2ω6,9, in some of the high saline soils, especially soil 6 (Fig. 1B). This soil also had the highest fungal growth rate, estimated with the Ac-in-erg method. This suggests that fungi would be more important in saline soils. Fungi as a group are usually considered to be more adapted to grow at lower soil water potentials than bacteria [33]. However, when comparing the effect of osmotic and matric potentials, it was found that although fungal appeared to be favoured by decreasing soil water content, they appeared less tolerant than bacteria to decreasing osmotic potential [9]. This is opposite to the present results, indicating that more saline soils have to be studied in order to establish how salinity affects the balance of fungi and bacteria in soil.

The most important environmental factor determining the PLFA composition of the studied soils was, however, the high pH. This was not directly evident when comparing the 12 different soils (Fig. 1A), since they had a rather narrow pH. However, using data from a broad pH gradient (from an agricultural soils in England; [34]) in a PCA plot together with soils from the present study, the PLFA pattern of the Indian soil was similar to the high pH soils from England (pH effect along PC1; Fig. 7). The Indian soils also were high in several unsaturated PLFAs, like 18:ω7, and relatively low in e.g. cy19:0, a pattern that earlier has been suggested to be indicative of high pH conditions in soil [34].

4.3. Effect of substrate addition

It has repeatedly been shown that high pH is relatively more conducive for bacterial then for fungal growth [7,8,15]. This was also found in the present study. In order to study if fungal growth could be induced even in the high pH soils studied here, different substrates of natural origin were added. Both straw and alfalfa addition increased fungal growth, showing that when substrate limitation was alleviated (Figs. 2 and 3), fungi could grow well in

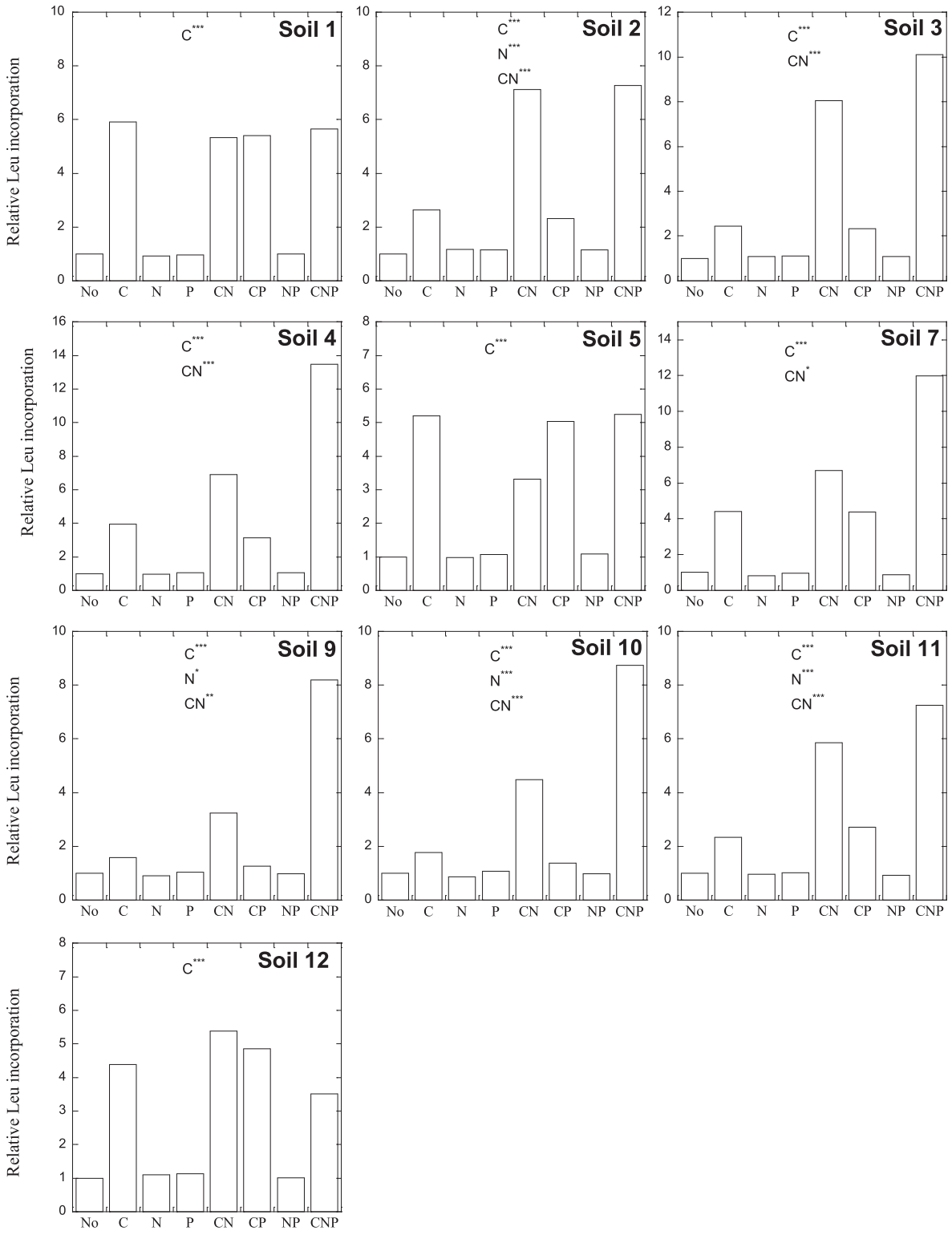

Fig. 4. Effect of adding nutrients (C as glucose-C, N as NH_4NO_3, P as K_2HPO_4) to estimate limiting factors on bacterial growth estimated as leucine incorporation in 10 soils from Pravaranagar (India). Nutrients were added in a full factorial design and bacterial growth measured after 72 h. All data were standardized to that in the control with no nutrients added.

these high pH soils. Previous studies have shown that straw addition would favour fungal growth more than alfalfa addition, and vice versa for bacteria [20]. This was also found here for bacteria (more than 3 times higher with alfalfa than straw, Fig. 3B), while both substrates were favoured by fungi (Fig. 3C and D).

4.4. Limiting nutrients

As expected, bacterial growth was C limited in all soils tested (Fig. 4), since due to frequent addition of organic and inorganic fertilizers to these soils, they were expected to be high in available

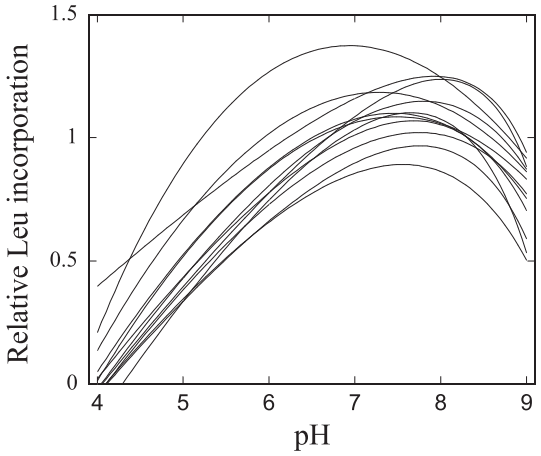

Fig. 5. Bacterial community response to pH. Growth of the bacterial community extracted from the 12 soils from Pravaranagar (India) was estimated after changing the solution pH of extracted bacteria by adding buffers. The data were standardized to one for the control with no buffer added (the natural pH). Lines were fitted using the CPM model (see Materials and Methods). Data points were omitted for clarity.

nutrients, including N and P [3]. Bacterial growth in soil has also most commonly being shown to be limited by lack of easily available C [26].

When comparing N and P, N appeared to be the secondary limiting substance, since no effect of adding P in combination with any other nutrient was found. In three soils, however, there were no extra growth when adding N in combination with C (Fig. 4, soils 1, 5 and 12). The most likely explanation for this is not that another nutrient was the secondary limiting one, but instead that N availability was very high, and the amount of C added was too low to induce limitation of a secondary limiting substance. A similar situation was earlier found in N fertilized forest soils [35]. A further indication of this is that these 3 soils had the largest increase in bacterial growth after adding only C (>5 times). The growth increase after adding only C has earlier been suggested to indicate the availability of the secondary limiting substance [35]. Thus, the high increase in bacterial growth after adding only C is a further indication of the high nutrient status of these soils.

4.5. Bacterial community pH tolerance

Earlier studies have shown that optimum pH for bacterial growth was approximately similar to the soil pH [6,7,36]. This was also found for the soils studied here (Fig. 5). However, the optimal pH for growth was more similar to that determined with KCl then with soil pH extracted in water. Thus, compared to pH_w, the optimum pH for bacterial growth was slightly lower. This differed from earlier studies (see references above). One reason could be that this is the first time bacterial pH tolerance in soils with pH > 8 have been studied, and at high soil pH the bacterial community may be more adapted towards neutral pH. However, in water a close correlation between water pH and optimum pH for bacterial growth was found even >pH 8 (E. Kritzberg and E. Bååth, unpublished). Another explanation is the problems to achieve buffering conditions above pH 9, since the only buffer used was sodium borate buffer of pH 9, which only resulted in around 15% decrease in bacterial growth (Fig. 5), and there were thus some problems in fitting the models.

4.6. Bacterial community tolerance to NaCl

Salinity has been shown to affect soil microorganisms, often resulting in decreased CO_2-evolution, enzymatic activity, microbial biomass, bacterial growth and microbial community composition in

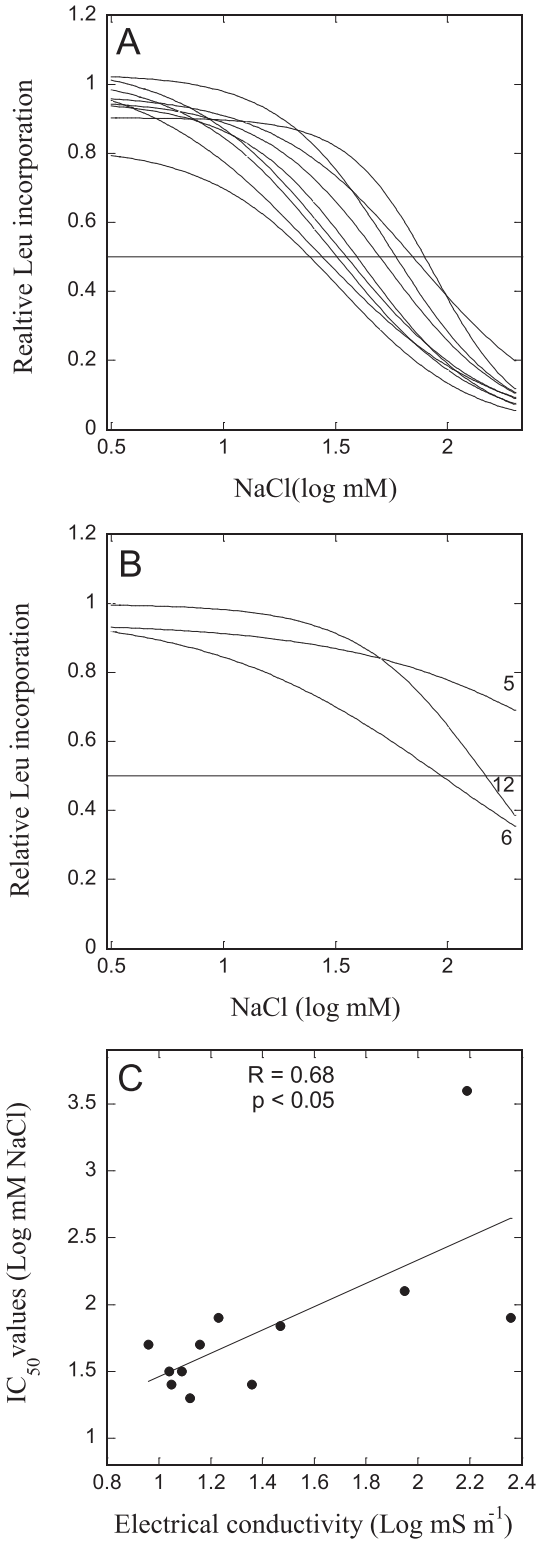

Fig. 6. Bacterial community tolerance to NaCl. Growth of the bacterial community extracted from the 12 soils from Pravaranagar (India) was estimated after changing the salt concentration. The data were standardized to one for the control with no salt added. Lines were fitted using a logistic equation. Data points were omitted for clarity. A) Soils with less tolerance to NaCl (soil no. 1–4 and 7–11). B) Soils with high tolerance to NaCl (soil no. 5, 6 and 12). C) Correlation between soil salinity ($EC_{1:5}$) and bacterial community tolerance to NaCl expressed as IC_{50} values.

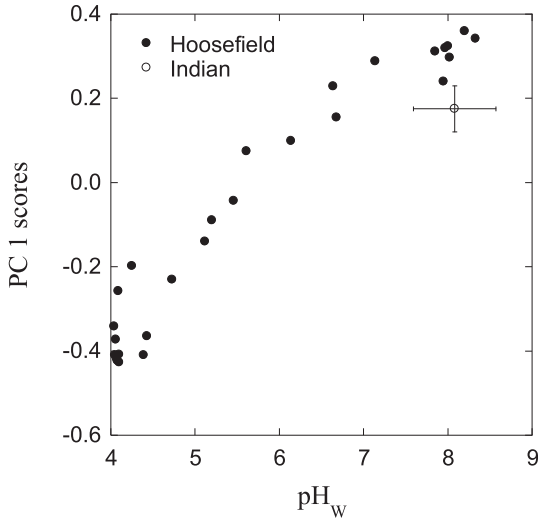

Fig. 7. Comparison of the phospholipid fatty acid (PLFA) pattern of the 12 soils from Pravaranagar (India) with the pattern of a pH gradient of English soils (Hoosefield, [26]). A PCA of the combined data were made. Mean and SE for the Indian soils are given.

soil [9–12,37,38]. Soil bacterial communities have, however, an ability to change in order to tolerate osmotic stress caused by salinity [17,38]. We partly detected an altered community composition in high salinity soils (along PC 1, Fig. 1). We also observed increasing bacterial community tolerance to NaCl in the 3 soil with highest salinity (Fig. 6B and C, soils 5, 6 and 12), indicating that the increased salinity had selected for bacterial communities more tolerant to high salt concentration, as found earlier by Ref. [17]. Rousk et al. [28] studied bacterial community tolerance to NaCl in 4 soils from an arid agroecosystem salinity gradient with the same technique as in the present study, but found no increased tolerance to NaCl. However, the most saline of their 4 soils had an $EC_{1:1}$ of around 400 mS m^{-1}, which would be around 4 times less as $EC_{1:5}$ [39] and thus similar to the lowest value of our 3 most saline soils. The difference between our studies was thus most likely that our most saline soil was >2 times more saline then their most saline soil.

5. Conclusions

We have demonstrated that both the high pH and the high salinity had affected the community composition (PLFA pattern) and the tolerance spectrum to pH and salinity, respectively. We have also shown that in these soils, high in pH and nutrients, bacteria were favoured compared to fungi. However, adding straw (and to some extent alfalfa) resulted in a significant increased fungal growth, stressing the importance of both fungi and bacteria for the functioning of these high pH soils. We also show that bacterial growth, as expected, were C limited, and where the large increase in growth after adding only C, indicated the high nutrient content in these soils. Our study emphasise the importance of using methods indicating growth of both bacteria and fungi. The growth based methods are also easy to perform, reproducible and could thus be used as a rapid way of studying not only microbial substrate and nutrient limitation in soils, but also to what extent environmental factors, like pH and salinity, have affected the microbial community.

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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.

KEYWORDS

Solvent extraction, spectrophotometric determination, o-methoxyphenyl thiourea, palladium.

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]

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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_2SO_4 5.0	0.02–0.4	2.01×10^4	Heating 10 min, Narrow Beer's range	16
2-Hydroxy-5-methylacetopheneoneisonicotinoylhydrazone	H_2SO_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-(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_2SO_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.

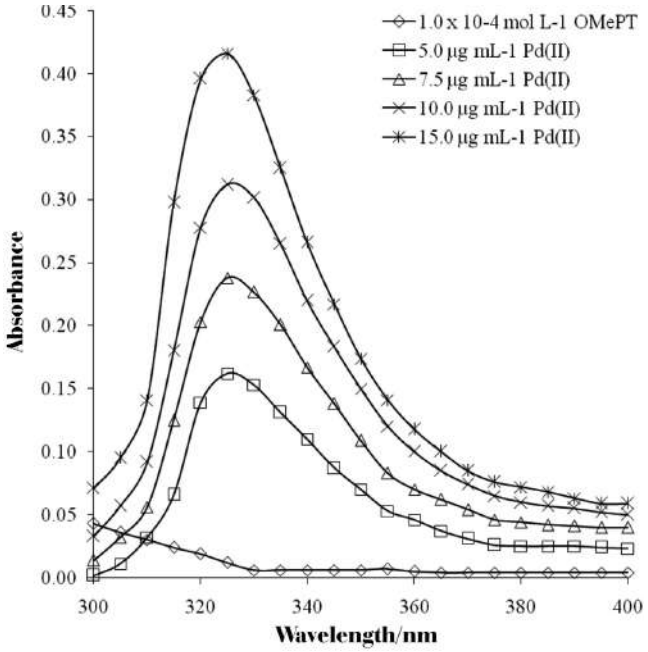

Figure 1 Absorbance spectra of Pd(II)-OMePT *vs*. OMePT reagent blank.

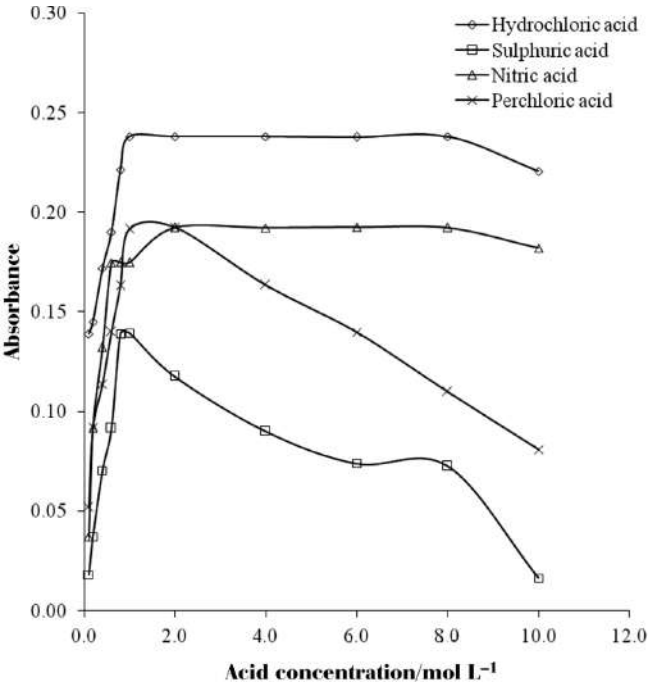

Figure 2 Effect of acid type and concentration on Pd(II)-OMePT complex formation.

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

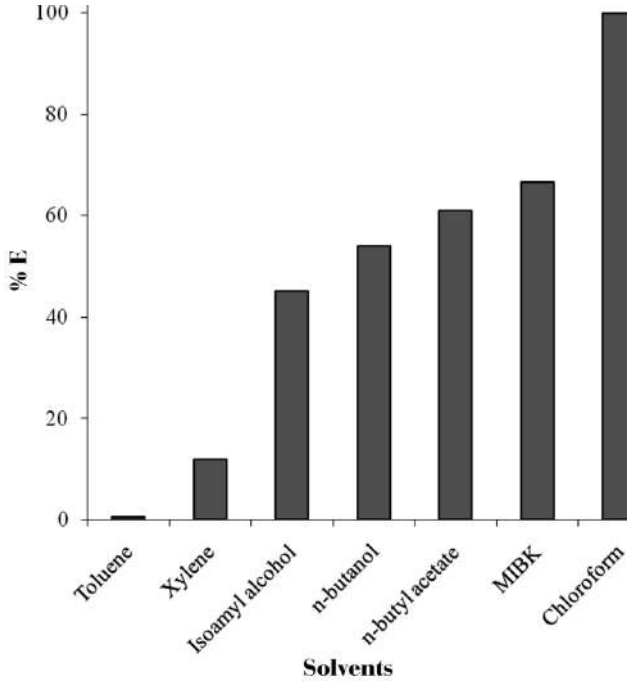

Figure 3 Effect of extraction solvent on Pd(II)-OMePT complex.

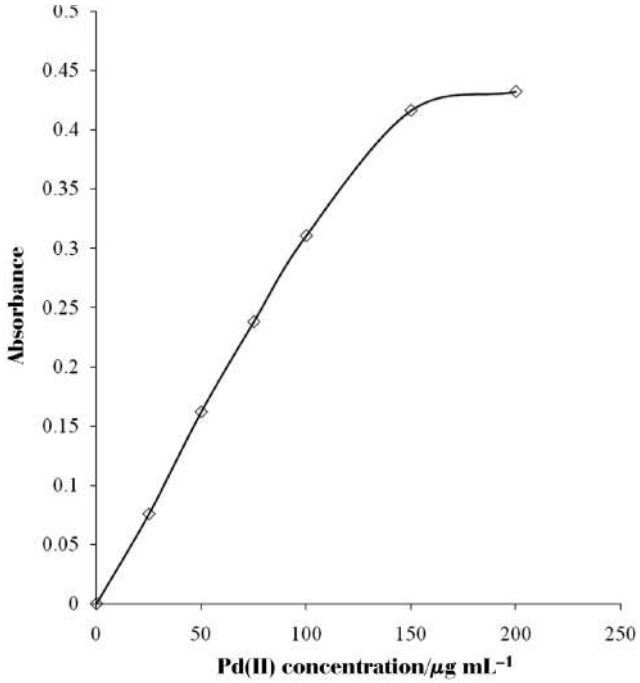

Figure 5 Applicability of Beer's law to Pd(II)-OMePT complex.

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

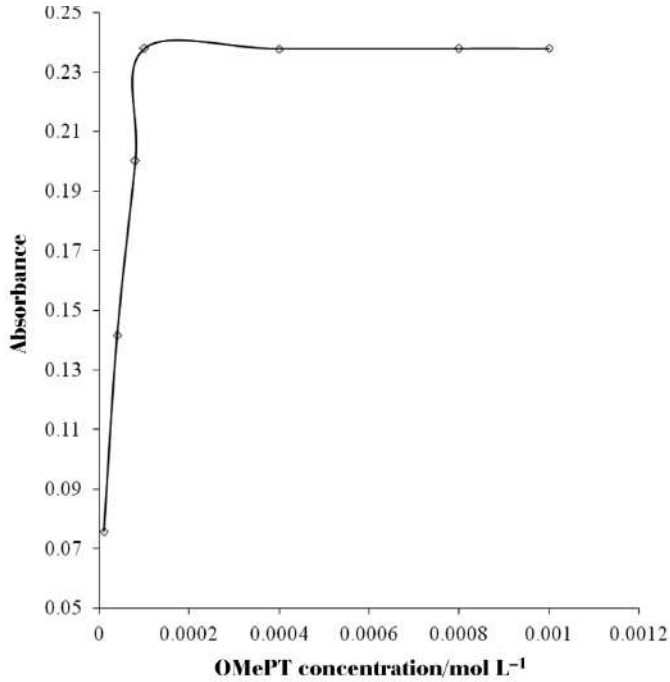

Figure 4 Effect of reagent concentration on Pd(II)-OMePT complex.

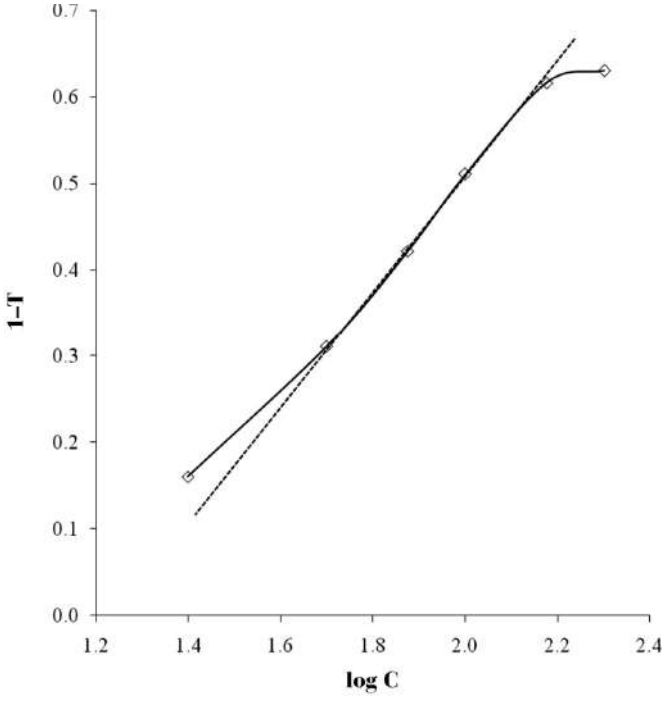

Figure 6 Ringbom's plot for Pd(II)-OMePT complex.

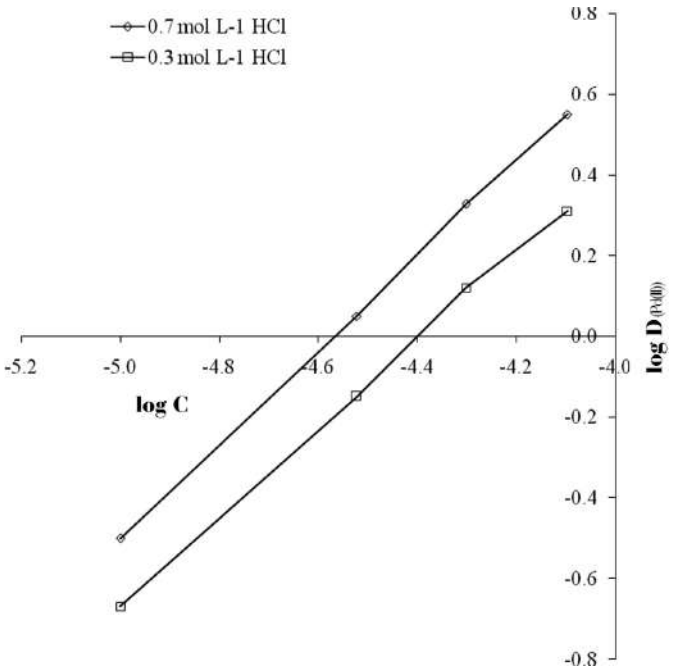

Figure 7 Plot of log $D_{Pd(II)}$ *vs.* log $C_{(OMePT)}$.

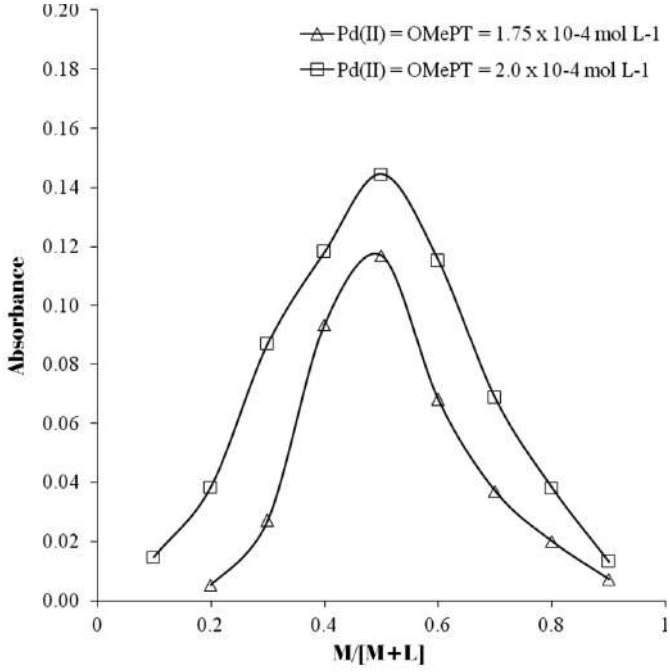

Figure 9 Job's continuous variation method for Pd(II)-OMePT complex.

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).

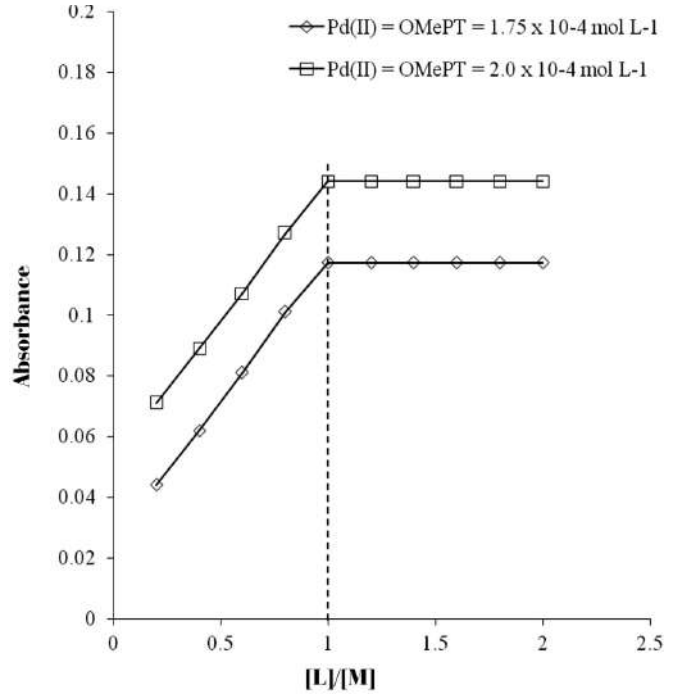

Figure 8 Mole ratio method for Pd(II)-OMPT complex.

4.1. Interference Study

Various amounts of foreign ions were added to a fixed amountof 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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Removal of hexavalent chromium from industrial effluents by natural ion exchanger

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In this study, removal of chromium (VI) from aqueous solution using *Tamarindous indicia* seeds has been investigated. The effects of *p*H, contact time, exchanger dose, have been studied at ambient temperature (25°C ± 2°C). The equilibrium process has been described by the Langmuir isotherm model with adsorption capacity for chromium (VI). The *Tamarindous indica* seeds are subjected to different modification methods (pulverization, formaldehyde and sulphuric acid treatment) and adsorption capacity of modified *Tamarindous indica* seeds for metal ion is obtained. The maximum exchange level have been attained 99% at *p*H 6.5 with exchanger dose 3.5 g and contact time 30 min. Method is applied for removal of chromium from industrial effluents.

Keywords: Chromium (VI), Natural ion exchange, Industrial effluents, Isothermal model, *Tamarindous indica*

Rapid industrialization affects the rise up in disposal of heavy metals in environment. The exceeding increase in the use of heavy metals leads to environmental as well as public health problems[1]. Toxic heavy metal ions discharge in waste water through various industrial activities as mining, refining of ores, fertilizer industries, tanneries, batteries, paper industries, pesticides, nuclear power plant and textile industries[2].

The electroplating and metal finishing plants discharge waste water contains hexavalent and trivalent chromium. Hexavalent chromium requires high cost chemicals for reduction, so was usually treated with ion exchange resin which offers greater advantages[3]. Trivalent chromium is essential in human nutrition (glucose metabolism). Most of the hexavalent compounds are toxic cause's lungs cancer. Chromium (VI) moves readily through the soil and aquatic environment which was strong oxidizing agent, being absorbed through the skin. The maximum concentration limits for chromium (VI), discharge in to ground water is 0.1 mg L^{-1} and in potable water is 0.05 mg L^{-1} (Ref 4). A number of technologies have been developed over the years to remove heavy metals from industrial waste water. The most important technology includes adsorption and coagulation[5], ion exchange[6], electro coagulation[7], adsorption8, bio sorption[9] and zeolite[10]. Ion exchange can be used to remove heavy metals from waste water using an ion exchange resin as synthetic ones derived from Dowex HCR-S (Ref 11), D-151 weak acid resin[12], amberlite 200 (Ref 13). The natural ion exchangers are Attapulgite[14], Kudzu (Pueraria Lobata Ohwi)[15], activated carbon[16], coconut husk[17], fly ash[18], coffee husk[19], fungal biomass[20], *Tamarindous indica* seeds[21], Tendu (*Diospyros melanoxylan*)[22], rise husk[23], *Lactobacillius bulgaricus*[24].

In the present study, adsorption of chromium (VI) by naturally occurring *Tamarindous indica* seeds powder is examined. The purpose of the study is to examine heavy metal removal by natural ion exchanger. The parameters that influence adsorption viz. *p*H, ion exchanger dose, temperature, contact time were investigated.

Experimental Section

Seed powder

Tamarindous indica seeds were pulverized after drying in sunlight and open air for one week. Small size pieces of dried seeds were ground and passed through the mesh size 200 unit. This powder was

treated with 39% formaldehyde and 0.1 mol L^{-1} sulphuric acid at 80°C, for 30 min. After cooling and washing with double distilled water, substrate was allowed to dry for overnight in open air. Dried powder was used for adsorption studies (Scheme 1). The properties of resin were reported in Table 1.

Sorbet

For adsorption study stock solution of chromium (1000 mg L^{-1}) was prepared by dissolving 4.8 g of chromium sulphate [Cr_2 $(SO_4)_3.6H_2O$] in double distilled water (DDW). The various concentrations were then obtained by diluting the stock solution with double distilled water.

Method for Separation of Chromium

Chromium solution [Cr_2 $(SO_4)_3.6H_2O$] having concentration 1.0 mg L^{-1} (25 mL) was transferred to a beaker. *p*H of this solution was adjusted to 6.5 ± 0.1 and was transferred to a 250 mL conical flask. In this solution 3.5 g natural adsorbent was added with successive shaking for 30 min. Solution was filtered using Whatman filter paper no. 41 and concentration of chromium remain in solution was determined using Shimadzu UV-visible spectrophotometer by standard method[25]. In this method, 0.6 mL of 7.0 mol L^{-1} hydrogen peroxide solution, 0.2 mL of 10^{-4} mol L^{-1} potassium cyanide and 5.5 mL of buffer solution (*p*H 6.5) were transferred in 25 mL standard volumetric flask. This solution was warmed at 60°C in a water bath for 10 min. The effluent from column was transferred in it after mixing the solution, absorbance were measured at 360 nm. The initial concentration C_o (mg L^{-1}) and equilibrium concentration at various time intervals C_e (mg L^{-1}) were determined and metal uptake q_e (mg L^{-1}) was calculated from the mass balance equation as:

$$q_e = (c_o - c_e)\frac{v}{m} \qquad \ldots(1)$$

where, C_o and C_e are the initial and equilibrium concentration of chromium solution (mg L^{-1}), ν is the solution volume (mL), and m is the adsorbent weight (g). The adsorption capacity was calculated using the equation 2.

$$\text{adsorption capacity} = \frac{(c_o - c_e)}{c_o} \times 100 \qquad \ldots (2)$$

The sorption equilibrium data for chromium on *Tamarindous indica* seeds powder was analyzed in terms of the Freundlich and Langmuir isotherm models. The Langmuir isotherm equation could be written as:

$$\frac{q_e}{q_m} = \frac{K_L C_e}{1 + K_L C_e} \qquad \ldots (3)$$

Where

q_e = the equilibrium concentration on adsorbent (mg g^{-1})

C_e = equilibrium concentration in solution (mg L^{-1})

q_m = maximum adsorption capacity (mg L^{-1})

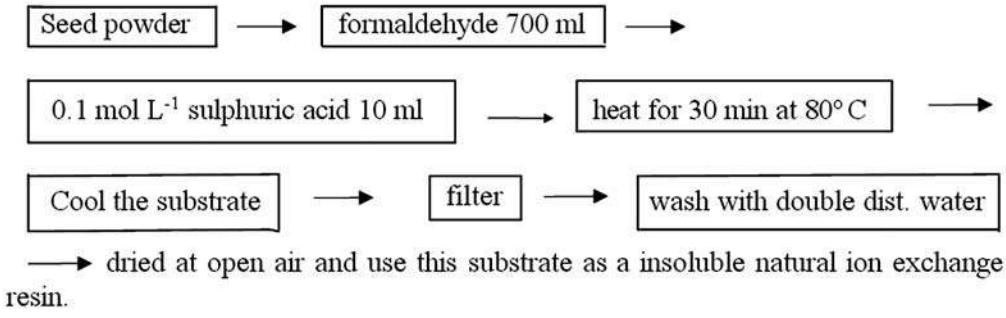
K_L = adsorption equilibrium constant (mg L^{-1})

This method is based on the assumption that the forces of interaction between adsorbed molecules are negligible and once a molecule occupies a site no further sorption take place.

Also, the logarithmic form of Freundlich equation may be written as:

Table 1—Properties of ion exchange resin

Parameters	Value
Physical form	Spherical
Bulk density	0.15 gm./cm^3
Ash content	10.4%
Moisture content	8.7%
Matter soluble in water	8.4%
Matter soluble in acid	18%
Water holding capacity	80.32%



Scheme 1

$$q_e = K_F C_e^{1/n} \quad \ldots(4)$$

where,

q_e = the equilibrium concentration of adsorbent (mg g^{-1})

C_e = equilibrium concentration in solution (mg L^{-1})

K_F = adsorption capacity

n = reaction energy

The Freundlich equation can be described by assuming a heterogeneous surface with adsorption on each class of sites. Although this expression is empirical, *1/n* reflects the curvature in the isotherm and may represent the energy distribution of adsorption sites.

The liberalized form of Freundlich sorption isotherm is:

$$\ln q_e = \ln K_F + \frac{1}{n} \ln C_e \quad \ldots(5)$$

By plotting ln q_e versus *ln* C_e K_F and n can be determined, if a straight line is obtained.

To study the effect of important parameters like contact time, resin amount, *p*H, initial metal concentration and temperature on the removal of Cr (VI) by natural ion exchanger, experiments were conducted at room temperature except those in which the effect of temperature. The parameters chosen in the experiments were reported in Table 2.

Results and Discussion

FTIR Analysis

The FTIR spectra of raw seeds powder, formaldehyde treated resin and Cr (VI) adsorbed resin have been studied. The fact that broad peak in between 3462 and 3281 cm^{-1} indicates presence of phenolic –OH group in both resin. IR absorption at 2924 cm^{-1} also indicates presence of =C–H group on the benzene ring. The 1600-1500 cm^{-1} absorption peak clearly indicates the presence of aromatic double bonds in both resin. The IR bonds in the region of 1149-1066 cm^{-1} indicate C–O bond in raw resin. One characteristic peak at 1739-1743 cm^{-1} indicates presence of ester group in both resins. Some peaks in the region of 1670-1612 cm^{-1} also are of due to olefinic bonds in raw and treated resin. The IR frequency at 2924 cm^{-1} is due to stretching vibration of $–CH_2–$ group in alkane. IR absorption at 2022 cm^{-1} in treated resin also suggest presence of $–CH_2–$ group in between two phenolic rings which is lower frequency than that of raw seeds powder. Hence due to adsorption of Cr (VI) ion color of product change because of d–d transition[27].

Table 2—Experimental parameter

Parameters	Studied ratio
Initial metal concentration (mg/L)	25, 50, 100, 250 and 500
*p*H	1.0, 1.5, 2.0, 2.5, 3.0, 3.5, 4.0, 4.5, 5.0, 5.5, 6.0 and 6.5
Solution temperature (K)	273, 298, 323 and 348

SEM and EDX Analysis

The morphological analysis of phenol formaldehyde resin was performed by SEM as shown in Figs 1(a)-1(c). Many small pores and particles >5µm diameter are observed on the surface of resin. Pores are does not observed in Fig. 1(c), clearly indicates that biosorption of chromium on phenol formaldehyde resin. EDX spectrum from Fig. 2(c), also showed a peak at 0.5 KeV, which confirmed that Cr (VI) was adsorbed on phenol formaldehyde resin, which was absent in Figs 2(a) and 2(b). It supports

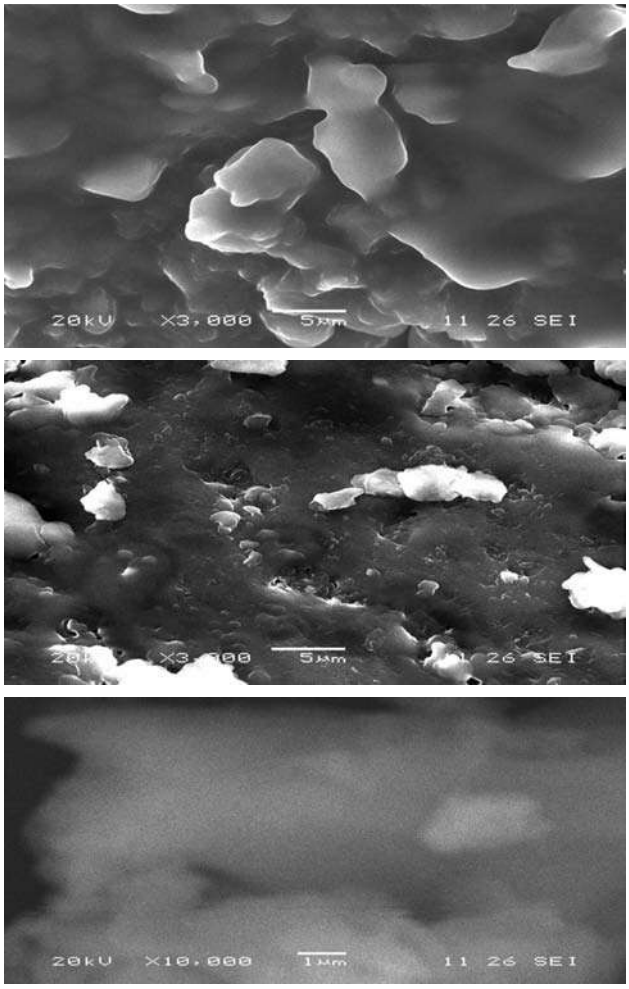


Fig. 1(a-c)—SEM Image of (a) raw seed powder; (b) phenol-formaldehyde resin and (c) phenol-formaldehyde resin after Cr (VI) adsorption

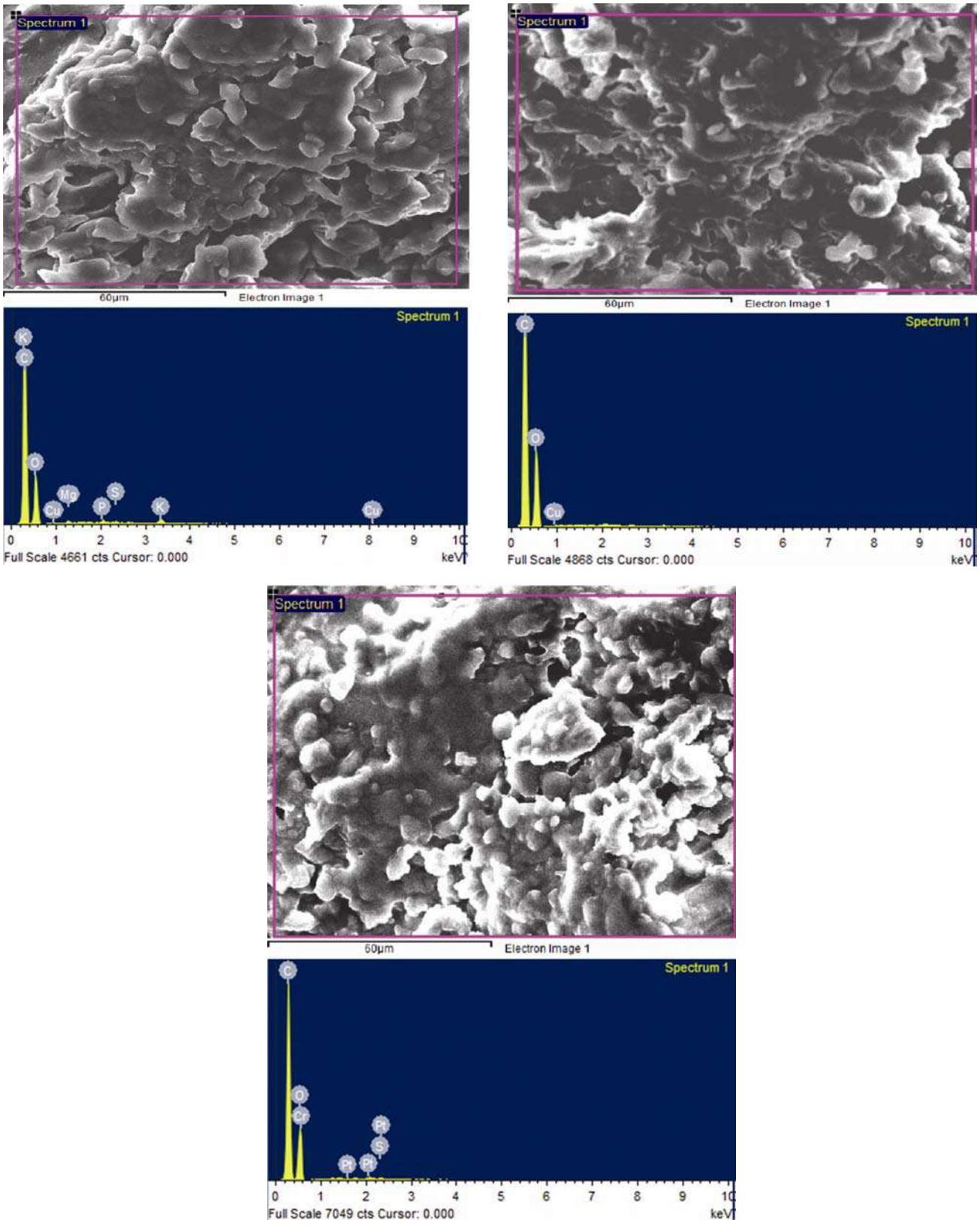


Fig. 2(a-c)—EDX spectrum of (a) raw seed powder; (b) phenol-formaldehyde resin and (c) chromium adsorbed resin

that the reaction of metal ion and phenolic –OH group on phenol formaldehyde resin surface may be partly ion exchange or complexation[28].

Effect of *p*H on ion exchange process

In order to establish the effect of *p*H on the ion exchange of chromium (VI) ion on natural resin, the batch equilibrium studies at different *p*H values were carried out in the range of 1.0-7.0 for a constant ion exchanger of 3.5 g L^{-1} and initial metal concentration of 25 mg/L at 298 K. The high values of *p*H were not studied because of precipitation of metal ion take place. Figure 3 shows the change in metal up take by natural ion exchange resin at different *p*H levels. It can be seen from Fig. 3, the *p*H of the aqueous solution is important control parameter in the ion exchange process[29]. The percentage removal of metal increased with *p*H 1.0-7.0 with maximum binding at *p*H 6.5. At this *p*H 99% removal of chromium was observed.

Effect of initial metal concentration on ion exchange process

The chromium (VI) metal solution (25 mL) of different concentrations ranging from 25 to 250 mg L^{-1} with 3.5 g of ion exchanger was stirred with ambient temperature (298 K) for a contact period of 30 min. The result obtained is shown in Fig. 4. It was also realized that the capacity of metal removed by natural ion exchanger at the equilibrium increased with the initial concentration of metal but the percent removal decreased with the increase in initial metal concentration. Apparently, the initial heavy metal ion concentration played an important role in affecting the capacity of metal exchange on natural resin. The higher the heavy metal concentration, stronger the driving forces of the concentration gradient and therefore the higher the adsorption capacity[30].

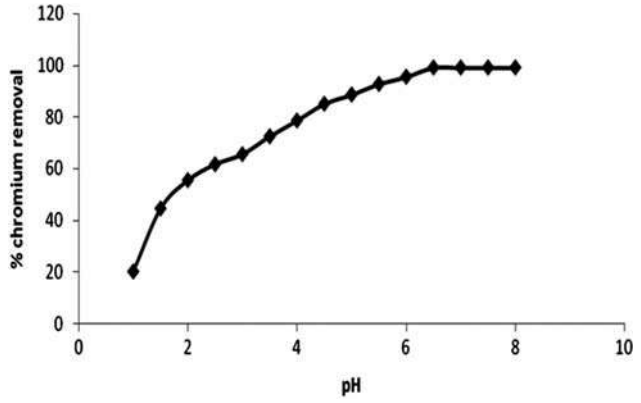


Fig. 3—Effect of *p*H on ion exchange process (293 K solution temperature, 1mg L^{-1} initial metal concentration and 3.5g resin dose)

Effect of solution temperature on ion exchange process

The effect of solution temperature on to chromium (VI) metal removal is shown in Fig. 5. The removal of metal ion increased slightly increasing temperature from 273 K to 348 K. It is seen from Fig. 5, when natural ion exchanger used for chromium (VI) removal with an increase in temperature from 273 K to 348 K, the ion exchange capacity increased from 52.36 to 99% with ini tial metal concentration. This indicated that the exchange reaction was endothermic and ion exchange mechanism favours high temperature. An increase the removal with the rise in temperature may be explained by active site on natural ion exchanger being more active at high temperature[31].

Effect of resin dose on ion exchange process

The percentage efficiency of chromium (VI) ion at different doses of ion exchanger was strongly acidic and shown in Fig. 6. The degree (%) of removal efficiency increased as the resin dose was increased. It might be concluded that by increasing the resin dose, the removal efficiency of heavy metal ion increased, while ion exchange density decreased with increase in resin dose. The decrease in ion exchange density may be due to the fact that some adsorption

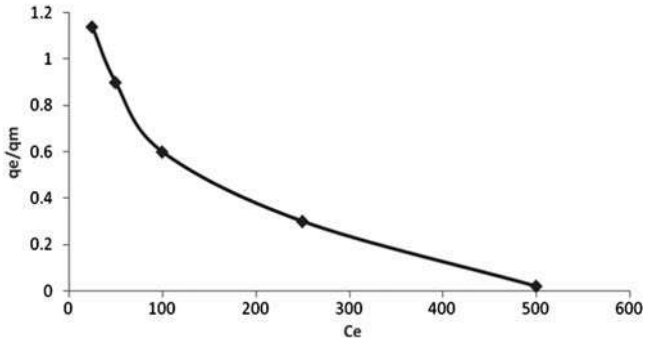


Fig. 4—Effect of initial metal concentration on ion exchange process (*p*H 6.5, 293 K solution temperature and 3.5 g resin dose)

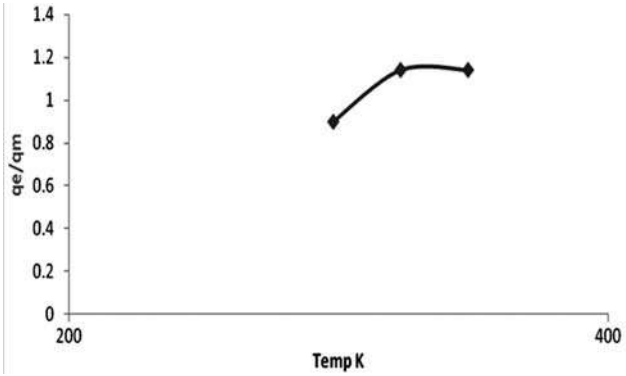


Fig. 5—Effect of solution temperature on ion exchange process (*p*H 6.5, 1 mg L^{-1} initial metal concentration, 3.5g resin dose)

site may remain unsaturated during the adsorption process, where as the number of sites available for adsorption increased by increasing the resin dose and that results in the increase of removal efficiency[32]. When increased resin dosage from 0.5 to 3.5 g, removal efficiency increased from 80.55 to 99 % for chromium (VI).

Effect of contact time on ion exchange process

The removal efficiency increased with increase in contact time. Other parameter such as adsorbent dose, *p*H and temperature of solution was kept optimum. It can be seen that chromium removal efficiency increased from 60.00 to 99%, when contact time increased from 10 to 30 min, the result obtained are shown in Fig. 7. Optimum contact time for chromium (VI) removal was found to be 30 min. Hence the ion exchanger requires shorter contact time. Greater availability of various functional groups on the surface of resin, which are required for interaction with anions and cations, significantly improved the binding capacity and the process proceeded rapidly. The result is important as equilibrium time is one of the important parameters for an economical wastewater treatment[33].

Sorption isotherm

The sorption isotherm for the removal of Cr from effluent on ion exchanger are found to be regular, positive and concave with respect to the concentration axis. The results show efficiency of ion exchanger for chromium removal from effluent. The sorption studies are carried out at 323 K to determine the sorption isotherms.

The isotherm parameters were evaluated using Langmuir and Freundlich isotherm models. The straight line obtained for two sorption isotherms indicated that the sorption of chromium (VI) fit to investigate isotherm models. The corresponding Langmuir and Freundlich parameters along with correlation coefficient are given in Table 4. The slope of the Freundlich isotherm was more linear than Langmuir isotherm, hence sorption isotherm fit better with Freundlich model.

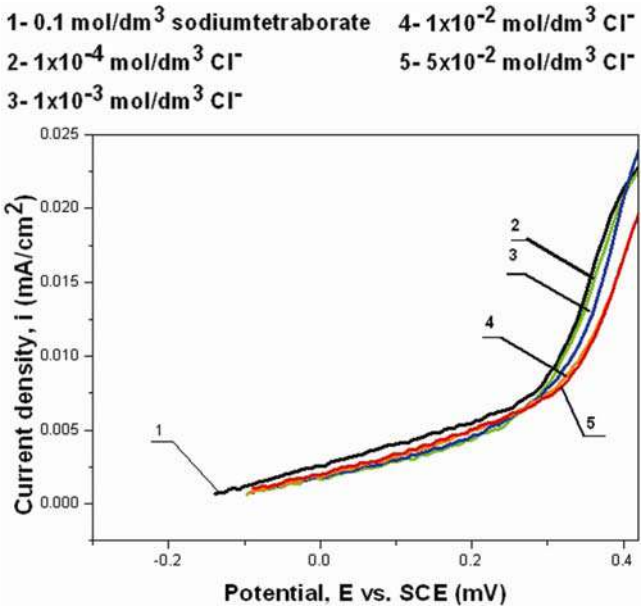


Fig. 6—Effect of adsorbent dose on ion exchange process (*p*H 6.5, 293 k solution temperature, 1 mg L^{-1} initial metal concentration)

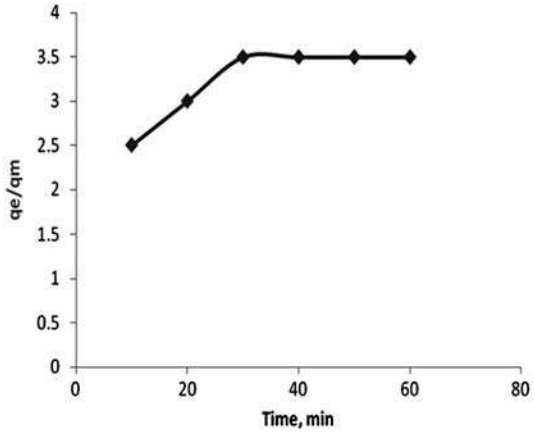


Fig. 7—Effect of contact time on ion exchange process (*p*H 6.5, 293 K solution temperature, 1 mg L^{-1} initial metal concentration, 3.5 g resin dose)

Table 3—Concentration of Cr (VI) in industrial effluent before and after treatment of ion exchange resin of 3.5 gm at *p*H 6.5, time 30 min and temperature 25°C

Industrial Sample	Effluent (mL)	Concentration before treatment (mg L^{-1})	Concentration after treatment (mg L^{-1})	%Removal
1	25	5.0	0.03	99.40
2	25	4.5	0.02	99.55
3	25	4.5	0.02	99.55
4	25	2.2	0.01	99.54
5	25	3.5	0.01	99.70

Table 4—Isothermal parameters of Cr (VI) adsorption

Langmuir Isotherm			Freundlich Isotherm		
q_m (mg L^{-1})	K_L (mg L^{-1})	R^2	1/n	K_F m mg g^{-1}	R^2
3.94	0.018	0.85	1	0.5	0.99

Application

Removal of chromium (VI) from industrial effluents

In order to assess the practical performance of natural ion exchanger for removal of hexavalent chromium from industrial effluent, an experiment was carried out after adjusting the *p*H 6.5 at which the maximum adsorption of hexavalent chromium can be achieved. Developed method was applied for removal of hexavalent chromium, from 5 different Pharmaceutical industrial effluents. The concentration of hexavalent chromium from these effluents was determined before treatment and after treatment with natural ion exchanger. It was observed that more than 99% of hexavalent chromium was removed from effluents. The results are reported in Table 3.

Conclusion

The purpose of this work is to study the possibility of removing hexavalent chromium from effluent through sorption by modified natural ion exchanger. The data reported here, show that *Tamarindous indica* seed powder is an effective sorbent for removing Cr from effluent. The sorption capacity of natural adsorbent is higher than the reported value of other adsorbents. Equilibrium studies are conducted for the adsorption of chromium from effluent by surface modified natural ion exchanger. The equilibrium data have been analyzed using Langmuir and Freundlich isotherm models, and results show that the sorption of hexavalent chromium occur at *p*H 6.5, which fits better to Freundlich isotherm model. It could be planned to use natural ion exchanger to economic polluted water treatment.

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Kinetic study for formation of thiazole by cyclisation

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The kinetic study of 3-chloroacetyl acetone with various thioureas has been carried out in ethanol. In this study thioureas used are m-methyl phenylthiourea, m-methoxy phenylthiourea, m-ethoxy phenylthiourea and m-chlorophenyl thiourea. The kinetic study reports second order rate constants for these reactions. The rate of reaction is first order with respect to thioureas and first order with respect to 3-chloroacetyl acetone. The effect of substituents on the rate of reaction is also studied. Thermodynamic parameters are used to explain the nature of reactions. The proposed reaction mechanism and details of Kinetics for various reactions were studied.

Keywords: Kinetics, Thiazole, Cyclisation

INTRODUCTION

Sulphur and nitrogen containing organic compounds are gaining importance in synthetic and pharmaceutical fields. Thiourea and their derivatives are well known intermediates in the synthesis of clinically important heterocycles like thiazoles, 4-thiozolidinones and benzothiozoles. Thioureas are commercially used in photographic films, plastics and textiles. Certain thiourea derivatives are insectides, rhodenticides and pharmaceuticals. Some of the thioureas are screened for anticancer activity. Thioureas have shown antibacterial [1], antipyretic [2], hypnotic [3] and fungicidal [4] activity. Thiazoles are found in medicaments [5] like vitamin-B, sulphathiozoles, promizole, niridazole, aminotrizole and tetramisole. Kinetics and mechanism of reaction between thiourea and iodate in buffer medium has been studied [6]. The kinetic study of reaction of thiourea with formaldehyde is also reported [7]. Reaction kinetics of gold dissolution in acid thiourea solution using ferric sulphate as oxidant was investigated with rotating disk technique [8]. The kinetics of formation of chromium(III) – iminodiacetic acid complex has been studied in temperature range 35 – 55 ^{0}C spectrophotometrically. The study shows rate of reaction is first order with respect to chromium(III) and rate of increases with increase in temperature [9]. The kinetics of oxidation of thiourea and *N*-substituted thioureas and the corresponding formamidine disulfides by sodium *N*-chloro-*p*-toluenesulfonamide or chloramine-T (CAT) in the presence of $HClO_4$ has been studied at 278 K [10]. The kinetics of the reaction between vitamin C (L-ascorbic acid) and ferric chloride hexahydrate was investigated in acidic medium at pH 3 spectrophotometrically. The order of the reaction was established by applying different methods. The order of the reaction with respect to each reactant was found was first and the overall second order was recommended for the reaction [11]. Kinetic investigation in rhodium(III) catalyzed oxidation of D-Mannitol in an acidified solution of potassium bromate in the presence of $Hg(OAc)_2$ as a scavenger, have been studied in the temperature range of 300 - 450 ^{0}C [12]. Kinetic and thermodynamic study on the adsorption behavior of Rhodamine B dye on Duolite C-20 resin has been reported. The effects of various experimental factors; sorbent amount, contact time, dye concentration and temperature, were studied by using the batch technique [13].

We have reported kinetic study of reaction of chloroacetone with p-substituted phenyl thioureas [14]. We have also reported kinetics of reaction of 3-chloroacetyl acetone with p-substituted phenyl thioureas [15]. Literature survey reveals that there is no work on kinetic study of reaction of 3-

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chloroacetyl acetone with m-substituted phenyl thioureas.

EXPERIMENTAL

Apparatus

The pH of thiazole hydrochloride solution was measured by digital pH meter. (EQUIPTRONICS, EQ-614A)

Reagents

All the reagents used were of analytical reagent grade unless otherwise stated; double distilled water was used throughout the experimental work.

Aryl thioureas were prepared by Frank and Smith method [16]. The 3-chloroacetyl acetone (Merck India), diethyl ether (Qualigens) were used for this work. The standard solutions of 3-chloroacetyl acetone and thioureas were prepared in double distilled absolute alcohol.

General procedure

Kinetic measurements were carried out at different concentrations of reactants and temperatures. A solution containing appropriate amount of thiourea which is thermostated at particular temperature was added in the solution containing appropriate amount of 3-chloroacetyl acetone at same temperature. At different time intervals definite volume of aliquot was added to a mixture of diethyl ether and water. It was shaken immediately and aqueous layer containing thiozole hydrochloride was separated, diluted to definite volume with distilled water. The pH of thiazole hydrochloride solution formed was measured by digital pH meter. Equal amounts of thiourea and 3-chloroacetyl acetone were mixed under the similar experimental conditions and kept overnight. The reaction mixture was then cooled and poured on crushed ice. It was extracted with ether to remove the unreacted reactants. The aqueous layer was neutralized by sodium hydroxide. The white solid obtained was crystallized from ethanol.

RESULTS AND DISCUSSION

The stoichiometric study indicates that one mole of thiourea reacts with one mole of 3-chloroacetylacetone. The rates of reaction were measured at different concentration of thioureas at constant concentration of 3-chloroacetylacetone. The plot of log (dc/dt) against log [3-chloroacetylacetone] is also straight line by keeping concentration of thioureas constant. The slope of the graph is 1.0 (Fig. 1).

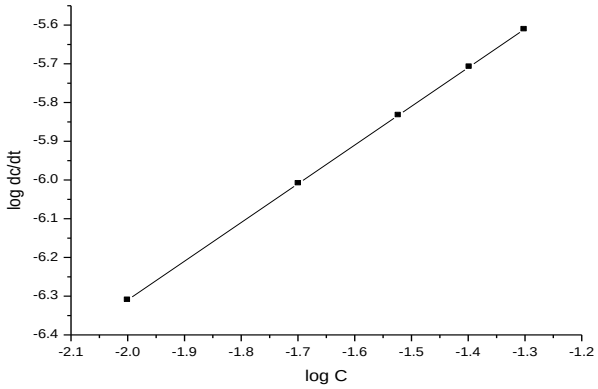

Fig. 1. Variation of log dc/dt with Log C

The plot of log (dc / dt) against log [thioureas by keeping concentration of 3-chloroacetylacetone constant it is also strate line and slop of the plot is one. The overall order of reaction is 2.

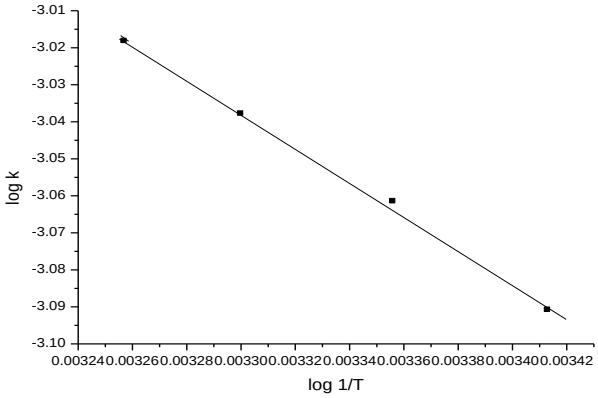

Fig. 2. Variation of log k with 1/T

By using Van't Hoffs differential method [17] the order of reaction with respect to 3-chloroacetylacetone and thioureas was also determined. Second order rate constants were determined at five different temperatures. The energy of activation (Ea*) was determined by plotting graph of log k verses 1/T (Fig. 2) and other thermodynamic parameter were calculated, [Table.1].

Table 1. Thermodynamic parameters for reaction of 3-chloroacetyl acetone with thioureas.

Thioureas	Ea* kJmol^{-1}	ΔH* kJmol^{-1}	-ΔS* kJ K^{-1}mol^{-1}	ΔF* kJ mol^{-1}
m-methyl phenyl & thiourea	30.17	28.67	0.043	20.14
m-mthoxy phenylthiourea	35.40	32.78	0.466	22.41
m-ethoxy phenylthiourea	37.47	35.76	0.0511	26.19
m-chloro phenyl thiourea	34.49	31.87	0.0501	23.32

The entropies of activation (ΔS*) of these reaction are negative indicates rigid nature of the transition state. The negative value of entropies of activation (ΔS*) also indicates that less stable noncyclic reactant convert into stable cyclic products [18]. Almost equal values of free energy of activation (ΔF*) for all thioureas indicates that probably a similar type of mechanism prevails in all cases [18]. When rate constant for the reaction are compared, the thiourea is found to be more reactive than the substituted phenyl thiouras. This may be due to the presence of II-electron in benzene ring. The phenyl thiourea and m-methyl phenyl thiourea show nearly same rate constants. This may be due to small effect of methyl group due to hyper conjugation and inductive effect. The m-ethoxy phenyl thiourea shows higher rate of reaction due to mesomeric effect. The m-chlorophenyl thiourea shows lower rate of reaction due to negative inductive effect of chloro group [19-20]. It is found that, the reaction is second order, first order with respect to thioureas and first order with respect to 3-chloroacetylacetone. The rate constants calculated from second order rate law are fairly constant [Table. 2].

Table 2. Second order rate contents for reaction of 3-Chloroacetyl acetone with thioureas
Thiourea = 0.05 mol dm^{-3} Temp = 313 ^oK

Thiourea	10^3 dm^3 mol^{-1} S^{-1} at 3-chloroacetylacetone mol dm^{-3}			
	0.05	0.04	0.03	0.02
m-methyl phenyl thiourea	0.96	0.98	0.94	0.99
m-methoxy phenyl thiourea	1.25	1.27	1.24	1.28
m-ethoxy phenyl thiourea	2.75	2.69	2.72	2.77
m-chloro phenyl thiourea	0.23	0.26	0.21	0.24

Based on these facts, the following general mechanism and rate expression is proposed.

$$S_1 + S_2 \underset{k_{-1}}{\overset{k_1 \text{ Slow}}{\rightleftharpoons}} [\text{Intermediate}] \xrightarrow[k_2]{\text{Fast}} \text{products} \quad (1)$$

S_1 stands for 3-chloroacetylacetone and S_2 stands for thioureas.

$$\text{Rate of reaction} = k_1 [S_1] [S_2] - k_{-1} [\text{Intermediate}] \quad (2)$$

On applying steady state approximation.

$$d / dt [\text{Intermediate}] = o = k_1 [S_1] [S_2] - k_{-1} [\text{Intermediate}] - k_2 [\text{Intermediate}] \quad (3)$$

$$[\text{Intermediate}] = \frac{k_1 [S_1] [S_2]}{k_{-1} + k_2} \quad (4)$$

Substituting the value of [Intermediate] in equation (2)

$$\text{Rate of reaction} = k_1 [S_1] [S_2] - \frac{k_1 k_{-1} [S_1] [S_2]}{k_{-1} + k_2} \quad (5)$$

$$\text{Rate of reaction} = \left\{ k_{-1} - \frac{k_{-1} k_1}{k_{-1} + k_2} \right\} [S_1] [S_2] \quad (6)$$

The order of reaction is two (Reaction mechanism). The derived rate law explains all the observed experimental facts.

CONCLUSION

The order of reaction between 3-chloroacetylacetone and thiourea is found to be two.

The proposed rate law also shows that the rate of reaction is two.

Nearly equal values of free energy (ΔF*) indicates that same type of reaction mechanism prevails.

Decrease in entropy (ΔS*) indicates that, from open chain reactants the cyclic product is formed.

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КИНЕТИЧНО ИЗСЛЕДВАНЕ НА ОБРАЗУВАНЕТО НА ТИАЗОЛ ЧРЕЗ ЦИКЛИЗАЦИЯ

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(Резюме)

Извършено е кинетично изследване на взаимодействието на 3-хлороацетилацетон с различни производни на тиокарбамида в етанол. Производните на карбамида са m-метил-фенилкарбамид, m-метоксифенилкарбамид, m-етоксифенилкарбамид и m-хлорофенилкарбамид. Порядъкът на реакциите е първи по отношение на тиокарбамидните производни, както и за 3- хлороацетилацетон. Изследван е и ефектът на заместителите върху скоростта на реакциите. Използвани са термодинамични параметри за обяснението на природата на реакциите. Изследван е предложеният механизъм на реакциите и подробности за кинетиката им.

Synthesis and Antimicrobial Activity of Some Novel [4-(1,2,3-thiadiazol-4-yl) phenoxy]methylene anchored 1,3,4-triazoles and 1,3,4-thiadiazoles

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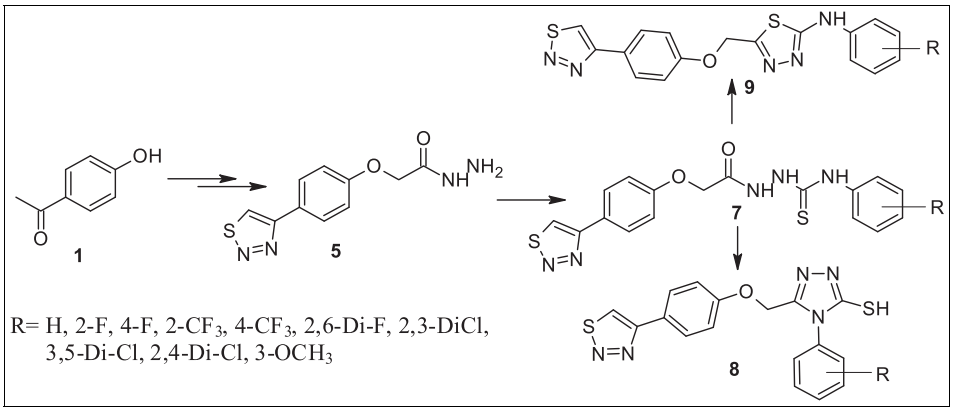

A series of novel [4-(1,2,3-thiadiazol-4-yl)phenoxy]methylene anchored 1,3,4-triazoles (**8a–h**) and 1,3,4-thiadiazoles (**9a–i**) were synthesized from thiosemicarbazide (**7a–j**). The structures of these newly synthesized compounds were confirmed on the basis of IR, ^{1}H-NMR, mass spectral techniques, and elemental analysis. The *in vitro* antimicrobial screenings of the synthesized compounds were carried out against four bacterial pathogens, namely *Staphylococcus aureus*, *Streptococcus pyogenes*, *Escherichia coli*, *Pseudomonas aeruginosa* and three fungal pathogens *Candida albicans*, *Aspergillus niger* and *Aspergillus clavatus*, using broth microdilution minimum inhibitory concentration method. The compounds **7d**, **7j**, **8a**, **9a, 9b**, and **9i** exhibited promising antibacterial activity against the tested strains, whereas some compounds were found to be active against one of the tested bacterial strains.

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INTRODUCTION

An azole is a class of five-membered nitrogen heterocycles containing at least one other non-carbon atom such as nitrogen, sulfur, or oxygen [1]. It has shown wide applications in medicinal chemistry due to their diverse therapeutic properties, which includes dyslipidemia, antiarthritis, anti-inflammatory, antidiabetes, anticoagulant, antiobesity, pesticides, antimicrobial, antihypertensive, anticonvulsant, antidepressants, antioxidants, and so on [2–6].

Thiadiazoles are widely exposed to therapeutic world because of their known antibacterial [7], antifungal [7], antitubercular [8], carbonic anhydrase inhibitors [9], anti-inflammatory [10], analgesic [10], antidepressant [11], anti-HIV [12], and anticancer [13] activities. 1,3,4-thiadiazole scaffold occurs in various drugs such as sulfamethizole (sulfonamide antibiotic), acetazolamide (carbonic anhydrase inhibitors), ceftezole (cephalosporin antibiotic), and so on.

The chemistry of triazoles received considerable attention because of their synthetic and biological importance. They have been found to exhibit antifungal [14], anti-inflammatory [15], anticancer [16], and anticonvulsant [17] activities. They have a higher affinity for fungal than mammalian target enzymes, which makes them less toxic than imidazole compounds such as ketoconazole and miconazole. Thiosemicarbazide are known for their antifungal [18], antibacterial [18], plant growth promoting [19], and antiviral [20] activities.

In view of broad spectrum of biological activities associated with thiadiazole and triazole system, it was thought worthwhile to combine such biologically important moieties into a single scaffold to produce a novel heterocycles and explore the effects toward their biological activities. In radiance of the aforementioned facts and in continuation of our investigations on the synthesis of biologically active heterocycles [21], herein we report the synthesis of novel 1,3,4-thiadiazole and 1,3,4-triazole analogues.

RESULTS AND DISCUSSION

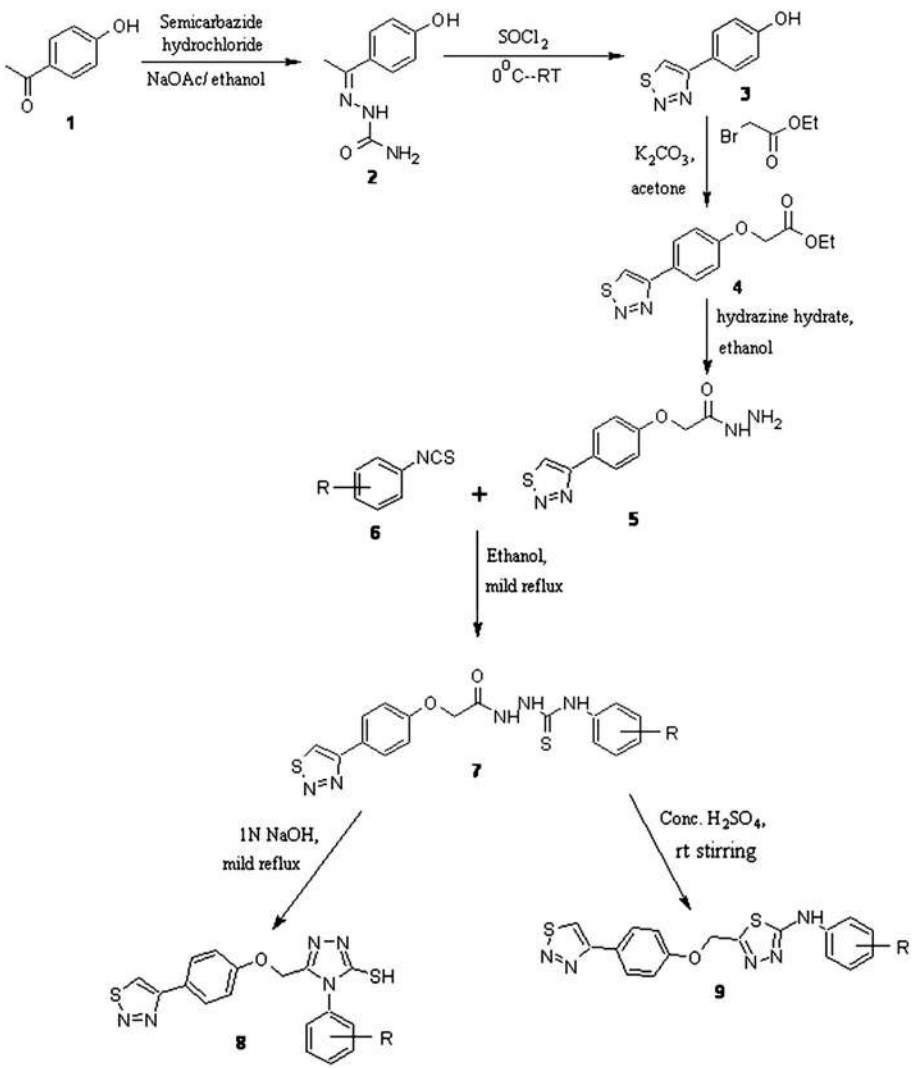
Chemistry. The 2-[4-(1,2,3-thiadiazol-4-yl)phenoxy] acetylhydrazide (**5**) was synthesized from 4-hydroxy

acetophenone as shown in Scheme 1. 4-hydroxy acetophenone (**1**) upon reaction with semicarbazide hydrochloride in presence of sodium acetate in ethanol gave 1-(4-hydroxyphenyl) ethan-1-one semicarbazone (**2**). The semicarbazone (**2**) on reaction with thionyl chloride gave 4-(1,2,3-thiadiazol-4-yl)phenol (**3**). Formation of (**3**) takes place by Hurd–Mori reaction [22]. The 4-(1,2,3-thiadiazol-4-yl)phenol (**3**) on reaction with ethylbromoacetate in presence of potassium carbonate in acetone gave ethyl [4-(1,2,3-thiadiazol-4-yl)phenoxy] acetate (**4**), which further on reaction with hydrazine hydrate in ethanol under reflux condition gave 2-[4-(1,2,3-thiadiazol-4-yl) phenoxy]acetylhydrazide (**5**).

The 2-[4-(1,2,3-thiadiazol-4-yl)phenoxy]acetylhydrazide (**5**) was treated with aryl isothiocyanates [23] (**6**) in ethanol to give thiosemicarbazides (**7**). The formation of compound (**7**) was confirmed by spectral techniques. ^{1}H-NMR spectrum of thiosemicarbazide (**7c**) showed characteristic signals for N–H at 8.92, 9.38, and 9.83 δ as broad singlets and sharp singlet at 4.78 δ for –O–CH_2 protons. The proton of 1,2,3-thiadiazole nucleus appeared at 9.22 δ. IR spectrum exhibited characteristic bands at 3294, 3232, 3116 cm^{-1} for N–H, 1705 cm^{-1} for C = O, and 1357 cm^{-1} for C = S functions. The compound shows molecular ion peak *m/z* at 403 (M^+) confirmed the structure of **7c**.

Thiosemicarbazide (**7**) on intramolecular cyclization with 1 N NaOH gave triazole (**8**). The ^{1}H-NMR spectrum of triazole (**8b**) showed characteristic signal at 14.18 δ for S–H proton while the signals due to NH protons of thiosemicarbazide were disappeared. This clearly indicates that thiosemicarbazide is cyclized under alkaline condition to get triazoles. The protons of –O–CH_2 group resonated at 5.04 and 5.11 δ as doublets indicating geminal coupling. The COSY ^{1}H-NMR spectrum of **8b** proves that O–CH_2 group protons show a geminal coupling of 12.80 Hz. The

Scheme 1. 254 × 187 mm (96 × 96 DPI).



similar type of geminal coupling is observed for O–CH_2 group protons in compounds **8d** and **8g** proved by COSY ^{1}H-NMR. The IR spectrum of **8b** exhibited characteristic band for S–H function at 2620 cm^{-1}. The compound showed molecular ion peak at *m/z* at 385 (M^+), which confirms the structure of **8b**.

Thiosemicarbazide (**7**) subjected to cyclodehydration in conc. H_2SO_4 afforded thiadiazoles (**9**). The ^{1}H-NMR spectrum of thiadiazole (**9c**) resonated a singlet at 10.31 δ for N–H proton. The singlet at 5.44 δ was observed because of the protons of –O–CH_2 group. The IR spectrum of **8b** exhibited a characteristic band for N–H function at 3412 cm^{-1}. The structure of **9c** was also confirmed by its mass spectral data. In its mass spectrum, the molecular ion peak was noticed at *m/z* at 385 (M^+) corresponding to its molecular weight.

Antimicrobial activity. The *in vitro* antibacterial activity of all synthesized compounds was evaluated against *Staphylococcus aureus*, *Streptococcus pyogenes*, *Escherichia coli*, and *Pseudomonas aeruginosa* using ampicillin as a standard. The investigation of antibacterial activity results revealed that the compounds showed moderate to good activity. Compounds **7d**, **7j**, **8a**, **9a**, **9b**, and **9i** showed broad spectrum activity against all tested bacterial strains. Compounds **7a**, **7e**, **7f**, **8b**, **8c**, **8d**, **8e, 9d**, **9e**, **9g**, and **9h** showed promising activity against *S. aureus* bacterial strain. Compounds **7f**, **7h, 8b**, and **9h** showed good activity against *P. aeruginosa*. Compounds **7c, 7g, 7i, 8g, 9c, 9d**, and **9e** showed good antibacterial activity against *S. pyogenes*, whereas only compound **8h** was found to be active against *E. coli*. Antifungal activity was evaluated against *Candida albicans*, *Aspergillus niger*, and *Aspergillus clavatus* fungal strains using griseofulvin as a standard. Among the synthesized compounds, **9e**, **9f**, and **9g** exhibited good antifungal activity against *C. albicans* fungal strain, whereas remaining compounds were found to be moderately active. Among the synthesized compounds, none of them showed promising activity against *A. niger* and *A. clavatus* fungal strains. In general, most of the tested compounds were found to be more active against gram-positive rather than gram-negative bacterial strains. Compounds showed moderate antifungal activity (Table 1).

Table 1

Antibacterial and antifungal activity data of synthesized compounds (**7a–j**), (**8a–h**) and (**9a–i**) indicated by MIC values (μg/ml).

	MIC, μg/mL						
	Gram-positive bacteria		Gram-negative bacteria		Fungi		
Compounds	*S. aureus*	*S.pyogenes*	*E. coli*	*P.aeruginosa*	*C.albicans*	*A.niger*	*A.clavatus*
7a	**200**	250	200	250	500	500	500
7b	250	200	250	250	500	500	1000
7c	250	**100**	250	500	1000	1000	1000
7d	**100**	**100**	**100**	**250**	1000	1000	1000
7e	**125**	125	125	200	1000	1000	>1000
7f	**200**	200	200	**62.5**	1000	500	1000
7g	250	**100**	250	250	>1000	>1000	>1000
7h	250	250	250	**100**	>1000	>1000	>1000
7i	1000	**62.5**	200	250	>1000	>1000	>1000
7j	**250**	**100**	**125**	**100**	>1000	>1000	>1000
8a	**125**	250	**100**	**125**	1000	500	500
8b	**100**	200	250	**62.5**	1000	500	1000
8c	**100**	250	250	200	500	250	250
8d	**200**	200	500	250	>1000	>1000	>1000
8e	**200**	250	500	200	1000	>1000	>1000
8f	250	500	250	250	>1000	>1000	>1000
8g	250	**100**	200	200	1000	>1000	>1000
8h	250	500	**100**	200	500	>1000	>1000
9a	**200**	**100**	200	**62.5**	>1000	500	500
9b	**250**	**125**	**125**	**100**	500	>1000	>1000
9c	250	**62.5**	250	200	500	>1000	>1000
9d	**100**	**100**	250	250	1000	500	500
9e	**100**	**100**	200	200	**250**	>1000	>1000
9f	250	250	125	250	**200**	>1000	>1000
9g	**200**	200	200	200	**250**	>1000	>1000
9h	**62.5**	125	250	**100**	500	>1000	>1000
9i	**100**	**100**	**100**	**100**	500	>1000	>1000
Ampicillin	250	100	100	100	—	—	—
Griseofulvin	—	—	—	—	500	100	100

MIC, minimum inhibitory concentration.

EXPERIMENTAL

General. All the chemicals used were of analytical grade. Melting points were taken in open capillaries and are uncorrected. The IR spectra were recorded in KBr on a Shimadzu FTIR-8400 spectrophotometer (Tokyo, Japan), and only characteristic peaks are reported in cm^{-1}. The ^{1}H-NMR spectra were recorded in DMSO-d_6 on a Bruker Avance spectrometer (Rheinstetten, Germany) using TMS as an internal standard at 400 MHz, and chemical shifts are reported in ppm. Mass spectra were scanned on a Finnigan mass spectrometer (San Jose, USA). Elemental analysis was performed on a Perkin–Elmer analyzer (Massachusetts, USA). Thin-layer chromatography (TLC) (on aluminum plates coated with silica gel 60 F254, 0.25 mm thickness, Merck) was used for monitoring the progress of reactions, purity, and homogeneity of the synthesized compounds.

General procedure for synthesis of 2-[4-(1,2,3-thiadiazol-4-yl) phenoxy]acetyl hydrazide (5). This compound was synthesized by following literature known methods [22].

General procedure for synthesis of aryl isothiocyanates (6). These compounds were synthesized by following literature known methods [23].

General procedure for synthesis of *N*-phenyl-2-{[4-(1,2,3-thiadiazol-4-yl)phenoxy] acetyl}hydrazine carbothioamide (7a–j)

Equimolar amount (0.01 mol) of acid hydrazide (**5**) and aryl isothiocyanate (**6**) were dissolved in ethanol (15 mL), and the reaction mixture was heated under reflux condition till completion of reaction (checked by TLC). After completion of reaction, the contents were allowed to cool; the solid obtained was filtered and recrystallized from ethanol to give pure thiosemicarbazides (**7a–j**). The characterization data of synthesized compounds are as follows.

***N*-phenyl-2-{[4-(1,2,3-thiadiazol-4-yl)phenoxy]acetyl}hydrazine carbothioamide (7a).** This compound was obtained as faint yellow solid (ethanol), yield 72%; mp 168–169°C; IR: 3290 (NH), 3210 (NH), 3122 (NH), 1688 (CO), 1605 (C=C), 1320 (CS), 1225 (C–O) cm^{-1}; ^{1}H-NMR: δ 4.74 (s, 2H, –CH_2–), 7.14–7.16 (m, 3H, Ar-H), 7.28–7.34 (m, 2H, Ar-H), 7.49–7.51 (m, 2H, Ar-H), 8.02 (d, 2H, J = 8.4 Hz, Ar-H), 9.01 (s, 1H, thiadiazole ring proton), 9.55 (bs, 2H, NH), 10.22 (bs, 1H, NH); MS: *m/z* 385 (M^+); *Anal*. Calcd for $C_{17}H_{15}N_5O_2S_2$: C, 52.97%; H, 3.92%; N, 18.17%. Found: C, 52.90%; H, 3.88%; N, 18.24%.

***N*-(2-fluorophenyl)-2-{[4-(1,2,3-thiadiazol-4-yl)phenoxy]acetyl} hydrazine carbothioamide (7b).** This compound was obtained as faint yellow solid (ethanol), yield 75%; mp 176-177°C; IR: 3285 (NH), 3219 (NH), 3126 (NH), 1699 (CO), 1601 (C=C), 1335 (CS), 1235 (C–O), 1140 (Ar-F) cm^{-1}; ^{1}H-NMR: δ 4.73 (s, 2H, –CH_2–), 7.10–7.16 (m, 5H, Ar-H), 7.90 (s, 1H, Ar-H), 8.03 (d, 2H, J = 8.7 Hz, Ar-H), 9.10 (s, 1H, thiadiazole ring proton), 9.41(bs, 1H, NH), 9.84 (bs, 1H, NH), 10.35 (bs, 1H, NH); MS: *m/z* 403 (M^+); *Anal*. Calcd for $C_{17}H_{14}FN_5O_2S_2$: C, 50.61%; H, 3.50%; N, 17.36%. Found: C, 50.55%; H, 3.61%; N, 17.29%.

***N*-(4-fluorophenyl)-2-{[4-(1,2,3-thiadiazol-4-yl)phenoxy]acetyl} hydrazine carbothioamide (7c).** This compound was obtained as off-white solid (ethanol), yield 69%; mp 173–174°C; IR: 3294 (NH), 3232 (NH), 3116 (NH), 1705 (CO), 1612 (C=C), 1357 (CS), 1222 (C-O), 1148 (Ar-F) cm^{-1}; ^{1}H-NMR: δ 4.78 (s, 2H, –CH_2–), 7.03–7.07 (m, 2H, Ar-H), 7.20 (d, 2H, J = 8.4 Hz, Ar-H), 7.49–7.52 (m, 2H, Ar-H), 8.11 (d, 2H, J = 8.4 Hz, Ar-H), 8.92 (bs, 1H, NH), 9.22 (s, 1H, thiadiazole ring proton), 9.38 (bs, 1H, NH), 9.83 (bs, 1H, NH); MS: *m/z* 403 (M^+); *Anal*. Calcd for $C_{17}H_{14}FN_5O_2S_2$: C, 50.61%; H, 3.50%; N, 17.36%. Found: C, 50.54%; H, 3.57%; N, 17.27%.

***N*-[2-(trifluoromethyl)phenyl]-2-{[4-(1,2,3-thiadiazol-4-yl) phenoxy]acetyl}hydrazine carbothioamide (7d).** This compound was obtained as faint yellow solid (ethanol), yield 78%; mp 177–178°C; IR: 3279 (NH), 3229 (NH), 3125 (NH), 1698 (CO), 1601 (C=C), 1333 (CS), 1233 (C–O) cm^{-1}; ^{1}H-NMR: δ 4.73 (s, 2H, –CH_2–), 7.14 (d, 2H, J = 8.3 Hz, Ar-H), 7.44–7.51 (m, 2H, Ar-H), 7.61–7.69 (m, 2H, Ar-H), 8.04 (d, 2H, J = 8.3 Hz, Ar-H), 9.26 (s, 1H, thiadiazole ring proton), 9.39 (bs, 1H, NH), 9.83 (bs, 1H, NH), 10.35 (bs, 1H, NH); MS: *m/z* 453 (M^+); *Anal*. Calcd for $C_{18}H_{14}F_3N_5O_2S_2$: C, 47.68%; H, 3.11%; N, 15.44%. Found: C, 47.77%; H, 3.22%; N, 15.33%.

***N*-[3-(trifluoromethyl)phenyl]-2-{[4-(1,2,3-thiadiazol-4-yl)phenoxy] acetyl}hydrazine carbothioamide (7e).** This compound was obtained as white solid (ethanol), yield 71%; mp 181–182°C; IR: 3289 (NH), 3213 (NH), 3101 (NH), 1688 (CO), 1604 (C=C), 1327 (CS), 1239 (C–O) cm^{-1}; ^{1}H-NMR: δ 4.74 (s, 2H, –CH_2–), 7.16 (d, 2H, J = 8.8 Hz, Ar-H), 7.42–7.44 (m, 1H, Ar-H), 7.49–7.53 (m, 1H, Ar-H), 7.84–7.86 (m, 2H, Ar-H), 8.06 (d, 2H, J = 8.8 Hz, Ar-H), 9.31 (s, 1H, thiadiazole ring proton), 9.89 (bs, 2H, NH), 10.35 (bs, 1H, NH); MS: *m/z* 453 (M^+); *Anal*. Calcd for $C_{18}H_{14}F_3N_5O_2S_2$: C, 47.68%; H, 3.11%; N, 15.44%. Found: C, 47.59%; H, 3.24%; N, 15.55%.

***N*-(2,6-difluorophenyl)-2-{[4-(1,2,3-thiadiazol-4-yl)phenoxy] acetyl}hydrazine carbothioamide (7f).** This compound was obtained as brownish solid (ethanol), yield 65%; mp 129–130°C; IR: 3277 (NH), 3225 (NH), 3090 (NH), 1694 (CO), 1599 (C=C), 1323 (CS), 1240 (C–O), 1141 (Ar-F) cm^{-1}; ^{1}H-NMR: δ 4.73 (s, 2H, –CH_2–), 6.95-6.99 (m, 2H, Ar-H), 7.14 (d, 2H, J = 8.5 Hz, Ar-H), 7.28–7.30 (m, 1H, Ar-H), 8.02 (d, 2H, J = 8.5 Hz, Ar-H), 8.84 (s, 1H, thiadiazole ring proton), 9.00 (bs, 2H, NH), 10.24 (bs, 1H, NH); MS: *m/z* 421 (M^+); *Anal*. Calcd for $C_{17}H_{13}F_2N_5O_2S_2$: C, 48.45%; H, 3.11%; N, 16.62%. Found: C, 48.52%; H, 3.22%; N, 16.53%.

***N*-(2,3-dichlorophenyl)-2-{[4-(1,2,3-thiadiazol-4-yl)phenoxy] acetyl}hydrazine carbothioamide (7g).** This compound was obtained as white solid (ethanol), yield 71%; mp 138–139°C; IR: 3283 (NH), 3235 (NH), 3101 (NH), 1681 (CO), 1603 (C=C), 1315 (CS), 1223 (C–O) cm^{-1}; ^{1}H-NMR: δ 4.74 (s, 2H, –CH_2–), 7.14 (d, 2H, J = 8.6 Hz, Ar-H), 7.25–7.29 (m, 1H, Ar-H), 7.39–7.52 (m, 2H, Ar-H), 8.04 (d, 2H, J = 8.6 Hz, Ar-H), 9.14 (s, 1H, thiadiazole ring proton), 9.46 (bs, 1H, NH), 9.90 (bs, 1H, NH), 10.39 (bs, 1H, NH); MS: *m/z* 454 (M^+), 456 (M^++2), 458 (M^++4); *Anal*. Calcd for $C_{17}H_{13}Cl_2N_5O_2S_2$: C, 44.94%; H, 2.88%; N, 15.41%. Found: C, 44.85%; H, 2.97%; N, 15.55%.

***N*-(3,5-dichlorophenyl)-2-{[4-(1,2,3-thiadiazol-4-yl)phenoxy] acetyl}hydrazine carbothioamide (7h).** This compound was obtained as white solid (ethanol), yield 66%; mp 202–203°C; IR: 3299 (NH), 3220 (NH), 3129 (NH), 1693 (CO), 1595 (C=C), 1340 (CS), 1243 (C–O) cm^{-1}; ^{1}H-NMR: δ 4.73 (s, 2H, –CH_2–), 7.08–7.12 (m, 1H, Ar-H), 7.15 (d, 2H, J = 8.6 Hz, Ar-H), 7.68–7.75 (m, 2H, Ar-H), 8.06 (d, 2H, J = 8.6 Hz, Ar-H), 9.29 (s, 1H, thiadiazole ring proton), 9.79 (bs, 1H, NH), 9.96 (bs, 1H, NH), 10.41 (bs, 1H, NH); MS: *m/z* 454 (M^+), 456 (M^++2), 458 (M^++4); *Anal*. Calcd for $C_{17}H_{13}Cl_2N_5O_2S_2$: C, 44.94%; H, 2.88%; N, 15.41%. Found: C, 45.01%; H, 2.76%; N, 15.50%.

***N*-(2,4-dichlorophenyl)-2-{[4-(1,2,3-thiadiazol-4-yl)phenoxy] acetyl}hydrazine carbothioamide (7i).** This compound was obtained as white solid (ethanol), yield 69%; mp 159–160°C; IR: 3291 (NH), 3230 (NH), 3117 (NH), 1694 (CO), 1610 (C=C), 1348 (CS), 1239 (C–O) cm^{-1}; ^{1}H-NMR: δ 4.75 (s, 2H, –CH_2–), 7.14 (d, 2H, J = 8.6 Hz, Ar-H), 7.25 (dd, 1H, J = 8.8 &

2.2 Hz, Ar-H), 7.42 (d, 1H, J = 2.2 Hz, Ar-H), 8.00–8.05 (m, 3H, Ar-H), 8.97 (s, 1H, thiadiazole ring proton), 9.26 (bs, 1H, NH), 9.71 (bs, 1H, NH), 10.34 (bs, 1H, NH); MS: *m/z* 454 (M^+), 456 (M^++2), 458 (M^++4); *Anal*. Calcd for $C_{17}H_{13}Cl_2N_5O_2S_2$: C, 44.94%; H, 2.88%; N, 15.41%. Found: C, 44.81%; H, 2.95%; N, 15.54%.

N-(3-methoxyphenyl)-2-{[4-(1,2,3-thiadiazol-4-yl)phenoxy] acetyl}hydrazine carbothioamide (7j). This compound was obtained as yellowish solid (ethanol), yield 73%; mp 150–151°C; IR: 3289 (NH), 3210 (NH), 3127 (NH), 1695 (CO), 1596 (C = C), 1339 (CS), 1240 (C–O) cm^{-1}; ^{1}H-NMR: δ 3.76 (s, 3H, Ar-OCH_3), 4.73 (s, 2H, –CH_2–), 6.72–6.74 (m, 1H, Ar-H), 7.02–7.04 (m, 1H, Ar-H), 7.14–7.22 (m, 4H, Ar-H), 8.06 (d, 2H, J = 8.8 Hz, Ar-H), 9.32 (s, 1H, thiadiazole ring proton), 9.67 (bs, 2H, NH), 10.30 (bs, 1H, NH); MS: *m/z* 415 (M^+); *Anal*. Calcd for $C_{18}H_{17}N_5O_3S_2$: C, 52.03%; H, 4.12%; N, 16.86%. Found: C, 51.95%; H, 4.24%; N, 16.97%.

General method for synthesis of 4-phenyl-5-{[4-(1,2,3-thiadiazol-4-yl)phenoxy]methyl}-4*H*-1,2,4-triazole-3-thiol (8a–h). Thiosemicarbazide (**7**) (0.001 mol) was taken in 1 N NaOH (10 mL), and the reaction mixture was heated under mild reflux condition till completion of reaction (checked by TLC). After completion of reaction, the contents were allowed to cool, poured into crushed ice, and acidified with glacial acetic acid. The product obtained was separated and recrystallized from DMF and water (1 : 1) to give pure triazoles (**8a–h**). The characterization data of synthesized compounds are as follows.

4-phenyl-5-{[4-(1,2,3-thiadiazol-4-yl)phenoxy]methyl}-4H-1,2,4-triazole-3-thiol (8a). This compound was obtained as yellow solid (1 : 1, DMF : H_2O), yield 76%; mp 217–218°C; IR: 2595 (SH), 1640 (C = N), 1601 (C = C), 1241 (C–O) cm^{-1}; ^{1}H-NMR: δ 5.03 (s, 2H, –CH_2–), 6.96 (d, 2H, J = 8.7 Hz, Ar-H), 7.45–7.55 (m, 5H, Ar-H), 7.98 (d, 2H, J = 8.7 Hz, Ar-H), 9.28 (s, 1H, thiadiazole ring proton), 14.02 (s, 1H, SH); MS: *m/z* 367 (M^+); *Anal*. Calcd for $C_{17}H_{13}N_5OS_2$: C, 55.57%; H, 3.57%; N, 19.06%. Found: C, 55.49%; H, 3.70%; N, 18.97%.

4-(2-fluorophenyl)-5-{[4-(1,2,3-thiadiazol-4-yl)phenoxy]methyl}-4H-1,2,4-triazole-3-thiol (8b). This compound was obtained as yellow solid (1 : 1, DMF : H_2O), yield 73%; mp 183–184°C; IR: 2620 (SH), 1640 (C = N), 1608 (C = C), 1240 (C–O), 1172 (Ar-F) cm^{-1}; ^{1}H-NMR: δ 5.04 (d, 1H, J = 12.8 Hz, O–CH_2– proton), 5.11 (d, 1H, J = 12.8 Hz, O–CH_2– proton), 6.96 (d, 2H, J = 8.4 Hz, Ar-H), 7.34–7.38 (m, 1H, Ar-H), 7.45–7.49 (m, 1H, Ar-H), 7.55–7.62 (m, 2H, Ar-H), 7.99 (d, 2H, J = 8.4 Hz, Ar-H), 9.47 (s, 1H, thiadiazole ring proton), 14.18 (s, 1H, SH); MS: *m/z* 385 (M^+); *Anal*. Calcd for $C_{17}H_{12}FN_5OS_2$: C, 52.97%; H, 3.14%; N, 18.17%. Found: C, 53.09%; H, 3.06%; N, 18.30%.

4-(4-fluorophenyl)-5-{[4-(1,2,3-thiadiazol-4-yl)phenoxy]methyl}-4H-1,2,4-triazole-3-thiol (8c). This compound was obtained as faint yellow solid (1 : 1, DMF : H_2O), yield 69%; mp 205–206°C; IR: 2601 (SH), 1633 (C = N), 1606 (C = C), 1231 (C–O), 1175 (Ar-F) cm^{-1}; ^{1}H-NMR: δ 5.03 (s, 2H, –CH_2–), 6.97 (d, 2H, J = 8.6 Hz, Ar-H), 7.24–7.28 (m, 2H, Ar-H), 7.47–7.50 (m, 2H, Ar-H), 7.99 (d, 2H, J = 8.6 Hz, Ar-H), 9.16 (s, 1H, thiadiazole ring proton), 14.03 (s, 1H, SH); MS: *m/z* 385 (M^+); *Anal*. Calcd for $C_{17}H_{12}FN_5OS_2$: C, 52.97%; H, 3.14%; N, 18.17%. Found: C, 52.85%; H, 3.25%; N, 18.06%.

4-[2-(trifluoromethyl)phenyl]-5-{[4-(1,2,3-thiadiazol-4-yl) phenoxy]methyl}-4H-1,2,4-triazole-3-thiol (8d). This compound was obtained as brownish solid (1 : 1, DMF : H_2O), yield 73%; mp 120–121°C; IR: 2591 (SH), 1622 (C = N), 1599 (C = C), 1233 (C–O) cm^{-1}; ^{1}H-NMR: δ 4.87 (d, 1H, J = 13.0 Hz, O–CH_2– proton), 5.07 (d, 1H, J = 13.0 Hz, O–CH_2– proton), 6.92 (d, 2H, J = 8.0 Hz, Ar-H), 7.54 (d, 1H, J = 7.8 Hz, Ar-H), 7.74–7.92 (m, 3H, Ar-H), 7.97 (d, 2H, J = 8.0 Hz, Ar-H), 9.30 (s, 1H, thiadiazole ring proton), 14.09 (s, 1H, SH); MS: *m/z* 435 (M^+); *Anal*. Calcd for $C_{18}H_{12}F_3N_5OS_2$: C, 49.65%; H, 2.78%; N, 16.08%. Found: C, 49.54%; H, 2.86%; N, 16.20%.

4-[3-(trifluoromethyl)phenyl]-5-{[4-(1,2,3-thiadiazol-4-yl)phenoxy] methyl}-4H-1,2,4-triazole-3-thiol (8e). This compound was obtained as brownish solid (1 : 1, DMF : H_2O), yield 77%; mp 200–201°C; IR: 2587 (SH), 1643 (C = N), 1610 (C = C), 1239 (C–O) cm^{-1}; ^{1}H-NMR: δ 5.06 (s, 2H, –CH_2–), 6.94 (d, 2H, J = 8.5 Hz, Ar-H), 7.18–7.82 (m, 4H, Ar-H), 7.98 (d, 2H, J = 8.5 Hz, Ar-H), 9.14 (s, 1H, thiadiazole ring proton), 14.11 (s, 1H, SH); MS: *m/z* 435 (M^+); *Anal*. Calcd for $C_{18}H_{12}F_3N_5OS_2$: C, 49.65%; H, 2.78%; N, 16.08%. Found: C, 49.59%; H, 2.65%; N, 16.19%.

4-(2,6-difluorophenyl)-5-{[4-(1,2,3-thiadiazol-4-yl)phenoxy] methyl}-4H-1,2,4-triazole-3-thiol (8f). This compound was obtained as brownish solid (1 : 1, DMF : H_2O), yield 68%; mp 189–190°C; IR: 2594 (SH), 1641 (C = N), 1616 (C = C), 1247 (C–O), 1179 (Ar-F) cm^{-1}; ^{1}H-NMR: δ 5.07 (s, 2H, –CH_2–), 6.92 (d, 2H, J = 8.8 Hz, Ar-H), 7.22–7.26 (m, 2H, Ar-H), 7.59–7.63 (m, 1H, Ar-H), 7.97 (d, 2H, J = 8.8 Hz, Ar-H), 9.21 (s, 1H, thiadiazole ring proton), 14.20 (s, 1H, SH); MS: *m/z* 403 (M^+); *Anal*. Calcd for $C_{17}H_{11}F_2N_5OS_2$: C, 50.61%; H, 2.75%; N, 17.36%. Found: C, 50.74%; H, 2.86%; N, 17.20%.

4-(2,3-dichlorophenyl)-5-{[4-(1,2,3-thiadiazol-4-yl)phenoxy] methyl}-4H-1,2,4-triazole-3-thiol (8g). This compound was obtained as faint yellow solid (1 : 1, DMF : H_2O), yield 76%; mp 210–211°C; IR: 2612 (SH), 1635 (C = N), 1601 (C = C), 1245 (C–O) cm^{-1}; ^{1}H-NMR: δ 4.98 (d, 1H, J = 13.04 Hz, O–CH_2– proton), 5.04 (d, 1H, J = 13.04 Hz, O–CH_2– proton), 6.92 (d, 2H, J = 8.8 Hz, Ar-H), 7.46–7.52 (m, 2H, Ar-H), 7.69–7.72 (m, 1H, Ar-H), 7.97 (d, 2H, J = 8.8 Hz, Ar-H), 9.24 (s, 1H, thiadiazole ring proton), 14.12 (s, 1H, SH); MS: *m/z* 436 (M^+), 438 (M^++2), 440 (M^++4); *Anal*. Calcd for $C_{17}H_{11}Cl_2N_5OS_2$: C, 46.79%; H, 2.54%; N, 16.05%. Found: C, 46.67%; H, 2.42%; N, 16.21%.

4-(3-methoxyphenyl)-5-{[4-(1,2,3-thiadiazol-4-yl)phenoxy] methyl}-4H-1,2,4-triazole-3-thiol (8h). This compound was obtained as faint yellow solid (1 : 1, DMF : H_2O), yield 68%; mp 182–183°C; IR: 2580 (SH), 1622 (C = N), 1596 (C = C), 1233 (C–O) cm^{-1}; ^{1}H-NMR: δ 3.79 (s, 3H, Ar-OCH_3), 5.03 (s, 2H, –CH_2–), 6.98–7.04 (m, 5H, Ar-H), 7.40–7.44 (m, 1H, Ar-H), 7.99 (d, 2H, J = 8.8 Hz, Ar-H), 9.20 (s, 1H, thiadiazole ring proton), 14.00 (s, 1H, SH); MS: *m/z* 397 (M^+); *Anal*. Calcd for $C_{18}H_{15}N_5O_2S_2$: C, 54.39%; H, 3.80%; N, 17.62%. Found: C, 54.51%; H, 3.71%; N, 17.72%.

General method for synthesis of *N*-phenyl-5-{[4-(1,2,3-thiadiazol-4-yl)phenoxy]methyl}-1,3,4-thiadiazol-2-amine (9a–i). Thiosemicarbazide (**7**) (0.001 mol) was dissolved in conc. H_2SO_4 (3 mL), and the reaction mixture was stirred at room temperature for 3 h. After completion of reaction (checked by TLC), the contents were poured over crushed ice. The solid obtained was separated and recrystallized from DMF and water (1 : 1) to give pure thiadiazoles (**9a–i**). The characterization data of synthesized compounds are as follows.

N-phenyl-5-{[4-(1,2,3-thiadiazol-4-yl)phenoxy]methyl}-1,3,4-thiadiazol-2-amine (9a). This compound was obtained as faint yellow solid (1 : 1, DMF : H_2O), yield 71%; mp 205–206°C; IR: 3421 (NH), 1608 (C = N), 1550 (C = C), 1249 (C–O) cm^{-1}; ^{1}H-NMR: δ 5.47 (s, 2H, –CH_2–), 7.00–7.02 (m, 2H, Ar-H), 7.19 (d, 2H, J = 8.0 Hz, Ar-H), 7.60–7.66 (m, 3H, Ar-H), 8.04 (d, 2H, J = 8.0 Hz, Ar-H), 9.45 (s, 1H, thiadiazole ring

proton), 10.02 (bs, 1H, NH); MS: *m/z* 367 (M^+); *Anal*. Calcd for $C_{17}H_{13}N_5OS_2$: C, 55.57%; H, 3.57%; N, 19.06%. Found: C, 55.45%; H, 3.66%; N, 19.15%.

N-(2-fluorophenyl)-5-{[4-(1,2,3-thiadiazol-4-yl)phenoxy]methyl}-1,3,4-thiadiazol-2-amine (9b). This compound was obtained as brownish solid (1 : 1, DMF : H_2O), yield 77%; mp 209–210°C; IR: 3415 (NH), 1602 (C = N), 1540 (C = C), 1236 (C–O), 1187 (Ar-F) cm^{-1}; ^{1}H-NMR: δ 5.44 (s, 2H, –CH_2–), 6.95–7.01 (m, 1H, Ar-H), 7.10–7.19 (m, 4H, Ar-H), 8.05 (d, 2H, *J* = 8.0 Hz, Ar-H), 8.40–8.44 (m, 1H, Ar-H), 9.20 (s, 1H, thiadiazole ring proton), 10.11 (bs, 1H, NH); MS: *m/z* 385 (M^+); *Anal*. Calcd for $C_{17}H_{12}FN_5OS_2$: C, 52.97%; H, 3.14%; N, 18.17%. Found: C, 53.09%; H, 3.23; N, 18.28%.

N-(4-fluorophenyl)-5-{[4-(1,2,3-thiadiazol-4-yl)phenoxy]methyl}-1,3,4-thiadiazol-2-amine (9c). This compound was obtained as faint yellow solid (1 : 1, DMF : H_2O), yield 70%; mp 247–248°C; IR: 3412 (NH), 1599 (C = N), 1545 (C = C), 1241 (C–O), 1178 (Ar-F) cm^{-1}; ^{1}H-NMR: δ 5.44 (s, 2H, –CH_2–), 7.03–7.08 (m, 2H, Ar-H), 7.18 (d, 2H, *J* = 8.8 Hz, Ar-H), 7.62–7.65 (m, 2H, Ar-H), 8.06 (d, 2H, *J* = 8.8 Hz, Ar-H), 9.28 (s, 1H, thiadiazole ring proton), 10.31 (bs, 1H, NH); MS: *m/z* 385 (M^+); *Anal*. Calcd for $C_{17}H_{12}FN_5OS_2$: C, 52.97%; H, 3.14%; N, 18.17%. Found: C, 52.85%; H, 3.04%; N, 18.24%.

N-[2-(trifluoromethyl)phenyl]-5-{[4-(1,2,3-thiadiazol-4-yl)phenoxy]methyl}-1,3,4-thiadiazol-2-amine (9d). This compound was obtained as faint yellow solid (1 : 1, DMF : H_2O), yield 67%; mp 198–199°C; IR: 3429 (NH), 1595 (C = N), 1551 (C = C), 1247 (C–O) cm^{-1}; ^{1}H-NMR: δ 5.38 (s, 2H, –CH_2–), 7.15 (d, 2H, *J* = 8.4 Hz, Ar-H), 7.26–7.30 (m, 1H, Ar-H), 7.58–7.66 (m, 2H, Ar-H), 7.94 (s, 2H, Ar-H & NH), 8.05 (d, 2H, *J* = 8.4 Hz, Ar-H), 9.15 (s, 1H, thiadiazole ring proton); MS: *m/z* 435 (M^+); *Anal*. Calcd for $C_{18}H_{12}F_3N_5OS_2$: C, 49.65%; H, 2.78%; N, 16.08%. Found: C, 49.73%; H, 2.87%; N, 15.97%.

N-[3-(trifluoromethyl)phenyl]5-{[4-(1,2,3-thiadiazol-4-yl)phenoxy]methyl}-1,3,4-thiadiazol-2-amine (9e). This compound was obtained as white solid (1 : 1, DMF : H_2O), yield 70%; mp 238–239°C; IR: 3425 (NH), 1591 (C = N), 1541 (C = C), 1243 (C–O) cm^{-1}; ^{1}H-NMR: δ 5.48 (s, 2H, –CH_2–), 7.20 (d, 2H, *J* = 8.0 Hz, Ar-H), 7.25–7.27 (m, 1H, Ar-H), 7.48–7.52 (m, 1H, Ar-H), 7.76–7.79 (m, 1H, Ar-H), 8.07 (d, 2H, *J* = 8.0 Hz, Ar-H), 8.15 (s, 1H, Ar-H), 9.34 (s, 1H, thiadiazole ring proton), 10.68 (bs, 1H, NH); MS: *m/z* 435 (M^+); *Anal*. Calcd for $C_{18}H_{12}F_3N_5OS_2$: C, 49.65%; H, 2.78%; N, 16.08%. Found: C, 49.76%; H, 2.67%; N, 16.22%.

N-(2,6-difluorophenyl)-5-{[4-(1,2,3-thiadiazol-4-yl)phenoxy]methyl}-1,3,4-thiadiazol-2-amine (9f). This compound was obtained as white solid (1 : 1, DMF : H_2O), yield 64%; mp 215–216°C; IR: 3423 (NH), 1596 (C = N), 1550 (C = C), 1225 (C–O), 1173 (Ar-F) cm^{-1}; ^{1}H- NMR: δ 5.38 (s, 2H, –CH_2–), 7.01-7.05 (m, 2H, Ar-H), 7.15 (d, 2H, *J* = 8.8 Hz, Ar-H), 7.21–7.28 (m, 1H, Ar-H), 7.93 (bs, 1H, NH), 8.04 (d, 2H, *J* = 8.8 Hz, Ar-H), 9.15 (s, 1H, thiadiazole ring proton); MS: *m/z* 403 (M^+); *Anal*. Calcd for $C_{17}H_{11}F_2N_5OS_2$: C, 50.61%; H, 2.75%; N, 17.36%. Found: C, 50.53%; H, 2.82%; N, 17.25%.

N-(2,3-dichlorophenyl)-5-{[4-(1,2,3-thiadiazol-4-yl)phenoxy]methyl}-1,3,4-thiadiazol-2-amine (9g). This compound was obtained as white solid (1 : 1, DMF : H_2O), yield 72%; mp 209–210°C; IR: 3429 (NH), 1599 (C = N), 1551 (C = C), 1239 (C–O) cm^{-1}; ^{1}H-NMR: δ 5.44 (s, 2H, –CH_2–), 7.16–7.20 (m, 3H, Ar-H), 7.25–7.29 (m, 1H, Ar-H), 8.05 (d, 2H, *J* = 8.8 Hz, Ar-H), 8.34 (d, 2H, *J* = 8.4 Hz, Ar-H), 9.12 (s, 1H, thiadiazole ring proton), 9.84 (bs, 1H, NH); MS: *m/z* 436 (M^+), 438 (M^++2), 440 (M^++4); *Anal*. Calcd for $C_{17}H_{11}Cl_2N_5OS_2$: C, 46.79%; H, 2.54%; N, 16.05%. Found: C, 46.70%; H, 2.48%; N, 16.20%.

N-(3,5-dichlorophenyl)-5-{[4-(1,2,3-thiadiazol-4-yl)phenoxy]methyl}-1,3,4-thiadiazol-2-amine (9h). This compound was obtained as white solid (1 : 1, DMF : H_2O), yield 69%; mp 239–240°C; IR: 3431 (NH), 1601 (C = N), 1548 (C = C), 1231 (C–O) cm^{-1}; ^{1}H-NMR: δ 5.46 (s, 2H, –CH_2–), 6.97–6.98 (m, 1H, Ar-H), 7.17 (d, 2H, *J* = 8.8 Hz, Ar-H), 7.67–7.68 (m, 2H, Ar-H), 8.04–8.07 (m, 2H, Ar-H), 9.12 (s, 1H, thiadiazole ring proton), 10.61 (bs, 1H, NH); MS: *m/z* 436 (M^+), 438 (M^++2), 440 (M^++4); *Anal*. Calcd for $C_{17}H_{11}Cl_2N_5OS_2$: C, 46.79%; H, 2.54%; N, 16.05%. Found: C, 46.64%; H, 2.62%; N, 16.15%.

N-(2,4-dichlorophenyl)-5-{[4-(1,2,3-thiadiazol-4-yl)phenoxy]methyl}-1,3,4-thiadiazol-2-amine (9i). This compound was obtained as white solid (1 : 1, DMF : H_2O), yield 73%; mp 211–212°C; IR: 3419 (NH), 1597 (C = N), 1539 (C = C), 1245 (C–O) cm^{-1}; ^{1}H-NMR: δ 5.46 (s, 2H, –CH_2–), 7.18 (d, 2H, *J* = 8.4 Hz, Ar-H), 7.31–7.34 (m, 1H, Ar-H), 7.46–7.47 (m, 1H, Ar-H), 8.07 (d, 2H, *J* = 8.4 Hz, Ar-H), 8.42–8.44 (m, 1H, Ar-H), 9.30 (s, 1H, thiadiazole ring proton), 9.87 (bs, 1H, NH); MS: *m/z* 436 (M^+), 438 (M^++2), 440 (M^++4); *Anal*. Calcd for $C_{17}H_{11}Cl_2N_5OS_2$: C, 46.79%; H, 2.54%; N, 16.05%. Found: C, 46.88%; H, 2.61%; N, 16.21%.

General procedure for *in vitro* antimicrobial screening. All newly synthesized compounds were evaluated for their antimicrobial activity by broth microdilution method according to the National Committee for Clinical Laboratory Standards [24]. The results were determined using minimum inhibitory concentration (MIC) values in μg/mL. Antibacterial activity was screened against two gram-positive (*S. aureus* MTCC 96 and *S. pyogenes* MTCC 443) and two gram-negative (*E. coli* MTCC 442 and *P. aeruginosa* MTCC 441) bacteria by using ampicillin as a standard antibacterial agent. Antifungal activity was screened against three fungal species (*C. albicans* MTCC 227, *A. niger* MTCC 282, and *A. clavatus* MTCC 1323) where griseofulvin was used as standard antifungal agent.

All MTCC cultures were collected from Institute of Microbial Technology, Chandigarh and tested against abovementioned known drugs. Mueller–Hinton broth was used as nutrient medium to grow and dilute the drug suspension for the test. Inoculum's size for test strain was adjusted to 10^8 colony-forming unit (CFU)/mL by comparing the turbidity. The control tube containing no antibiotic was immediately subcultured (before inoculation) by spreading a loopful evenly over a quarter plate of medium suitable for the growth of the test organism and put for incubation at 37°C overnight. The tubes were then incubated overnight. The MIC of the control organism was read to check the accuracy of the compound concentration. The MIC was defined as the lowest concentration of the antibiotic or test sample allowing no visible growth. All tubes showing no visible growth (same as control tube) were subcultured and incubated overnight at 37°C. The amount of growth from the control tube before incubation (which represents the original inoculums) was compared. Subcultures might show the following: similar number of colonies indicating bacteriostatic, a reduced number of colonies indicating a partial or slow bactericidal activity and no growth if the whole inoculum has been killed. The test must include a second set of the same dilutions inoculated with an organism of known sensitivity. DMSO was used as diluents to obtain the desired concentration of compounds to test upon standard bacterial strains. Each synthesized compound was diluted obtaining 2000 μg/mL concentrations as a stock solution. Serial dilutions were prepared

in primary and secondary screening. In primary screening, 500, 250, and 200 μg/mL concentrations of the synthesized compounds were taken. The compounds found active in primary screening were further tested in a second set of dilutions 100, 62.5, 50, and 25 μg/mL concentrations against all microorganisms.

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Spectrophotometric study of interaction of *o*-methylphenyl thiourea with iridium(III) and development of a precise determination method from hydrochloric acid media

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A spectrophotometric determination of iridium(III) is studied using *o*-methylphenyl thiourea (OMPT). Trivalent iridium has been determined spectrophotometrically as its 1:1 [iridium(III):OMPT] complex in aqueous hydrochloric acid media (0.6 M). The complex exhibits maximum absorption from 512 nm to 522 nm with molar absorptivity 0.663×10^3 L mol^{-1} cm^{-1} and sandell's sensitivity 0.289 µg of iridium(III) cm^{-2} ; beer's law is obeyed up to 300 µg/mL. The relative standard deviation for ten replicate samples at 40 µg/mL level of iridium(III) is found to be 0.54 and the limit of detection of the method is 0.018 µg/mL. Iridium(III)-OMPT complex is found stable for more than 8 days.

Keywords: Iridium, *o*-Methylphenyl thiourea, Spectrophotometry, Synthetic mixtures

Iridium, the member of platinum group metals, has widespread applications with the principal use as a hardening agent in platinum alloys. Iridium is used in high temperature applications such as crucibles, thermocouples, jewellery, dental alloys, electrical equipments, spark plugs, corrosion resistant glassware's and extrusion dies for high melting point glasses. Iridium in combination with platinum (platinum-iridium microelectrode) has been used as a biosensor for isocitrate dehydrogenase[1]. It is also being used as a permanent modifier in determination of lead in blood and urine[2]. Iridium is also being used as the endurable chemical modifier in electro thermal AAS determination of cadmium in water and vegetable food[3].

Owing to trace abundance, enhanced properties and large number of applications of iridium, it demands the need of highly efficient analytical procedure for determination of iridium at trace and ultra trace level and still is a challenge to the analyst. Various sophisticated techniques have been applied for determination of iridium such as atomic-laser induced fluorescence[4], isotope dilution inductively coupled plasma mass spectrometry[5], double focusing magnetic sector field inductively coupled plasma mass spectrometry[6], controlled potential coulometry[7] and voltammetry[8]. These advanced instrumental techniques lack with the drawbacks of hardly available instrumentation, high cost of working, maintenance and tedious analysis procedures. Comparatively spectrophotometric methods have applications even at trace concentrations with advantages such as high sensitivity, simple instrumentation, easy handling, low cost, quantitative recovery and precision of results with good accuracy.

A wide variety of reagents have been proposed for spectrophotometric determination of iridium by Marckzenko[9] and Sandell[10]. Extractive spectrophotometric determination was carried out using phenthrenequinone monoxime[11] and 3-hydroxy-2-methyl-1-phenyl-4-pyridone[12]. A large number of catalytic-kinetic spectrophotometric determination methods are reported[13-20]. Derivative spectrophotometry was used for determination of iridium[21-24]. Solvent extraction of iridium was carried out based on ion-association species formation by cyanex 923[25] and N-*n*-octylaniline[26]. Though large number of procedures is reported the major drawbacks harden their applicability. The catalytic kinetic methods have narrow beer's range, require highly controlled conditions and have restricted applications. The spectrophotometric methods lack with large number of interferences from foreign ions, complex formation after heating, long equilibration time, less stability of the complex and rarely available reagent.

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In our earlier study, the extraction spectrophotometric determination of palladium(II)[27] and rhodium(III)[28] using OMPT has been reported. In present communication, as the part of further extension of work, the extraction spectrophotometric determination method for iridium(III) is reported.

Limited procedures are available for direct spectrophotometric determination of iridium. The parameters for spectrophotometric determination of iridium in reported procedures are compared with the parameters of proposed method (Table 1)[29-36].

Experimental Procedure

Apparatus

A uv-visible spectrophotometer (Model SL-159 ELICO Limited, Hyderabad, India) with matched 10 mm quartz cells was used for absorbance measurements. Contech make electronic balance (Model CA-123) was used for weighing purpose. Calibrated glassware were used after getting cleaned by soaking in acidified solution of potassium dichromate followed by washing with soap water and rinsing two times with distilled water.

Reagents

All the reagents used were of analytical reagent grade. *O*-Methylphenyl thiourea (OMPT) was synthesized as per the method reported by Frank and Smith[37]. The ethanolic stock reagent solution (0.1 M) was prepared after dissolving 0.830 g of OMPT in ethanol and diluted up to mark with ethanol in a 50 mL volumetric flask. The working reagent solution (0.004 M) was prepared from the stock reagent solution using ethanol solvent.

The standard stock solution of iridium(III) was prepared after dissolving 1 g of iridium trichloride ($IrCl_3$) (Loba Chemie, Mumbai, India) in 15-20 mL hydrochloric acid (1 M). The solution was then diluted up to mark in a 250 mL volumetric flask with distilled water and standardized gravimetrically[38]. The working standard solution of iridium(III) (400 µg/mL) was prepared from the standard stock solution.

Table 1 — Comparison of present method with other spectrophotometric determination methods of iridium(III)

Reagent	λ_{max} nm	Condition	Beer's law validity range	Molar absorptivity L $mol^{-1}cm^{-1}$	Remark	References
Perazine dimalonate	515	Phosphoric acid media	Up to 24.0 µg mL^{-1}	9.93×10^3	Instant red radical cation formation, analysis of synthetic mixtures	28
5-(5-nitro-2-pyridylazo)-2,4-diamino toluene	564	*p*H 5.4 acetate buffer	0.0-0.1 µg mL^{-1}	5.1×10^4	Narrow beer's range	29
Potassium tetrahydrofurfurylxanthate	380 - 387	*p*H 6.5-9.5	3.5-23 µg mL^{-1}	5.013×10^3	Co-precipitation separation using microcrystalline naphthalene	30
N,N'-Dipyridylthiourea	335	Not given	Not given	1.89×10^4	Determination of osmium and iridium	31
1-Phenyl-4,4,6-trimethyl-(1h,4h)-pyrimidine-2-thiolates	430	Not given	3.8-4.2 mg L^{-1}	3.879×10^3	Simultaneous determination of palladium and iridium	32
2-Mercapto-4-methyl-5-phenylazopyrimidne	280	2.0 M nitric acid	0.6-9.0 µg mL^{-1}	0.95×10^4	Heating at 60°C for 5 min followed by 80-90°C, solid phase extraction, determination of tellurium, palladium and iridium	33
Malachite Green Crystal Violet	627 595	HCl media HCl media	Not given Not given	1.55×10^5 1.06×10^5	Flotation spectrophotometric determination, rhodium, platinum and palladium interferes	34
25,26,27,28-Tetrahydroxy-5,11,17,23-tetra-[4-(N-hydroxy-phenylazo]calyx [4]arenes	290	3.0 M nitric acid	1.0-13.0 µg mL^{-1}	2.03×10^4	Stirring at 25°C for 1 h, standing 30 min	35
O-Methylphenyl thiourea	512 - 522	0.6 M HCl	Up to 300 µg mL^{-1}	0.663×10^3	Wide Beer's range, instant complex formation, determination in both aqueous phase and organic phase possible, stability >8 days	Present study

Standard solutions of different metal ions for interference study were prepared after dissolving weighed quantity of their salts in distilled water or dilute hydrochloric acid. Standard solutions of anions were prepared after dissolving their respective alkaline metal salts in distilled water.

Procedure

An aliquot of solution containing 400 µg of iridium(III) was taken in a 10 mL volumetric flask and 4 mL OMPT (0.004 M) in ethanol was added. To this mixture hydrochloric acid and distilled water were added to make the solution 0.6 M in hydrochloric acid at 10 mL volume. The pink colored iridium(III)-OMPT complex formation takes place instantly at room temperature. This complex was measured in aqueous phase at 516 nm or the complex extracted into 10 mL chloroform was measured at 516 nm against the reagent.

Results and Discussion

Spectral and physico-chemical characteristics

Iridium(III) forms pink colored 1:1 [Iridium(III):OMPT] complex in 0.6 M hydrochloric acid media. This complex shows maximum absorption at 516 nm. The iridium(III)-OMPT complex is found stable for more than 8 days. The optimum conditions for the determination of iridium(III) have been established after studying the determination parameters such as reagent solvent, hydrochloric acid concentration, OMPT concentration, standing time, extraction solvent, equilibration time and interference of various foreign ions. Stoichiometry of the iridium(III)-OMPT complex has been ascertained from slope ratio method and is found to be 1:1 [Iridium(III):OMPT]. The spectral and physico-chemical characteristic along with the precision data is reported (Table 2).

Table 2 — Spectral and physico-chemical characteristics along with precision data of iridium(III)-OMPT complex

Parameter	Value
HCl concentration	0.6 M
Reagent solvent	Ethanol
Reagent concentration	4 mL, 0.004 M
λ_{max}	516 nm
Extraction solvent	Chloroform
Equilibration time	5 s
Molar absorptivity	0.663×10^3 L mol^{-1} cm^{-1}
Sandell's sensitivity	0.289 µg cm^{-2}
Beer's law range	up to 300 µg/mL
Ringbom's optimum range	40 to 280 µg/mL
Limit of detection	0.018 µg/mL
Relative standard deviation	0. 54%
Stoichiometry	1:1 [Iridium(III):OMPT]
Stability of complex	> 8 days
Correlation coefficient	0.99

Absorption spectra

The absorption spectra of iridium(III)-OMPT complex shows a constant maximum absorbance in the wavelength ranging from 512 nm to 522 nm (Fig. 1). The wavelength of maximum absorption (λ_{max}) is kept fixed as 516 nm.

Effect of acid concentration

The extraction of iridium(III) was studied using different mineral acid media such as hydrochloric, sulphuric, nitric and perchloric acid in the range 0.1-3.0 M acid concentration. There is no complex formation found in nitric acid media while the complexation occurs in other acids studied. The complete complexation of Ir(III)-OMPT complex with maximum absorbance is obtained in hydrochloric acid media in the range 0.6-3.0 M (Fig. 2). Hence, all further measurements are performed at 0.6 M hydrochloric acid concentration.

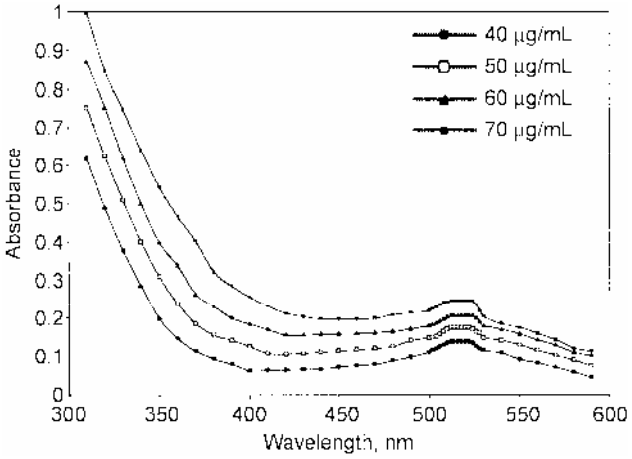

Fig. 1 — Absorption spectra of iridium(III)-OMPT complex

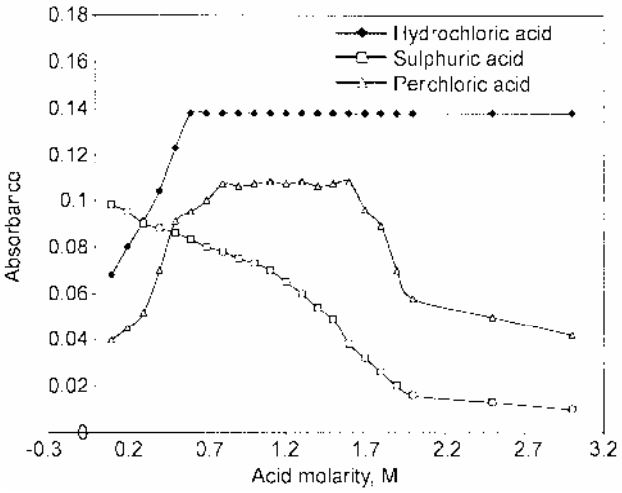

Fig. 2 — Effect of acid concentration on iridium(III)-OMPT complex formation

Effect of reagent solvent

The optimum range of reagent solvent such as ethanol, dimethylformamide, dimethyl sulphoxide and 1,4 dioxan was varied in terms of percentage keeping other optimum parameters constant. The results show that for each reagent solvent (up to 30% v/v) a slight turbid pink colored solution is obtained and for 30-70% solvent, a clear transparent phase is obtained with a constant absorbance value. Amongst the reagent solvents studied quantitative recovery with maximum absorbance value is obtained for ethanol. The 40% ethanol solvent is found fixed for the spectrophotometric determination study.

Choice of extraction solvent

Various extraction solvents were tested for extractive spectrophotometric determination of iridium(III). The percentage extraction of iridium is as follows *n*-butanol (62.3), n-butyl acetate (65.9), isoamyl alcohol (75.4), MIBK (78.9), 1,2-dichloroethane (79.7) and chloroform (99.9). Amongst the solvents studied complete extraction with maximum absorbance is obtained in chloroform.

Effect of standing time and order of addition

After adding the reagent (OMPT) to iridium(III) in hydrochloric acid media the iridium(III)-OMPT complex formation occurs instantly with no standing time or heating required for complex formation. Order of addition of either iridium(III), reagent (OMPT) or hydrochloric acid is not found so critical.

Effect of equilibriation time and stability of complex

A single step extraction is found sufficient for complete extraction of the complex from aqueous phase to organic phase, thus 5 s extraction time is recommended to ensure complete extraction of the complex.

Stability of the complex has been studied for more than 8 days with absorbance measurement carried out in the interval of 1 h each. The results show that the iridium(III)-OMPT complex is stable for more than 8 days.

Beer's law, molar absorptivity, Sandell's sensitivity and correlation coefficient

Beer's law is found to be obeyed in the concentration range up to 300 µg/mL (Fig 3). Ringbom's plot is drawn as log *C* of iridium(III) versus (1-*T*), where *T* is the transmittance (Fig. 4). This plot is sigmoid shape with linear segment at intermediate absorbance values 40-280 µg/mL.

The molar absorptivity and Sandell's sensitivity of the complex are 0.663×10^3 L mol^{-1} cm^{-1} and 0.289 µg cm^{-2} respectively. The correlation coefficient value with a independent variable as iridium(III) concentration in µg/mL and dependent variable as absorbance is found to be 0.99, indicating the clear linearity between these two values.

Effect of reagent concentration and stoichiometry of complex

The effect of reagent concentration was studied by varying OMPT concentration in ethanol from 0.0001 M to 0.1 M. The absorbance value increases from 0.0001 M to 0.004 M OMPT and further it remains constant.

The stoichiometry of iridum(III)-OMPT complex was ascertained from log-log plot, drawn between log of *o*-methylphenyl thiourea concentration (log *C*) and log of distribution ratio of iridium(III) (log *D*) at 0.5 M and 0.6 M hydrochloric acid concentration. The

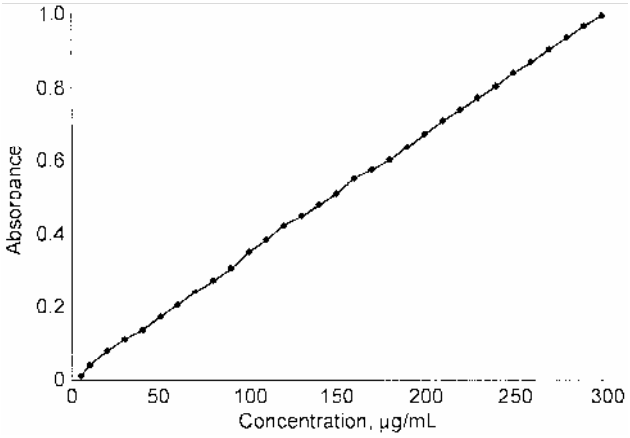

Fig. 3 — Validity of Beer's law

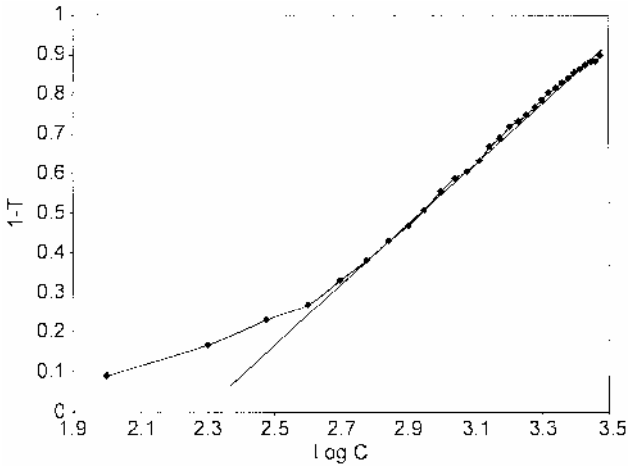

Fig. 4 — Ringbom's plot for optimum concentration of Ir(III)-OMPT complex

slope values at 0.5 M and 0.6 M hydrochloric acid are found to be 1.07 and 1.1 respectively (Fig. 5). It predicts the probable stoichiometry of extracted species as 1:1 [Iridium(III):OMPT] (Fig. 6).

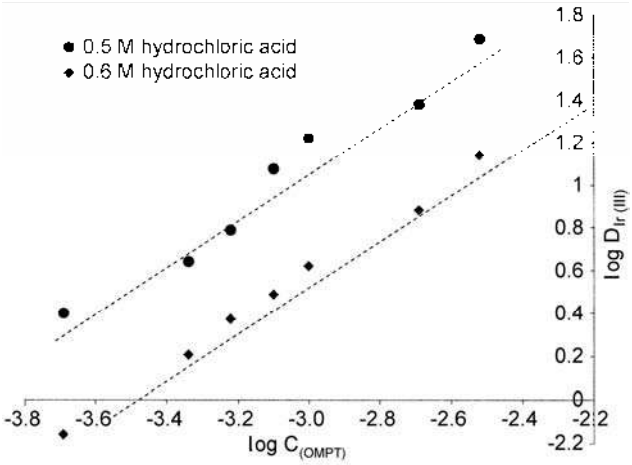

Fig. 5 — Plot of log C $_{(OMPT)}$ *vs* log D $_{Ir\ (III)}$

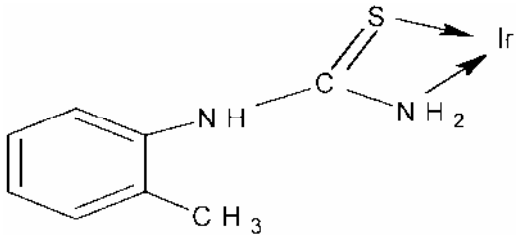

Fig. 6 — Probable structure of iridium(III):OMPT (1:1) complex

Precision, accuracy and detection limit

To access reproducibility of the results and accuracy of the method, absorbance measurement of ten identical solutions containing 400 µg iridium(III) was carried out as per the proposed method. Relative standard deviation is found to be 0.54%. The detection limit of iridium(III) for proposed method as the amount corresponding to thrice the standard deviation of blank value is 0.018 µg /mL.

Effect of foreign ions

Proposed method permits higher tolerance limits to various foreign ions. The only ions interfering in the method are palladium(II) and osmium(VIII) (Table 3). The tolerance limit value for various foreign ions is same for the direct spectrophotometric determination and extractive spectrophotometric determination of iridium(III) from hydrochloric acid media.

Applications of method

Analysis of synthetic mixtures corresponding to platinum-iridium alloy

Selectivity of the method was checked by applying it for the determination of iridium(III) in synthetic mixtures corresponding to platinum-iridium alloy (70:30). The composition of synthetic mixtures corresponding to platinum-iridium alloy was prepared in the laboratory and the amount of iridium(III) was determined following the recommended procedure. The results are in agreement with those obtained by atomic absorption spectrometer (Table 4).

Table 3 — Effect of foreign ions

Foreign ions	Added as	Tolerance limit, mg	Foreign ions	Added as	Tolerance limit, mg
Mn(II)	$Mncl_2.6H_2o$	15.0	Rh(III)	$RhCl_3$	3.2
Cd(II)	$Cdcl_2.2H_2o$	13.0	Ru(III)	$RuCL_3.6H_2O$	3.0
Fe(III)	$(NH_4)Fe(SO_4)_2.12H_2O$	5.5	Pt(IV)	$H_2PtCl_6.H_2O$	3.1
Hg(II)	$Hgcl_2$	5.0	Ce(IV)	$Ce(SO_4)_2.4H_2O$	4.0
Bi(III)	$BiCl_3$	12.0	Pb(II)	$PbCl_2$	18.0
Ni(II)	$NiCl_2.6H_2O$	6.5	V(V)	V_2O_5	40.0
Cu(II)	$CuSO_4.5H_2O$	8.0	U(VI)	$UO_2(CH_3COO)_2$	30.0
Al(III)	$AlCl_3.6H_2O$	25.0	Co(II)	$CoCl_2.6H_2O$	13.0
Cr(III)	$CrCl_3$	40.0	Ba(II)	$BaCl_2.6H_2O$	100
Zn(II)	$ZnSO_4.7H_2O$	20.0	Ca(II)	$CaCl_2.2H_2O$	100
Se(IV)	SeO_2	10.0	Sr(III)	$SrCl_3.6H_2O$	100
La(III)	$LaCl_3.7\ H_2O$	25.0	Tl(III)	Tl_2O_3	6.0
Li(I)	LiCl	16.0	Bromide	KBr	100
Ti(III)	$(Ti_2SO_4)_3$	18.0	Fluoride	NaF	100
Mg(II)	$MgCl_2.6H_2O$	11.0	Phosphate	Na_3PO_4	100
Sn(II)	$SnCl_2.2H_2O$	4.0	Sulphate	K_2SO_4	100
Ga(III)	$GaCl_3$	8.5	Succinate	$(CH_3COONa)_2.6H_2O$	100
Au(III)	$HAuClO_4.H_2O$	3.5	Citrate	$C_6H_8O_7.H_2O$	100
Mo(VI)	$(NH_4)_5MO_7.2H_2O$	14.5	Malonate	$CH_2(COONa)_2$	100
Sb(III)	Sb_2O_3	3.5	Tartrate	$(CHOH:COOH)_2$	100
W(VI)	$Na_2WO_4.2H_2O$	20.0	Oxalate	$(COOH)_2.2H_2O$	100
In(III)	$InCl_3.4H_2O$	6.0	E.D.T.A.	Na_2EDTA	100

Table 4 — Separation of iridium(III) from synthetic mixture corresponding to platinum-iridium alloy

Composition	Amount of iridium(III) µg			Relative standard deviation %
	Taken	Found		
		PM*	AAS	
Platinum-iridium (70:30)	400	397.84	398.90	0.42
	500	497.85	496.56	0.57
	600	596.40	597.64	0.48

* Average of four determinations, PM- Present method, AAS-Atomic absorption spectrometer.

Table 5 — Analysis of binary synthetic mixtures

Metal ions	Amount µg	Recovery[a] %	Relative standard deviation, %	Chromogenic ligand
Ir(III)	400	98.81	0.84	OMPT
Zn(II)	20	99.91	0.21	Dithizone[b]
Ir(III)	400	99.64	0.59	OMPT
Mn(II)	300	99.72	0.38	Permanganate[b]
Ir(III)	400	99.91	1.03	OMPT
W(VI)	300	99.80	0.28	Thiocynate[b]
Ir(III)	400	99.46	0.72	OMPT
Cu(II)	40	99.51	0.25	Dithizone[b]
Ir(III)	400	99.82	0.41	OMPT
Co(II)	500	99.77	0.31	Thiocynate[b]
Ir(III)	400	99.82	0.73	OMPT
Fe(III)	75	99.94	0.48	1,10-phenenthroline[b]

[a]Average of four determinations, [b]Reference 9.

Separation of iridium(III) from binary synthetic mixtures

The proposed method has dual application as direct spectrophotometric determination and extractive spectrophotometric determination using chloroform solvent, the merit of extractive spectrophotometric determination was applied for the separation of iridium(III) from associated metal ions such as Zn(II), Mn(II), W(VI), Cu(II), Co(II), Fe(III), Hg(II), Ni(II) and Au(III). After quantitative extraction of iridium(III) the aqueous phase was evaporated to moist dryness followed by 3 mL concentrated hydrochloric acid treatment, again evaporated to moist dryness and the residue obtained was cooled, dissolved in distilled water and the added metal ions were determined by standard procedures[9] (Table 5).

Table 6 — Separation of iridium(III) from multicomponent synthetic mixtures

Composition, µg	Recovery* %	Relative standard deviation %
Ir(III) 400; Ni(II) 50; Co(II) 50; Hg(II) 50	99.21	1.03
Ir(III) 400; Fe(III) 50; Mn(II) 50; Zn(II) 10	99.64	0.83
Ir(III) 400; Cu(II) 40; W(VI) 50; Co(II) 50	99.86	0.42
Ir(III) 400; Au(III) 50; Zn(II) 10; Ni(II) 50	99.92	0.34
Ir(III) 400; Au(III) 50; Hg(II) 50; Co(II) 50	99.86	0.42
Ir(III) 400; Ni(II) 50; Mn(II) 50; Co(II) 50	99.46	0.72
Ir(III) 400; Zn(II) 10; Hg(II) 50; W(VI) 50	99.64	0.59
Ir(III) 400; Hg(II) 50; Co(II) 50; Fe(III) 50	99.64	0.59
Ir(III) 400; Au(III) 50; Cu(II) 40; Mn(II) 50	99.28	0.60
Ir(III) 400; Zn(II) 10 ; Ni(II) 50; Fe(III) 50	99.10	0.73
Ir(III) 400; Co(II) 50 ; Fe(III) 50 ; W(VI) 50	99.46	0.73
Ir(III) 400; W(VI) 50 ; Hg(II) 50; Mn(II) 50	99.64	0.84
Ir(III) 400; Cu(II) 40 ; Zn(II) 10; Co(II) 50	99.82	0.42

* Average of four determinations.

Separation of iridium(III) from synthetic multicomponent mixtures

Synthetic multicomponent mixtures with varying composition of associated metal ions and fixed iridium(III) content (400 µg) were taken and the recommended procedure was followed. Iridium(III) was separated quantitatively and the results are found in a good agreement with the amount of iridium(III) present (Table 6).

Conclusion

O-Methylphenyl thiourea (OMPT) is a sensitive and selective reagent for spectrophotometric determination of iridium(III). Method merits with determination at lower hydrochloric acid concentration (0.6 M). The determination of iridium is possible in both aqueous and organic phase. The iridium(III)-OMPT complex is highly stable. Instant complex formation permits rapid determination at room temperature.

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Rapid and selective determination of osmium(IV) by UV-visible spectrophotometry using *o*-methylphenyl thiourea as a chromogenic chelating ligand: sequential separation of osmium(IV), rhodium(III) and platinum(IV)

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The objective of this research work was to develop a simple, highly sensitive and precise method for spectrophotometric determination of osmium(IV). *O*-Methylphenyl thiourea (OMPT) coordinates with osmium(IV) as a 1:1 (osmium(IV)–OMPT) complex in hydrochloric acid media (0.8 mol l^{-1}). The novelty of the investigated method is instant complex formation at room temperature with no need of heating or standing. The complex is stable for more than 8 days. The method is applicable over a wide linearity range (up to 110 µg ml^{-1}). A low reagent concentration is required (2 ml, 0.009 mol l^{-1} in ethanol). The complex exhibits maximum absorption in the range of wavelength 510–522 nm and 514 nm was selected for further study. The molar absorptivity was 1.864×10^3 l mol^{-1} cm^{-1}, Sandell's sensitivity was 0.102 µg of osmium(IV) cm^{-2}. Proposed method was successfully applied for separation and determination of osmium(IV) from binary and ternary synthetic mixtures containing associated metal ions. A scheme for mutual separation of osmium(IV), rhodium (III) and platinum(IV) is developed.

Keywords: osmium(IV); spectrophotometry; ternary mixture separation

1. Introduction

Osmium is a rare element found in metallic state together with other platinum group metals and coinage metals. Its abundance is 5 µg kg^{-1} in the earth's crust [1]. Osmium has a strong oxidising property, toxic nature, minimum natural abundance and widespread applications. Hence, it demands a simple method for the determination of osmium content in various sample matrices.

Many reagents are reported for determination of osmium using spectrophotometry. The 3-methyl-2,6-dimercapto-1,4-thiopyrone [2] forms a complex with osmium. The laborious and lengthy procedure hardens the applicability of this method. Indirect spectophotometric determination is reported based on the oxidation effect of osmium on iodine [3]. Method suffers from large number of interferences. Osmium and ruthenium were determined simultaneously by second derivative spectrophotometry [4] and third derivative spectrophotometry [5]. Methods suffer with determination in concentrated perchloric acid and sulphuric acid. Osmium was determined in the presence of other platinum group metals with mono azodyes [6]. Method needs heating in a boiling water bath. Osmium was determined based on its catalytic property.

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Different organic species were oxidised by osmium and the osmium content was determined using gallocyanine [7], Carminic acid [8], Methylene blue [9], Janus green [10], diantipyrlmethane derivatives [11], tribromineo-arsenazo-ascorbic acid [12], basic dyes: methylene blue, butyl rhodamine and nile blue [13], chlorophosphonazo [14] and diantipyryl-(p-dimethylamino)–phenylmethane [15]. These reagents are sensitive, but their determination methods suffer from drawbacks such as a shorter pH range for determination, low molar absorptivity, interferences from associated metal ions, less stability of the complex, complex formation after heating and need of highly controlled determination conditions.

In the present investigation a new reagent *o*-methylphenyl thiourea (OMPT) is studied which forms a stable 1:1 complex with osmium. The complex formation is instant with addition of reagent (2 ml, 0.009 mol l^{-1}) to osmium (IV) (200 μg) in 0.8 mol l^{-1} hydrochloric acid media. The merit of absorbance measurements in both aqueous phase and organic phase signifies the applicability of the method for the separation and determination of osmium from associated metal ions present in natural occurrence along with osmium. The investigated method has positive merits compared to reported methods for spectrophotometric determination of osmium and is shown in Table 1 [16–26].

2. Experimental

2.1 *Apparatus and glassware*

A UV-visible spectrophotometer (Elico make model, Mumbai, SL-159) with matched 10 mm quartz cells was used for absorbance measurements. Contech make electronic balance model CA-123 was used for weighing purpose. Calibrated glassware was used and was cleaned by soaking in acidified solution of potassium dichromate followed by washing with soap water and rinsing two times with distilled water.

2.2 *Chemicals and reagents*

2.2.1 *O-Methylphenyl thiourea solution*

O-Methylphenyl thiourea (OMPT) was synthesised as per the method reported by Frank and Smith [27] and recrystallised from ethanol solvent. The purity of OMPT was confirmed by taking its ^{1}HNMR spectrum (Figure 1).

^{1}H NMR Data: Proton resonance assignment for the pure product was made using tetramethylsilane (TMS) as an internal standard. ^{1}H NMR (400 MHz, $CDCl_2$); 2.33 (3H, singlet, CH_3); 5.68–6.24 (2H, broad singlet, NH_2); 7.23–7.32 (4H, multiplet, Ar-H); 7.92 (1H, broad singlet, NH).

The structural formula of OMPT is given in Figure 2. The stock solution of OMPT (0.1 mol l^{-1}) was prepared by dissolving 0.830 g OMPT in 20 ml ethanol and was made up to mark in a 50 ml calibrated volumetric flask with ethanol solvent. The working reagent solution (0.009 mol l^{-1}) was prepared from the stock reagent solution using ethanol solvent.

2.2.2 *Foreign ion solution*

Standard solutions of different metal ions for interference study were prepared in distilled water or dilute hydrochloric acid. Standard solutions of different anions were prepared after dissolving their respective alkaline metal salts in distilled water. The synthetic mixtures containing osmium (IV) and other commonly associated metal ions were prepared by combining their definite compositions together.

Table 1. Comparison of present method with other spectrophotometric determination methods of osmium (IV).

Reagent	λmax (nm)	Condition	Beer's Law validity range	Molar Absorptivity ($l\ mol^{-1}\ cm^{-1}$)	Remark	Reference
2,4-Dimethoxybenzaldehyde isonicotinylhydrazone-2-thione	393	pH 5.0	0.951–11.412 μg ml^{-1}	1.48×10^4	Determination in the presence of surfactant, limited Linearity range for determination	16
Crystal violet	600	6.0 mol l^{-1} HCl	0.04–1.0 μg ml^{-1}	2.0×10^5	Heating 1.5 h, lengthy procedure of precipitation, flotation and determination, no interfering ions studied except ruthenium	17
Rhodamine B	560	0.5 mol l^{-1} HCl	0.05–0.4 μg ml^{-1}	4.1×10^5	Separation by flotation, limited Linearity range for determination	18
Congo red	340	pH 3.5	0.09–6.7 mg l^{-1}	–	Limited linearity range for determination	19
Ethyl thiourea + Thiocytochrome complex [$NH_4(Cr(CNS)_4$(aniline)]	535 to 540	5 ml concentrated hydrochloric acid	68.4–548 mg l^{-1}	7.93×10^2	5 ml concentrated hydrochloric acid used, laborious lengthy procedure of flotation, precipitation, filtration, dissolution and determination, no applications studied	20
4-(2-pyridylazo)–resorcinol	540	2.5 ml, pH 6.5 phosphate buffer	0–11 μg ml^{-1}	2.4×10^4	Heating at 50°C for 30 min, cooling 5 min, associated metal ions interfere, determination in the presence of mixed surfactant	21

(*continued*)

Table 1. Continued.

Reagent	λmax (nm)	Condition	Beer's Law validity range	Molar Absorptivity (l mol^{-1} cm^{-1})	Remark	Reference
Paragallopthalein + Hydrogen peroxide	535	2 ml, pH 7.2, sorenson buffer	0–0.5 ng ml^{-1}	2.5×10^9	Heating at 60°C for 40 min, cooling 10 min, higher molar absorptivity but very limited Linearity range for determination, presence of surfactant Brij 35	22
Ethylene thiourea	490	pH 1.0	0.03–3.0 μg ml^{-1}	6.87×10^4	Limited linearity range for determination, characterisation of solid complex	23
D-Arabinotetrahydroxybutylimidazoline-2-thione	530	0.01–3.6 mol l^{-1} H_2SO_4	1.0–47.0 μg ml^{-1}	4.5×10^3	Sensitive determination, sulphuric acid media	24
Orange G	540	0.2 mol l^{-1} acetate buffer, pH 5.8	0.01–7.0 μg ml^{-1}	1.1×10^4	Heating 30 min, limited linearity range for determination	25
5-Chloro-2-hydroxythiobenzhydrazide	510	pH 2.5–5.0	1.8–14.4 μg ml^{-1}	1.056×10^4	Standing 30 min, complex precipitation using naphthalene (20% V/V), limited Linearity range for determination	26
O-Methylphenyl thiourea	510 to 522	0.8 mol l^{-1} HCl	Up to 110 μg ml^{-1}	1.86×10^3	Selective and sensitive, wide linearity range, instant complexation, stability of complex >8 days, absorbance measurement in both aqueous and organic phase	Present method

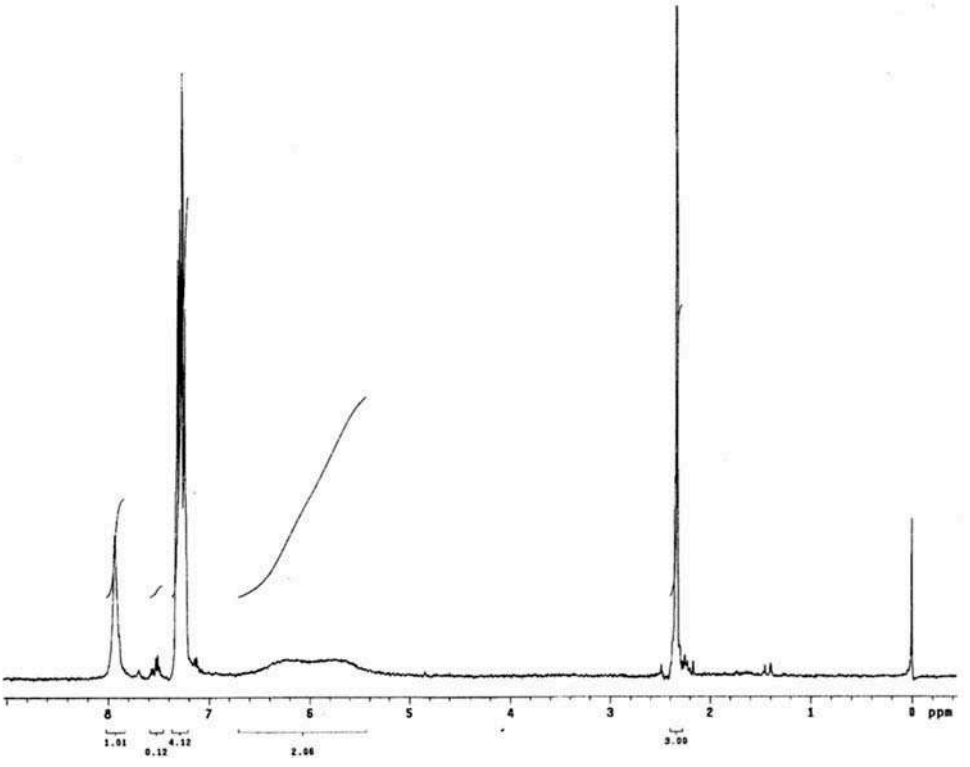


Figure 1. ^{1}H NMR Spectrum of *o*-Methylphenyl thiourea (OMPT).

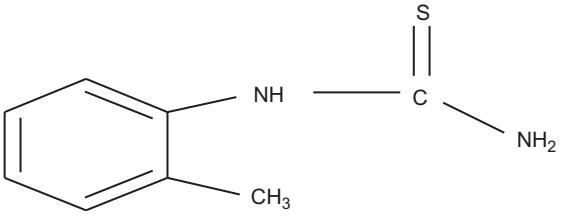


Figure 2. Structural formula of OMPT.

2.2.3 *Osmium(IV) solution*

A standard stock solution of osmium(IV) was prepared after dissolving 1.0 g osmium tetroxide (Loba Chemie Pvt Ltd, Mumbai, India, Purity = 99.9%) after careful crushing a hermetically closed glass ampoule containing the osmium tetroxide in 100 ml, 1.0 mol l^{-1} hydrochloric acid in a beaker under cover. This solution was made up to mark in a 200 ml volumetric flask with 1.0 mol l^{-1} hydrochloric acid following the reported method [28]. This solution was standardised gravimetrically [29]. Quantitative conversion of osmium into the stable $OsCl_6^{2-}$ as H_2OsCl_6 species was carried out by heating the solution for a minimum of 20 min at 90–100°C [5, 30]. Standard working solutions of osmium(IV) was prepared by dissolving an aliquot of osmium(IV) initial stock solution in 1.0 mol l^{-1} hydrochloric acid. Osmium(IV) present in the form $OsCl_6^{2-}$ does not undergo hydrolysis at room temperature in the hydrochloric acid media when the hydrochloric acid concentration is greater than 0.5 mol l^{-1} [31].

2.3 *General analytical procedure*

In a 10 ml volumetric flask an aliquot of solution containing osmium(IV) (200 μg) was taken. A 2 ml, 0.009 mol l^{-1} OMPT in ethanol was added to the volumetric flask containing osmium(IV). To this mixture 0.7 ml hydrochloric acid was added and diluted up to mark with distilled water, making the solution 0.8 mol l^{-1} with respect to hydrochloric acid at 10 ml volume. The instant pink-coloured osmium(IV)–OMPT complex formation takes place at room temperature and it was measured at 514 nm against the reagent blank. The absorbance measurement of the complex was also possible in the chloroform solvent. The osmium(IV)–OMPT complex was extracted into 10 ml chloroform and the absorbance was measured at 514 nm against the reagent blank.

3. Results and discussion

3.1 *Spectral characteristics*

The pink coloured osmium (IV)–OMPT complex shows same absorbance value in both the aqueous phase before extraction and the organic phase (chloroform) after extraction with maximum absorbance value in the range of 510–522 nm both in aqueous and organic phase respectively. Thus 514 nm was fixed as the wavelength of maximum absorbance (λ_{max}) for further absorption measurements (Figure 3).

The spectral and physico-chemical characteristic of the osmium(IV)–OMPT complex is given in Table 2.

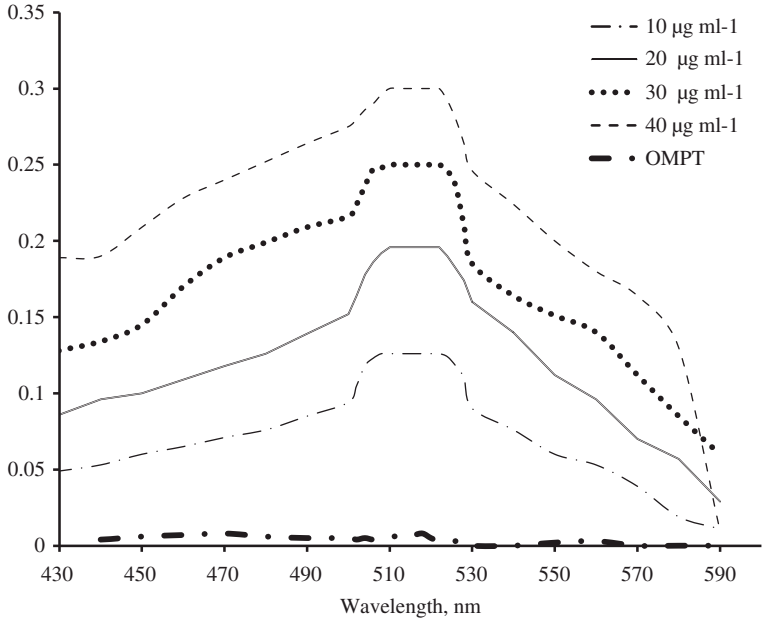


Figure 3. Absorption spectra: C (osmium(IV)) = 10 μg ml^{-1}, 20 μg ml^{-1}, 30 μg ml^{-1}, 40 μg ml^{-1}; C (HCl) = 0.8 mol l^{-1}, V (OMPT) = 2 ml, 0.009 mol l^{-1}.

Table 2. Spectral and physico-chemical characteristics along with precision data of osmium (IV)–OMPT complex.

Spectral characteristics and precision	Parameters
hydrochloric acid concentration	0.8 mol l^{-1}
reagent solvent	Ethanol
reagent concentration	2 ml, 0.009 mol l^{-1}
extraction solvent	Chloroform
equilibration time	single step extraction
λ_{max}	514 nm
molar absorptivity	1.864×10^3 l mol^{-1} cm^{-1}
Sandell's sensitivity	0.102 μg cm^{-2}
Beer's law range	up to 110 μg ml^{-1}
Ringbom's optimum range	27.54–91.20 μg ml^{-1}
limit of detection	0.60 μg ml^{-1}
limit of quantitation	1.79 μg ml^{-1}
relative standard deviation	0. 54%
stoichiometry of the complex	1:1 (Os(IV):OMPT)
stability of complex	> 8 days
correlation coefficient	0.99

3.2 *Effect of hydrochloric acid*

The osmium(IV)–OMPT complex formation takes place in hydrochloric acid, perchloric acid and sulphuric acid media at room temperature. In nitric acid media a faint yellow-coloured solution was obtained with no absorbance at 514 nm. Among the mineral acids studied, complete complexation and maximum absorbance was obtained in hydrochloric acid media. The concentration of hydrochloric acid was varied from 0.1 to 7.0 mol l^{-1}. A constant and maximum absorbance value was obtained from 0.8 to 3.2 mol l^{-1} and further at higher hydrochloric concentration above 3.2 mol l^{-1} absorbance decreases rapidly with negligible absorbance at 5.5 mol l^{-1} and above 5.5 mol l^{-1} there was no complex formation. Thus 0.8 mol l^{-1} HCl was fixed for further study.

3.3 *Effect of reagent solvent*

Various reagent solvents were studied viz: ethanol, DMF, DMSO and 1,4 dioxan. The optimum range was varied in terms of percentage from 4% to 40% (V/V). Maximum absorbance was obtained in ethanol solvent and the absorbance value remained constant over the range of 4–28% (V/V) ethanol. Hence, 20% (V/V) ethanol in aqueous phase was fixed for further investigations. In the presence of 1,4 dioxan higher absorbance values were obtained while in the presence of DMF and DMSO the complex formation was poor (Figure 4).

3.4 *Effect of o-methylphenyl thiourea concentration and order of addition*

The OMPT concentration was varied from 0.002 to 0.2 mol l^{-1} (2 ml in ethanol used). The absorbance value increases up to 0.008 mol l^{-1} OMPT and further remains constant. To ensure complete complexation 2 ml, 0.009 mol l^{-1} OMPT in ethanol was used for further study.

The order of addition of the reagent or osmium(IV) or hydrochloric acid shows no any adverse effect on the complex formation and thus no effect on the absorbance of the complex.

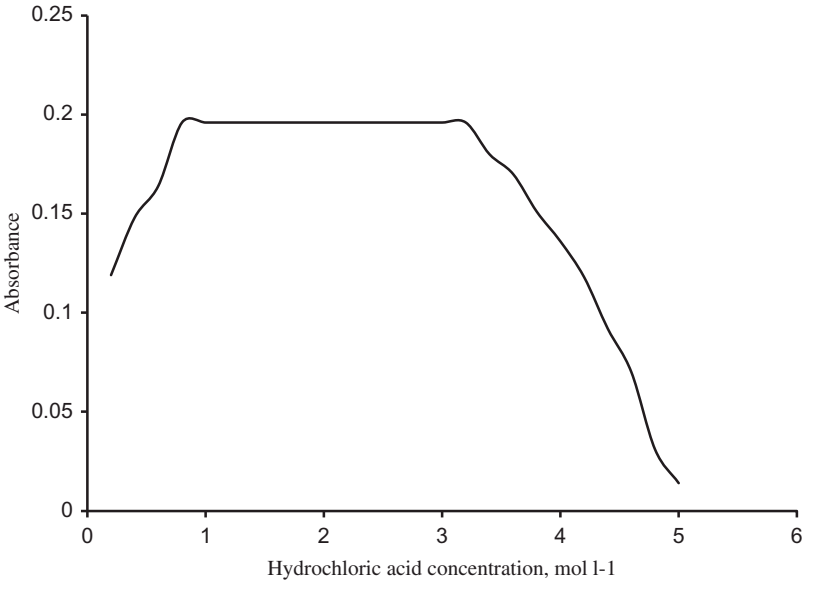


Figure 4. Effect of reagent solvent %: C (osmium(IV)) = 20 μg ml^{-1}; C (HCl) = 0.8 mol l^{-1}, V (reagent solvent) = 4 % to 40 % in ethanol; λ_{max} = 514 nm.

3.5 *Choice of extraction solvent*

The osmium(IV)–OMPT complex shows the same absorbance values in the aqueous phase before extraction and in the chloroform solvent after extraction. The percentage extraction (%E) increases in the order as n-butanol (55.10) < n-butyl acetate (55.61) < isoamyl alcohol (61.22) < MIBK (66.84) < 1,2 dichloroethane (72.45) < chloroform (99.99). There was no extraction in benzene, toluene, xylene and carbon tetrachloride.

3.6 *Stability of the complex*

The recommended method was followed for determination of osmium(IV) (200 μg). The absorbance value was determined with a time interval of 1 h each. The complex was stable for more than 8 days with no change of absorbance.

3.7 *Beer's law, molar absorptivity, Sandell's sensitivity, correlation coefficient*

Beer's law was obeyed over the concentration range up to 110 μg ml^{-1} (Figure 5). Ringbom's plot was drawn as log C of osmium(IV) concentration (C) versus (1-T) where T is the transmittance (Figure 6). The plot was sigmoid shape with a linear segment at intermediate absorbance values of 27.54–91.20 μg ml^{-1} and with a slope value of 0.62. Molar absorptivity and Sandell's sensitivity of the complex are 1.864×10^3 L mol^{-1} cm^{-1} and 0.102 μg cm^{-2} respectively. The correlation coefficient values of osmium(IV)–OMPT complex with an independent variable as concentration in μg ml^{-1} and dependent variable as absorbance was found to be 0.99. The slope and intercept for the best fitted line are 0.00576 and 0.074 respectively. Hence the content of osmium(IV) in real samples can be determined using the straight line equation $Y = 0.00576\,X + 0.074$.

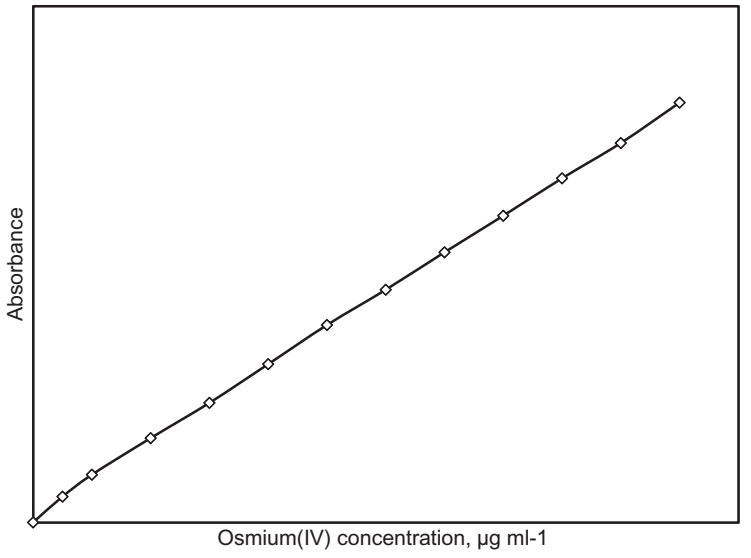


Figure 5. Validity of Beer's law: C (osmium(IV)) = 0.0 to 110 µg ml^{-1}; C (HCl) = 0.8 mol l^{-1}, V (OMPT) = 2 ml, 0.009 mol l^{-1}; λ_{max} = 514 nm.

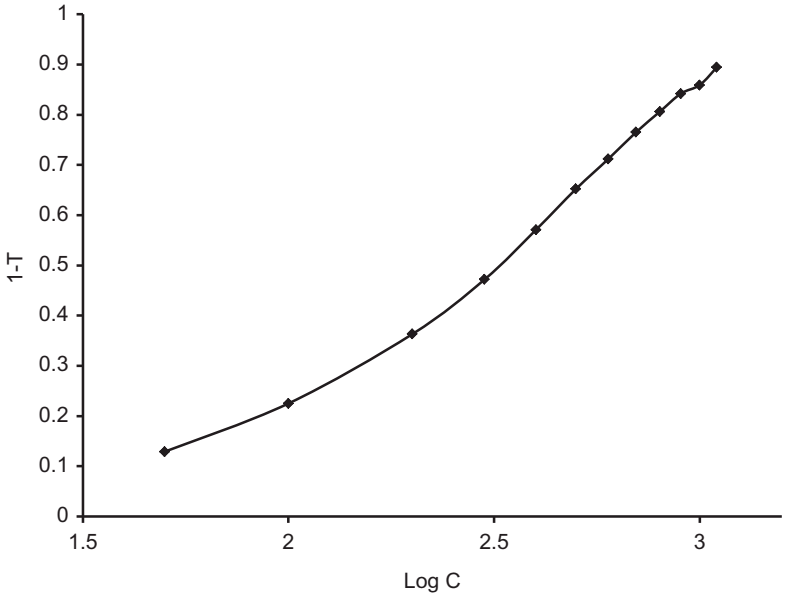


Figure 6. Ringbom's plot for optimum concentration of Os(IV)-OMPT Complex C (osmium (IV)) = 0.02 to 110 µg ml^{-1}; C (HCl) = 0.8 mol l^{-1}, V (OMPT) = 2 ml, 0.009 mol l^{-1}; λ_{max} = 514 nm.

3.8 *Stoichiometry of the complex*

Stoichiometry of osmium(IV)–OMPT complex was ascertained using slope ratio method by plotting the graph of log $C_{(OMPT)}$ against log $D_{(Os(IV))}$ at 0.4, 0.6 and 0.8 mol l^{-1} hydrochloric acid concentration gives the slope values as 1.20, 1.09 and 0.80 respectively (Figure 7). Hence

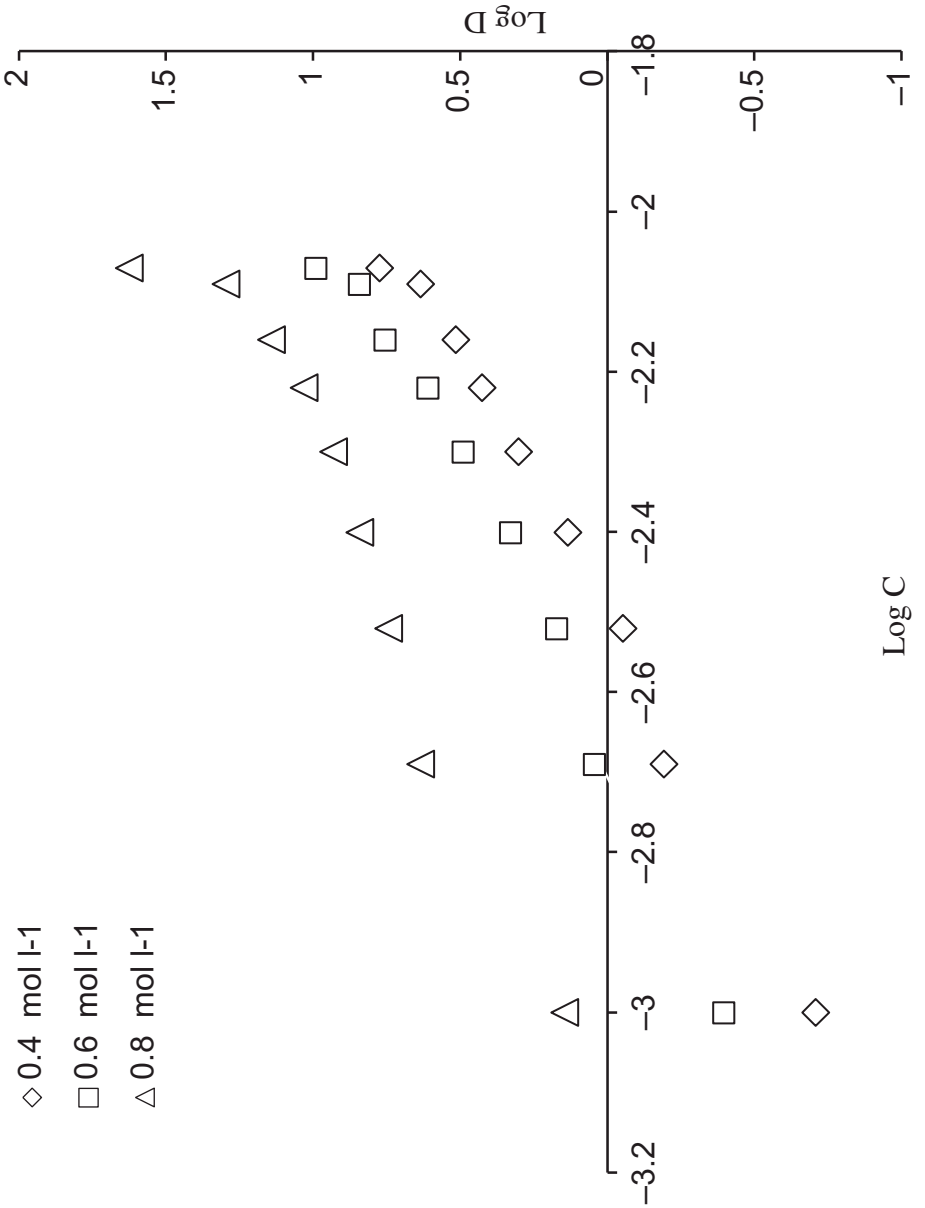


Figure 7. Plot of log $D_{Os[\ VIII]}$ Vs log $C_{[OMPT]}$: C (osmium(IV)) = 20 µg ml^{-1}; C (HCl) = 0.4 mol l^{-1}, 0.6 mol l^{-1}, 0.8 mol l^{-1}, V (OMPT) = 2 ml, 0.009 mol l^{-1}; λ_{max} = 514 nm.

the probable stoichiometry of the extracted species is 1:1 (Os(IV):OMPT). This stoichiometry of the complex was also checked by mole ratio method (Figure 8) and job's continuous variation method (Figure 9).

OMPT act as a multidentate ligand with two nitrogen atoms on either side of thiocarbonyl group and the sulphur atom of the thiocarbonyl group. They are potentially capable of forming coordinate bond through both sulphur and nitrogen. The methyl group attached at the ortho position to the thiourea group increases the intensity of absorption. It acts as an auxochrome and deepens the colour after complex formation. Sulphur from thio group (-C = S) and nitrogen from amine group ($-NH_2$) coordinate with osmium(IV) to form a 1:1 (osmium(IV):OMPT) complex. Based on this investigation probable structure recommended for the complex is reported in Figure 10.

3.9 *Precision, accuracy, limit of detection and limit of quantitation*

Ten identical solutions containing osmium(IV) (200 µg) were taken and the recommended procedure was followed. The relative standard deviation for ten identical determinations was 0.54%. The limit of detection (LOD) and limit of quantitation (LOQ) was determined using the formula:

$$\mathrm{LOD} = 3.3\,\mathrm{S}/\mathrm{b}$$

$$\mathrm{LOQ} = 10\,\mathrm{S}/\mathrm{b}$$

where S is the standard deviation of the intercept of the regression line and b is the slope. The LOD and LOQ values were 0.60–1.79 µg ml^{-1} respectively.

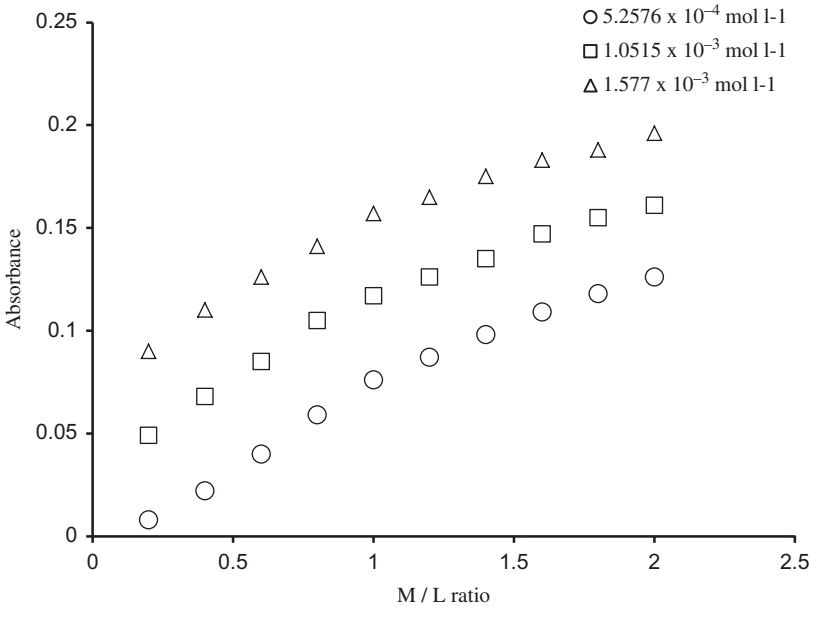


Figure 8. Mole ratio method: C (osmium(IV)) = C (OMPT) = 5.2576×10^{-4} mol l^{-1}, 1.0515×10^{-3} mol l^{-1}, 1.577×10^{-3} mol l^{-1}; C (HCl) = 0.8 mol l^{-1}; λ_{max} = 514 nm.

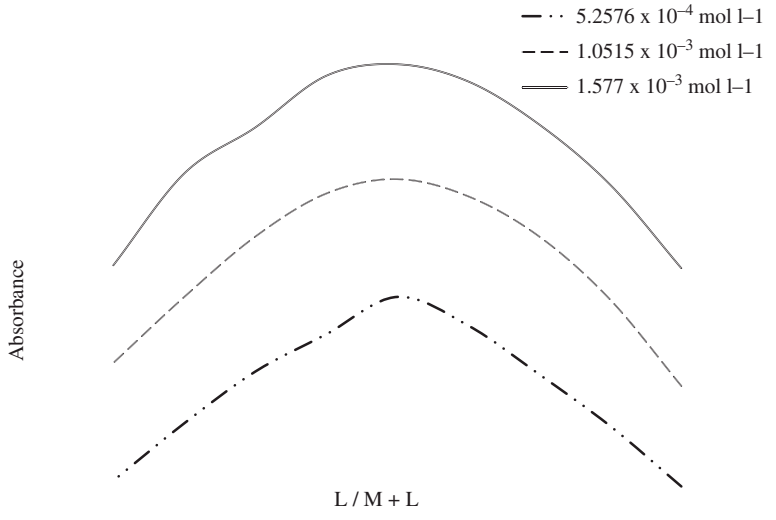


Figure 9. Job's continuous variation method : C (osmium(IV)) = C (OMPT) = 5.2576 × 10^{-4} mol l^{-1}, 1.0515 × 10^{-3} mol l^{-1}, 1.577 × 10^{-3} mol l^{-1}; C (HCl) = 0.8 mol l^{-1}; λ_{max} = 514 nm.

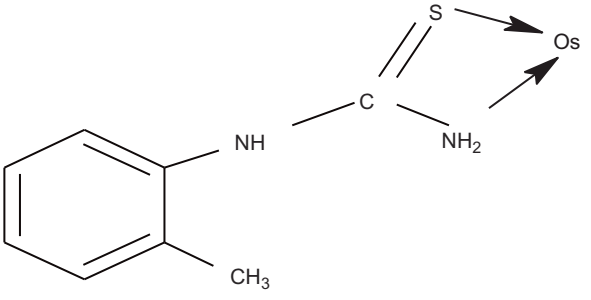


Figure 10. Probable structure of osmium(IV)-OMPT (1:1) complex.

3.10 *Effect of foreign ions*

Effects of various foreign ions on the spectrophotometric determination of osmium(IV) was studied (maximum level tested was 50–100 mg for cations and anions respectively). Selectivity of the method was examined by determination of the osmium(IV) content (200 μg) in the presence of the added cations and anions within a relative error of ±2%. The enveloped method has a maximum tolerance limit to various foreign ions. The two elements interfering in the determination were palladium(II) and iridium(III) (Table 3).

4. Applications of the proposed method

4.1 *Separation of osmium(IV) from binary synthetic mixtures*

Proposed method was applied for separation of osmium(IV) from associated metal ions Viz : Zn (II), Mn(II), Pb(II), Mo(VI), W(VI), Cu(II), Co(II), Fe(II), Bi(III), Cd(II), Hg(II), Ni(II) and Au (III). Osmium(IV) was separated from these metal ions as per recommended procedure. After quantitative extraction of osmium(IV) the aqueous phase was evaporated to moist dryness

Table 3. Effect of foreign ions: total osmium(IV) content is 200 µg.

Foreign Ions	Added as	Tolerance limit (mg)	Foreign Ions	Added as	Tolerance limit (mg)
Mn(II)	$MnCl_2.6H_2o$	15.0	Rh(III)	$RhCl_3$	3.2
Cd(II)	$CdCl_2.2H_2o$	25.0	Ru(III)	$RuCl_3.6H_2O$	2.6
Fe(III)	$(NH_4)Fe(SO_4)_{2..}12H_2O$	8.5	Pt(IV)	$H_2PtCl_6.H_2O$	3.0
Hg(II)	$HgCl_2$	14.0	Ce(IV)	$Ce(SO_4)_2.4H_2O$	3.5
Bi(III)	$BiCl_3$	15.0	Pb(II)	$PbCl_2$	15.0
Ni(II)	$NiCl_2.6H_2O$	12.0	V(V)	V_2O_5	30.0
Cu(II)	$CuSO_4.5H_2O$	18.0	U(VI)	$UO_2(CH_3COO)_2$	35.0
Al(III)	$AlCl_3.6H_2O$	34.0	Co(II)	$CoCl_2.6H_2O$	10.0
Cr(III)	$CrCl_3$	50.0	Ba(II)	$BaCl_2.6H_2O$	100
Zn(II)	$ZnSO_4.7H_2O$	65.0	Ca(II)	$CaCl_2.2H_2O$	100
Se(IV)	SeO_2	35.0	Sr(III)	$SrCl_3.6H_2O$	100
La(III)	$LaCl_3.7H_2O$	35.0	Tl(III)	Tl_2O_3	7.0
Li(I)	LiCl	20.0	Bromide	KBr	100
Ti(III)	$(Ti_2SO_4)_3$	14.0	Fluoride	NaF	100
Mg(II)	$MgCl_2.6H_2O$	15.0	Phosphate	Na_3PO_4	100
Sn(II)	$SnCl_2.2H_2O$	3.5	Sulphate	K_2SO_4	100
Ga(III)	$GaCl_3$	6.5	Succinate	$(CH_3COONa)_{2.}6H_2O$	100
Au(III)	$HAuClO_4.H_2O$	3.5	Citrate	$C_6H_8O_7.H_2O$	100
Mo(VI)	$(NH_4)_5MO_7.2H_2O$	25.0	Malonate	$CH_2(COONa)_2$	100
Sb(III)	Sb_2O_3	1.5	Tartrate	$(CHOH:COOH)_2$	100
Be(II)	$BeSO_4.4H_2O$	10.0	Oxalate	$(COOH)_2.2H_2O$	100
In(III)	$InCl_3.4H_2O$	7.0	E.D.T.A.	Na_2EDTA	100

followed by addition of 3 ml concentrated hydrochloric acid. The residue was cooled, dissolved in distilled water and the added metal ions were determined by reported procedures [32] (Table 4).

4.2 *Separation of osmium(IV) from ternary synthetic mixtures*

Ternary synthetic mixtures with various compositions of associated metal ions and fixed osmium(IV) content (200 µg) were taken and the proposed method was applied. Osmium(IV) was separated quantitatively as the osmium(IV)–OMPT complex extracted into chloroform, whereas the added metal ions remained in the aqueous phase. The results obtained were in a good agreement with the amount of osmium(IV) present (Table 5).

4.3 *Sequential separation of osmium(IV), rhodium(III) and platinum(IV)*

Method permits sequential separation of osmium(IV), rhodium(III) and platinum(IV) from their synthetic mixtures by taking the advantage of difference in their complex formation and extraction conditions using OMPT. The aqueous solutions containing a mixture of osmium (IV)(100, 150, 200 µg), rhodium(III)(50 µg) and platinum(IV)(100 µg) were mixed and osmium (IV) was separated as per recommended procedure using chloroform solvent, while the rhodium (III) and platinum(IV) remained in the aqueous phase. The aqueous phase was evaporated to moist dryness and the residue was dissolved in acetate buffer (pH 5.4). To this mixture 2 ml, 0.01 mol l^{-1} OMPT in ethanol was added and was made up to mark with acetate buffer pH 5.4

Table 4. Analysis of binary synthetic mixtures.

Metal ion	Amount taken (μg)	Recovery[a] (%)	RSD (%)	Chromogenic ligand	Reference
Os(IV)	200	99.49	0.72	OMPT	–
Zn(II)	20	99.69	0.10	dithizone	29
Os(IV)	200	99.24	0.72	OMPT	–
Mn(II)	200	99.57	0.57	permanganate	29
Os(IV)	200	99.49	0.59	OMPT	–
Pb(II)	50	99.93	0.17	dithizone	29
Os(IV)	200	99.62	0.51	OMPT	–
Mo(VI)	40	99.81	0.25	thiocynate-$Sncl_2$	29
Os(IV)	200	99.62	0.51	OMPT	–
W(VI)	200	99.80	0.16	thiocynate	29
Os(IV)	200	99.49	0.59	OMPT	–
Cu(II)	30	99.82	0.23	dithizone	29
Os(IV)	200	99.23	0.72	OMPT	–
Co(II)	200	99.42	0.90	thiocynate	29
Os(IV)	200	99.72	0.73	OMPT	–
Fe(III)	50	99.32	0.48	1,10-phenenthroline	29
Os(IV)	200	99.24	0.72	OMPT	–
Bi(III)	400	99.42	0.24	iodide	29
Os(IV)	200	99.47	0.24	OMPT	–
Cd(II)	40	98.11	0.89	dithizone	29
Os(IV)	200	99.49	0.72	OMPT	–
Hg(II)	500	99.37	0.28	dithizone	29
Os(IV)	200	99.11	0.94	OMPT	–
Ni(II)	75	99.28	0.26	DMG	29
Os(IV)	200	99.23	0.72	OMPT	–
Au(III)	100	99.38	0.59	$Sncl_2$	29

[a]average of four determinations.

Table 5. Separation of osmium(IV) from ternary synthetic mixtures.

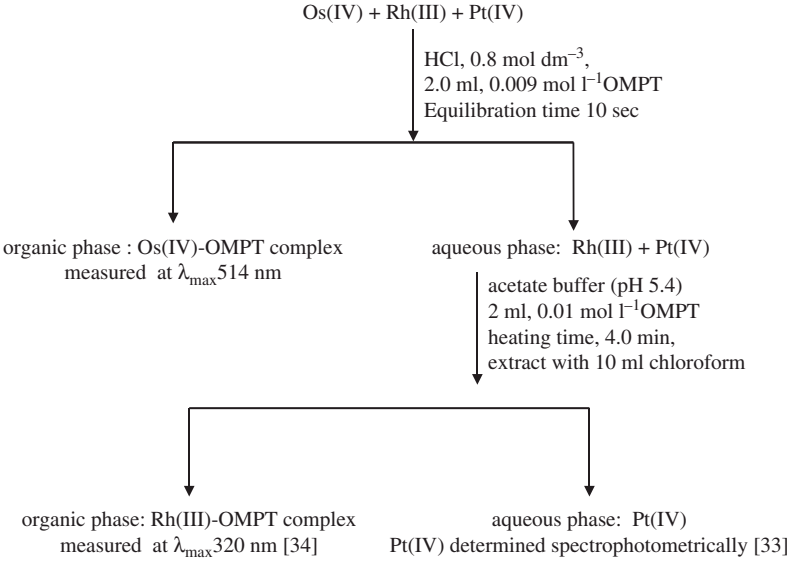
Composition (μg)	Recovery[a] (%)	RSD (%)
Os(IV) 200; Zn(II) 20; Mn(II) 75	99.62	0.51
Os(IV) 200; Pb(II) 50; Mo(VI) 20	99.62	0.78
Os(IV) 200; W(VI) 30; Cu(II) 30	99.49	0.73
Os(IV) 200; Co(II) 50; Fe(III) 50	99.36	0.51
Os(IV) 200; Bi(III) 50; Cd(II) 40	99.72	0.29
Os(IV) 200; Hg(II) 50; Ni(II) 50	99.11	0.67
Os(IV) 200; W(VI) 30; Ni(II) 50	99.23	0.72
Os(IV) 200; Co(II) 50; Cu(II) 30	99.75	0.42
Os(IV) 200; Au(III) 50; Hg(II) 50	99.36	0.30

[a]average of four determinations.

in a 25 ml volumetric flask. This solution was heated on the boiling water bath for 4 min and the yellow-coloured rhodium(III)–OMPT complex formation takes place. The yellow-coloured complex was extracted into 10 ml chloroform and was determined spectrophotometrically [33]. The raffinate containing platinum(IV) was evaporated to moist dryness, cooled, dissolved in distilled water and the platinum(IV) content was determined spectrophotometrically as per standard methods [32] (Table 6) (Scheme 1).

Table 6. Sequential separation of osmium(IV), rhodium(III) and platinum(IV).

Mixture	Amount taken (μg)	Chromogenic ligand	Recovery[a] (%)	RSD (%)
Os(IV) + Rh(III) + Pt(IV)	Os (100)	OMPT	99.40	0.81
	Rh (50)	OMPT	99.90	0.24
	Pt (100)	$SnCl_2$	99.66	0.76
Os(IV) + Rh(III) + Pt(IV)	Os (150)	OMPT	99.62	0.95
	Rh (50)	OMPT	99.48	0.42
	Pt (100)	$SnCl_2$	99.34	0.54
Os(IV) + Rh(III) + Pt(IV)	Os (200)	OMPT	99.62	0.29
	Rh (50)	OMPT	99.69	0.30
	Pt (100)	$SnCl_2$	99.36	0.94



Scheme 1. Sequential separation of osmium(IV), rhodium(III) and platinum(IV).

5. Conclusion

The present investigated method is highly selective and sensitive with determination at trace level. Determination of osmium is possible in both aqueous and organic phase merits the applicability of the method in various sample matrices. Fast analysis is possible with instant complex formation and spectrophotometric determination. Analysis of binary, ternary synthetic mixtures and mutual separation of osmium(IV), rhodium(III) and platinum(IV) proves the wide range applicability of the method. Low hydrochloric acid concentration (0.8 mol l^{-1}), minimum volume for determination (10 ml), instant complex formation and complex formation at room temperature with no need of heating or standing, proves the method is beneficial for rapid determination of osmium with low expenditure.

Supplementary material

Supplementary material relating to this article is available online.

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Separation of divalent lead from ayurvedic (herbal) medicines and alloys using extraction chromatography

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A selective, sensitive, less expensive and more precise method has been developed for the separation of lead(II) using N-***n***-octylaniline (liquid anion exchanger) coated silica gel as stationary phase. The quantitative extraction of lead(II) is found with 0.087 molL^{-1} N-***n***-octylaniline and 0.007 - 0.15 mol/L^{-1} ascorbic acid at ***p***H 9.0. The extracted lead(II) has been eluted from the column with 0.5 mol/L^{-1} hydrochloric acid and analyzed by spectrophotometric method. The probable composition of the extracted species is deduced from log-log plots and extracted species is found to be $[2RR'NH_2^+.Pb(C_6H_7O_6)_4^{2-}]_{(org.)}$. The optimum extraction conditions are evaluated from a critical study of effects of ***p***H, ascorbic acid concentration, N-***n***-octylaniline concentration and elution time. The proposed method is found simple and efficient as it avoids large number of cation and anion interferences. Lead(II) is successfully separated from binary mixtures with bismuth(III), gold(III) and osmium(VIII). The method is also extended for separation of lead(II) from ayurvedic medicine and synthetic mixtures corresponding to alloys.

Keywords: Alloys, Ayurvedic medicine, Extraction chromatography, Lead(II), N-***n***-octylaniline

Lead is a toxic and relatively rare element (10^{-3} wt%), but is well known for its technical importance. Lead and its compounds constitute one of the most important industrial health hazards and also the major soil contaminant. It has low reactivity and solubility and due to this reason lead poisoning occurs in many cases, where lead is dispersed, like sanding lead based paint, long term exposure in the case of pewter tableware. Even in trace level, it decreases enzymatic and kidney function and causes neuromuscular difficulties[1]. Obviously, trace level separation of metallic toxicant lead(II) poses a challenging problem to the analytical chemists.

The most widely used techniques for the separation and preconcentration of trace level of lead(II) includes reverse osmosis[2], liquid–liquid extraction[3,4], coprecipitation[5,6], ion-exchange[7], adsorption[8,9], cloud point extraction[10], electrochemical deposition[11] and solid phase extraction (SPE)[12-14]. Solid phase extraction is an effective alternative, when the metals are in large volumes of relatively low concentrations. Extraction chromatographic separation of lead(II) was carried out with Versatic 911[15] and Versatic10[16] (liquid cation exchangers) coated on silanised silica gel from acetate buffer media. The effect of ***p***H on Rf values in ion exchange paper chromatography has been studied. The method was used for separation of lead(II) from synthetic multi-component mixtures, industrial waste and standard alloy samples using its preconcentration on the column. Lead can be separated by extraction chromatography using bis (2-ethyl hexyl) phosphoric acid coated on silica gel as a stationary phase in 0.01 mol/L^{-1} hydrochloric acid[17]. Modified silica gel by thiosalicylic acid was used as a reagent for extraction and concentration of lead ions from aquatic samples and determined with FAAS[18]. To desorb the lead ions, 4.0 mol/L^{-1} nitric acid is required. 4-propyl-2-thiouracil[19] coated on activated charcoal was preconcentrate copper(II), nickel(II), cobalt(II) and lead(II). These metals were simultaneously determined by AAS but separation was not achieved. The separation of lead(II) from cadmium(II), bismuth(III), indium(III) and vanadium(V) was carried out with 60% acetone from a column of AG5OW-X8 cation-exchange resin[20] by taking advantage of difference in their stripping agents. Extraction of lead, nickel, zinc and copper was carried out with hexamethyleneammonium hexamethylenedithio-carbamate (HMA-HMDC) and reversed-phase liquld

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chromato graphy using Cosmosil 5 C-18, (4.6×250 mm) column. This method was used to determine these metals from citrus leaves and rice flour[21].

Uranium(VI) and lead(II) were extracted from sodium salicylate solution with high molecular-weight amines, viz. aliquat 336, TOA, TIOA, amberlite LA-1 or amberlite LA-2 in xylene[22]. This method permits separation of uranium and lead from binary mixtures with commonly associated metal ions and from air samples. Cyanex 302[23] was used as an extractant for solvent extraction of lead(II) in phosphoric acid media. In this method, extraction of lead was strongly dependent on phosphoric acid concentration. 2-Octylaminopyridine[24] was used as an extractant for solvent extraction separation of lead(II) in sodium succinate media at ***p***H 10. Though lead(II) is separated from other toxic metals, excess reagent gives adverse effect on extraction which requires multiple striping and minimum equilibration time of 4 min. Tributyl phosphine oxide[25] was used for solvent extraction of lead(II) from salicylate media. The method was applied for separation of lead(II) and copper(II) from various samples. Lead(II) was quantitatively extracted with tributyl phosphate[26] in 3.0 mol/L hydrochloric acid but method suffers from high reagent concentration (30%) and it requires lithium chloride (2 mol/L^{-1}) as a salting out agent.

The extensive use of organic solvents is no longer desirable as these are expensive and harmful to the environment and health. A number of methods have been developed which are solvent free or low solvent consumption methods. Among these, solid phase extraction reduces the limitations of liquid-liquid extraction (LLE). Recently in our laboratory N-***n***-octylaniline was applied for solid phase extraction of aluminium(III)[27], copper(II)[28], gold(III)[29], palladium(II)[30], ruthenium(III)[31] and manganese(II)[32]. In the present work, extraction of lead(II) was achieved from ascorbic acid media with N-***n***-octylaniline (liquid anion exchanger) coated on silica gel as a stationary phase. Lead(II) was quantitatively extracted from 0.01 molL^{-1} ascorbic acid at ***p***H 9.0 and eluted with 0.5 mol/L^{-1} hydrochloric acid. The method is applied for separation of lead(II) from binary mixtures, ayurvedic (herbal) medicine and synthetic mixtures corresponding to alloys.

Experimental Procedure

Apparatus

An Elico spectrophotometer model SL-159 with 10 mm path length quartz cell and a control hydrodynamic ***p***H meter were used to measure absorbance and adjust the required ***p***H.

Reagents

All the chemicals used were of analytical grade. Double distilled water was used throughout the experimental work. A stock solution of lead(II) was prepared by dissolving 0.39937g of lead(II)nitrate [$Pb(NO_3)_2$], (make Qualigens) in 250 mL of distilled water and standardized using gravimetric method[33]. A working solution containing 50 µg mL^{-1} lead(II) was prepared by further dilution.

Ascorbic acid (Vitamin C) and hydrochloric acid were provided by Merck India Ltd. and 4-(2-pyridylazo) resorcinol disodium salt (PAR) by S.D. Fine Chem. Ltd. Other standard solutions of different metal ions used for the study of effect of foreign ions on the extraction were prepared by dissolving their corresponding salts in dilute hydrochloric acid. The solutions of anions were prepared by dissolving respective sodium salts in distilled water. The N-***n***-octylaniline was prepared by the method reported by Gardlund[34] and its dilutions were prepared in chloroform.

Preparation of anion exchange material

A portion of 5.0 g sililated silica gel[35] was soaked with 0.087 mol L^{-1} N-***n***-octylaniline which was previously equilibrated with ascorbic acid (0.01 mol/L^{-1}) at ***p***H 9.0 for 10 min, the solvent was evaporated to get nearly dried gel using rotary vacuum evaporator. The slurry of N-***n***-octylaniline coated silica gel in distilled water was prepared by centrifugation at 2000 r min^{-1}. Then the coated silica gel was packed into chromatographic column to give a 6.0 cm bed height. The bed was covered with a glass wool plug.

General procedure for extraction and estimation of lead(II)

An aliquot solution containing 100 µg lead(II) was made up to 25.0 mL by adjusting the concentration of ascorbic acid to 0.01 mol/L^{-1} and ***p***H 9.0. It was passed through the column containing 0.087 mol/L^{-1} N-***n***-octylaniline coated on silica gel at a flow rate of 1.0 ml min^{-1}. After extraction, lead(II) was eluted with 25 mL (0.5 mol/L^{-1}) hydrochloric acid and determined by spectrophotometric method[36].

Results and Discussion

Effect of ascorbic acid concentration on extraction of lead(II)

Hundred microgram (100.0 g) lead(II) in 25.0 mL aqueous solution was extracted by varying ascorbic acid concentration from 0.001 mol/L^{-1} to 0.70 mol/L^{-1}

with 0.087 mol/L^{-1} N-***n***-octylaniline as the stationary phase on silica gel. The percentage extraction of lead(II) initially increases with increase in ascorbic acid concentration, becomes quantitative at 0.007-0.15 mol/L^{-1} and then decreases (Fig. 1). Hence, all the extractions were carried out at 0.01 molL^{-1} ascorbic acid at ***p***H 9.

Effect of *p*H on extraction of lead(II)

The extraction of lead(II) was studied in a ***p***H range 4.5-12 (Table 1). Metal ion was quantitatively extracted in 0.01 mol/L^{-1} ascorbic acid media at the ***p***H range 5-10. This shows that the equilibrium at ***p***H range 5-10 is favorable for the formation of ion-pair complex from ascorbic acid medium. Hence, all the extractions were carried out at ***p***H 9.

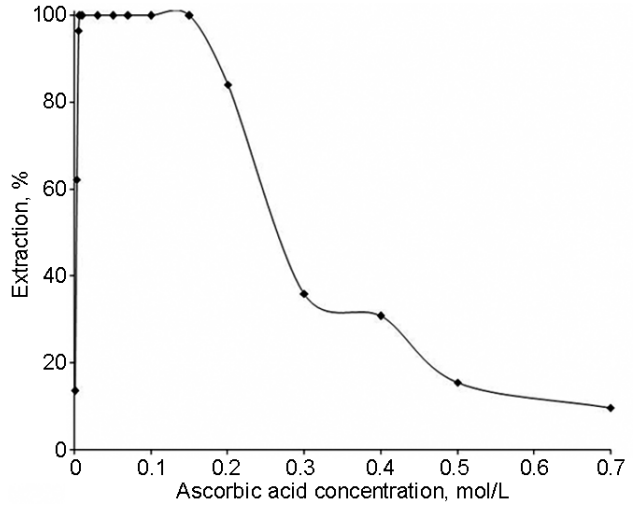

Fig. 1—Extraction of lead(II) as a function of ascorbic acid concentration

Table 1—Extraction behavior of lead(II) as a function of ***p***H [Pb(II) 100 µg; ascorbic acid 0.01 mol L^{-1}; eluent 0.5 mol L^{-1} hydrochloric acid; N-***n***- octylaniline 0.087 mol $L^{-1}$and flow rate 1.0 mL min^{-1}]

pH	Percentage extraction (%E)	Distribution coefficient (K_d)
4.5	42.0	0.72
4.75	759	3.15
5	99.9	999.0
6	99.9	999.0
7	99.9	999.0
8	99.9	999.0
9	99.9	999.0
10	99.9	999.0
11	89.6	8.62
12	44.7	0.81

Effect of flow rate on percentage extraction of lead(II)

The effect of flow rate on percentage extraction of lead(II) has been studied from 0.5 mL min^{-1} to 4.0 mL min^{-1}. It is observed that the increase in flow rate is inversely proportional to percentage extraction. Therefore, normal flow rate is kept 1.0 mL min^{-1} for further extraction studies.

Effect of N-*n*-octylaniline concentration on extraction of Pb(II)

The concentration of N-***n***-octylaniline varies from 0.022 mol/L^{-1} to 0.109 mol/L^{-1} over ascorbic acid concentration 0.005-0.05 mol/L^{-1} at 1.0 mL min^{-1} flow rate for lead(II). It is found that for quantitative extraction of lead(II), 0.087 mol/L^{-1} N-***n***-octylaniline is sufficient in 0.01-0.05 mol/L^{-1} ascorbic acid media. An increase in N-***n***-octylaniline concentration increases the percentage extraction of lead(II). Log-log plot of N-***n***-octylaniline concentration versus log of distribution coefficient (Fig. 2) at 0.005-0.007 mol/L^{-1} of ascorbic acid gives slopes 2.3 and 2.4 respectively. The probable composition of metal to amine ratio is calculated as 1:2. It indicates that the probable extracted species is $[2RR'NH_2^+.\ Pb(C_6H_7O_6)_4^{2-}]_{org}$. The extraction mechanism can be explained as follows:

$$[RR'NH]_{org.} + [C_6H_8O_6]_{aq.} \rightleftharpoons [RR'NH_2^+\ C_6H_7O_6^-]_{org} \quad \ldots(1)$$

$$2[RR'NH_2^+.\ C_6H_7O_6^-]_{org.} + [Pb(C_6H_7O_6)_4^{2-}]_{aq.} \rightleftharpoons [2RR'NH_2^+.Pb(C_6H_7O_6)_4^{2-}]_{org.} + [(C_6H_7O_6)_2^-]_{aq} \quad \ldots(2)$$

where R= $-C_6H_5$ R'= $-CH_2\ (CH_2)_6CH_3$

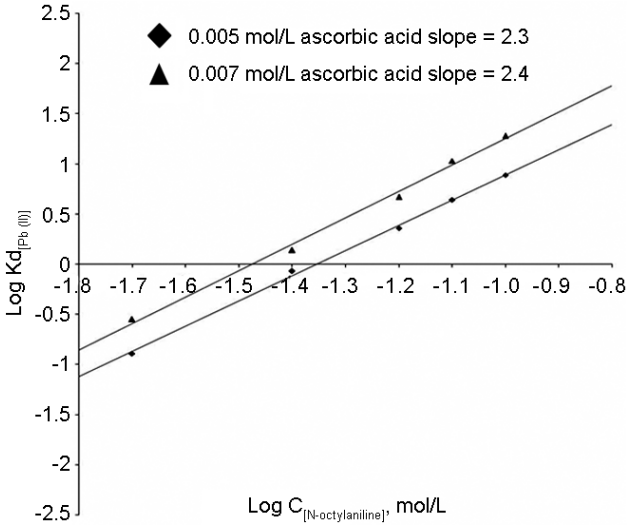

Fig. 2—Log-log plot of distribution coefficient versus N-***n***-octylaniline concentration at 0.005 and 0.007 mol L^{-1} ascorbic acid

Effect of eluting agent

The elution study of lead(II) was carried out using hydrochloric acid (0.05-5.0 mol/L^{-1}), sulphuric acid (0.1-2.5 mol/L^{-1}), perchloric acid (0.05-6.0 mol/L^{-1}), hydrobromic acid (0.1-3.0 mol/L^{-1}), nitric acid (0.1-3.0 mol/L^{-1}), sodium hydroxide (0.1-3.0 mol/L^{-1}) and ammonia (0.1-2.5 mol/L^{-1}). The elution of lead(II) is found quantitatively from column in 0.5 mol/L^{-1} hydrochloric acid. Maximum elution of lead(II) is observed in sulphuric acid 99.9%, perchloric acid 99.9%, hydrobromic acid 99.9% and nitric acid 99.3%. In sodium hydroxide and ammonia there is no elution of metal ion. Hydrochloric acid is used for elution of lead(II) in further study.

Effect of foreign ions

Various amounts of foreign ions have been added to a fixed amount of lead(II) (100 µg) to study the effect of interference according to the recommended procedure. The tolerance limit is set at the amount required to cause ± 1.5% error in the recovery of lead(II) (Table 2). It is observed that the method is free from interference for large number of cations and anions. The cations showing interferences in the method are uranium(VI), zinc(II), iron(III) and mercury(II).

Applications

Analysis of lead(II) from synthetic mixtures corresponding to alloys

Validity of the method is confirmed by applying it for the separation of lead(II) from synthetic mixtures corresponding to alloys. However, the real samples are not available at the working place, which forces us to use synthetic mixtures corresponding to the composition of alloys. The composition of alloys has been prepared for sealing alloy, wood-metal alloy, lead-bismuth alloy, bismuth solder alloy and solder alloy in laboratory and the proposed method has been applied for the separation of lead(II) (Table 3). The results obtained are in good agreement with the certified values.

Table 2—Effect of foreign ions
[Pb(II) 100 µg; ascorbic acid 0.01 mol L^{-1}; ***p***H 9.0; eluent 0.5 mol L^{-1} hydrochloric acid; N-***n***- octylaniline concentration 0.087 mol $L^{-1}$and flow rate 1.0 mL min^{-1}]

Foreign ion	Added	Tolerance limit µg, lead(II)	Foreign ion	Added	Tolerance limit, µg lead(II)
Sb(III)	Sb_2O_3	300	W(IV)	$Na_2WO_4.2H_2O$	300
Cr(VI)	$K_2Cr_2O_7$	300	In(III)	$InCl_3$	150
Cu(II)	$CuSo_4.5H_2O$	50	Ni(II)	$NiCl_2.6H_2O$	300
Mn(II)	$MnCl_2.6H_2O$	50	Ir(III)	$IrCl_3.xH_2O$	300
V(V)	V_2O_5	50	Fe(II)	$FeSO_4.7H_2O$	50
Tl(III)	$TlNO_3$	100	Bi(III)	$Bi(NO_3)_3$	300
Cd(II)	$3CdSO_4.8H_2O$	50	Os(VIII)	O_SO_4	100
Sn(II)	$SnCl_2$	200	Rh(III)	$RhCl_3.xH_2O$	300
Mo(VI)	$(NH_4)_6Mo_7O_{24}.2H_20$	300	Ru(III)	$RuCl_3.xH_2O$	300
Ag(I)	$AgNO_3$	300	EDTA	EDTA(Disodium salt)	100
Mg(II)	$MgCl_2.6H_2O$	300	Tartrate	$C_6H_6O_6$	300
Co(II)	$CoCl_2.6H_2O$	50	Malonate	$CH_2(COONa)_2$	300
Ti(IV)	TiO_2	300	Oxalate	$(COOH)_2.2H_2O$	300
Ga(III)	$GaCl_3$	300	Succinate	$(CH_2COONa)_2. 6H_2O$	300
Al(III)	$AlCl_3$	200	Citrate	$C_6H_8O_7.H_2O$	300
Au(III)	$HAuClO_4.H_2O$	100	Thiourea	SN_2H_4C	200

Table 3—Analysis of lead(II) from synthetic mixtures corresponding to alloys
[Ascorbic acid 0.01 mol L^{-1}; ***p***H 9.0; eluent 0.5 mol L^{-1} hydrochloric acid; N-***n***-octylaniline concentration 0.087 mol L^{-1} and flow rate 1.0 mL min^{-1}]

Alloy sample composition	Pb(II) taken, µg	Pb(II) found, µg	Mean (***n***=3)	Recovery, % (***n***=3)	Confidence limit	RSD, % (***n***=3)
Sealing alloy (Bi 58; Pb 36; Sb 6)	100.0	99.5, 99.4,99.6	99.5	99.5	99.47 –99.53	0.10
Wood metal alloy (Bi 50; Pb 26; Sn 13.3; Cd 10)	100.0	99.5, 99.3,99.6	99.5	99.5	99.46 –99.54	0.15
Lead bismuth alloy (Pb 84.6; Bi 15.4)	100.0	99.4, 99.5,99.5	99.5	99.5	99.49 –99.52	0.06
Bismuth solder alloy (Bi 27.5; Pb 27.5 Sn 45)	100.0	99.6, 99.7,99.6	99.6	99.6	99.56 –99.64	0.15
Solder alloy (Pb 40 ; Sn 60)	100.0	99.7, 99.7,99.6	99.7	99.7	99.69 –99.72	0.06

Table 4—Separation of lead(II) from binary mixtures
[N-***n***-octylaniline 0.087 mol L^{-1}; eluent 25 ml 0.5 mol L^{-1} hydrochloric acid; ascorbic acid 0.01 mol L^{-1}; ***p***H 9.0 and flow rate 1.0 mL min^{-1}]

Mixture*	Chromogenic ligand	Taken, µg	Found, µg	Recovery, %	Confidence limit	RSD, %
Pb(II) + Bi(III)	PAR	100.0	99.66	99.7	99.60 – 99.72	0.22
	KI	100.0	99.58	99.6	99.53 – 99.63	0.21
Pb(II) + Au(III)	PAR	100.0	99.71	99.7	99.64 – 99.78	0.26
	$SnCl_2$	100.0	99.51	99.5	99.43 – 99.59	0.30
Pb(II) + Os(VIII)	PAR	100.0	99.78	99.8	99.72 – 99.84	0.23
	Thiourea	100.0	99.80	99.8	99.76 – 99.84	0.14

* Lead(II) gets extracted; and bismuth(III), gold(III) and osmium(VIII) remain in aqueous phase.

Table 5—Separation of lead(II) from ayurvedic (herbal) medicine (n=3)
[Ascorbic acid 0.01 mol L^{-1}; ***p***H 9.0; eluent 0.5 mol L^{-1} hydrochloric acid; N-***n***-octylaniline concentration 0.087 mol $L^{-1}$and flow rate1.0 mL min^{-1}]

Pharmaceutical sample	Pb(II)		Recovery, %	Confidence limit	% RSD
	Added, µg	Found, µg			
Nag Bhasma (Batch No. 2109) [Koral Pharmaceuticals]	100.0	99.43	99.4	99.30 –99.56	0.52
Ekangweer Ras (Batch No. 165) [Shree baidyanath Ayurved Bhavan Pvt. Ltd.]	280.0	278.0	99.3	277.94 –278.06	0.36
Garbhapal Ras (Lot No. 52 GM10) [Shree Bhuvaneshwari Aushadhashram Gondal]	80.0	79.5	99.4	79.45 –79.56	0.19
Tribang Bhasma (S.Y.S.) (Batch No. 106), [Shree Akshar Pharmaceuticals Pvt. Ltd.]	247	245.4	99.4	245.37 –245.43	0.20

Separation of lead(II) from binary mixtures

Synthetic binary mixtures of lead(II) with bismuth(III), gold(III) and osmium(VIII) were prepared. The separations of these mixtures were carried out using the proposed method. The results are reported in Table 4.

Separation of lead(II) from ayurvedic samples

The ayurvedic samples like Nag Bhasma, Ekangweer Ras, Garbhapal Ras, Tribang Bhasma containing lead(II) were prepared as solutions by wet digestion[37] method. The solution was filtered and then diluted to 50 ml and analysed for lead content by the proposed method. The results are found in good agreement with the certified values (Table 5).

Conclusion

Method is simple, rapid and reproducible. Extraction of lead(II) requires low concentration of N-***n***-octylaniline. Method is free from large number of foreign ions. The method gives separation of lead(II) from alloys, viz. sealing alloys, wood metal alloy, lead bismuth alloy, bismuth solder alloy and solder alloy. It permits separation of lead(II) from ayurvedic samples and associated metals, viz. bismuth(III), gold(III) and osmium(VIII).

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"DETERMINATION OF WATER QUALITY INDEX IN INDUSTRIAL AREA OF WALUNJ MIDC AURANGBAD MAHARASHTRA, INDIA"

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Abstract:

The Present study intended to calculate Water Quality Index (WQI) of industrial areas of well water samples in Aurangabad industrial area, Maharashtra India were monitored. The quality of bore waters was assessed by comparing with existing standard for important parameters. Water Quality Index calculated from thirteen parameters of physicochemical parameters taken together varied from 76.38 – 266.88ppm indicating level of nutrient load and pollution in the bore waters. Result of this study indicates that all the bore well water of the study areas are permissible limit except S3, S4 and S6 (Deolali, Pandharpur and Naralibag). The water was not confirming to drinking standards and hence it is suggested that to take all the necessary precautions before the water are sent into public distribution system. It is concluded that WQI can be used as tool in comparing the water quality of different source.

Key wards: *Maharashtra, chemical properties, industrial areas, India, Aurangabad, WQI.*

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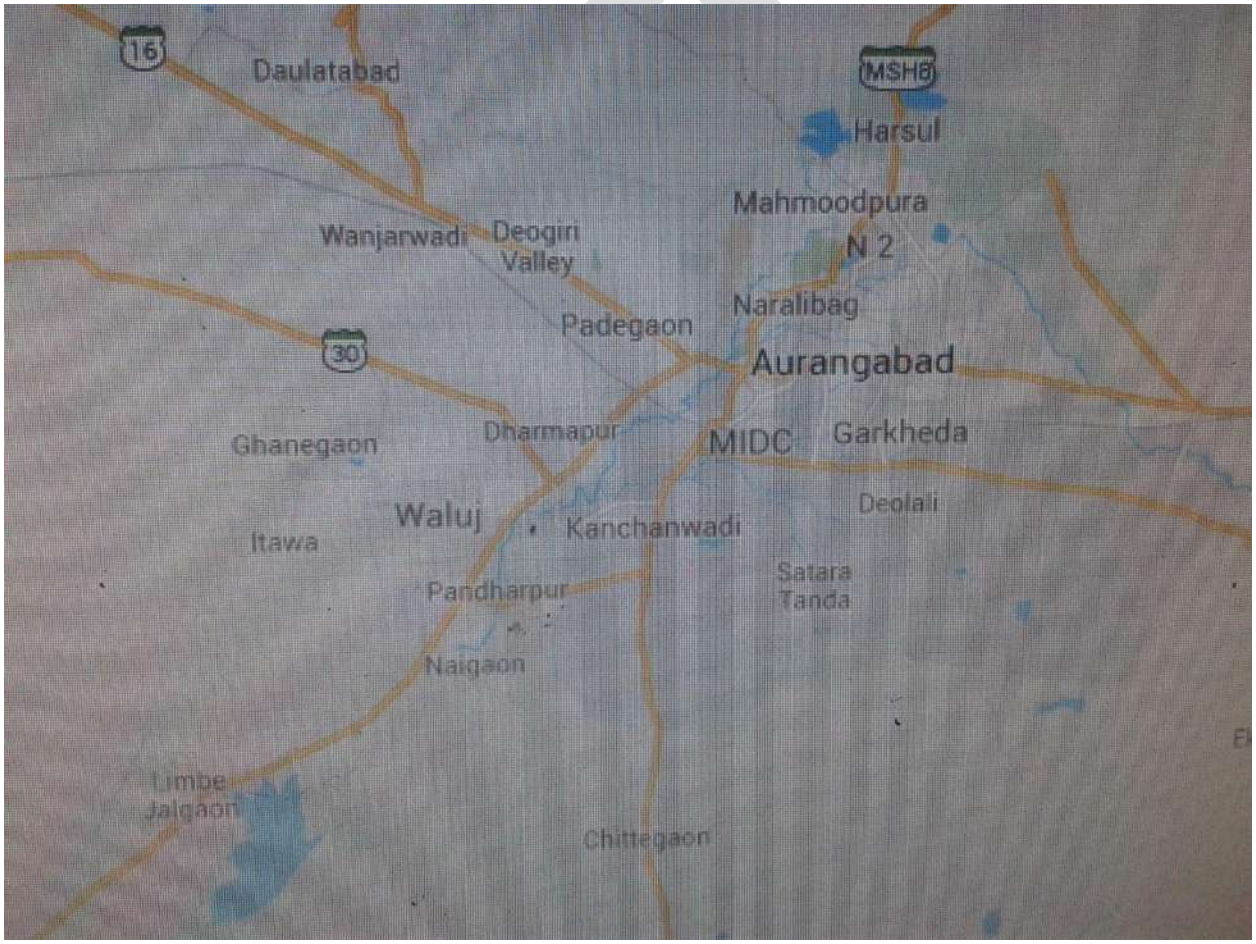
Introduction:

Water is one of the most important factors for every living organism on this planet. The 3 % of global fresh water is large enough to meet the requirements of the man for millions of years. Water pollution is a phenomenon that is characterized by the deterioration of its quality as a result of various human activities[1]. Water is generally used for drinking, fisheries and other domestic's purposes in this area. The available fresh water to man is hardly 0.3 to 0.5 % of the total water available on the earth and therefore its judicious use in imperatives Waluj is industrial area and a municipal corporation in Indian state of Maharashtra[2,3]. Is a special economic zone, the problem of industrial zone has been considerably serious in India. Due to the externally rapid rate of industrial development which is providing one of the major sources of employment for the growing population of the country. This promotes the leading of chemicals and contaminates the ground water[4]. As of 2011 census, Aurangabad Municipal Corporation had a population of 3,701,282.

The 1/3 of the inhabitant people depends on mainly ground water in residential and industrial area. In industrial belt several major industries such as fertilizers, power oil, chemical and gas etc., the industries discharge their treated effluents into unlined canals, rivers through drains and some store in ash ponds or slurry ponds. Water Quality index (WQI) provides a single number that expresses overall water quality at a certain locations and time based on several water quality parameters[6,7]. The WQI was first developed by Horton in the early 1970 is basically a mathematical means of calculating a single value from multiple test results [8,9]. The index results represent the level of water quality in a given water basin, such as ponds, lake, river or stream. Srinivas et al. (2013) carried out the determination of water quality index (WQI) in residential area of Ferozabad village, Gulbarga Taluka and District, Karnataka, INDIA. This promotes the leading of chemicals and contaminates the ground water[10]. The objective of Water Quality Index is to turn complex water quality data into information that is understandable and used the public. A single number cannot tell the whole story of water quality parameters that are not included in the index. However, a water quality index based on some very important parameters can provide a single indicator of water quality[11, 12]. In general, water quality indices incorporate data from multiple water quality parameters in to a mathematical equation that rates the health of a lake and river with number[13].

Study area: The Aurangabad city is the capital of Marathwada of Maharashtra. Located mainly in Godavari River basin and partly in the Tapi River basin. The district is located between 19 and 20 degrees north longitude and 74 and 76 degrees east latitude of Maharashtra. Aurangabad is declared Tourism capitals of Maharashtra and nicknamed city of gates. The present study deals with the assessment of the quality of ground water in industrial areas of Waluj MIDC, Aurangabad Maharashtra, India. Aurangabad situated between the latitude$19^0.53^!$ North and longitude $75^0.23^!$ East.

The study was carried at the10 sampling locations of industrial areas of Aurangabad. It is rich in small waste bodies and most of all agricultural lands are dependent on those water sources.



Location Map of the study area.

Experimental:

The water sample were collected in satirized polythene air tight containers and was analyzed for water quality parameters like PH, electrical conductivity, total dissolved solids, total solids , dissolved oxygen, biological oxygen demand, total alkalinity, total hardness, sulphate, phosphate, nitrates and chlorides, as per standard method prescribed by American public health association (APHA)[14]. All the chemicals and reagents were of analytical grade. Double distilled water was used for the preparation of solutions. The study was carried out at the 10 locations of industrial areas of Waluj MIDC area, Aurangabad. The sampling stations selected for the analysis of ground water are, S1 - Waluj MIDC area, S2 - Dharmpur, S3 - Deolali, S4 - Pandharpur, S5 - Garkheda, S6 – Naralibag, S7 - Mahmoodpura, S8 - Naigaon, S9- Kanchanwadi and S10 - Padegaon. .

Bore water samples were collected in the all sampling stations. In this study, for the calculation Water Quality Index, 13 important parameters were chosen. The WQI has been calculated by using the standards of the drinking water quality recommended by the World Health Organization (WHO)[15]. Indian Council Of Medical Research (ICMR)[16], and Bureau of Indian Standards (BIS) [17] have been used for the calculations of WQI of the water body.

Further, quality rating or sub index (qn) was calculated using the following expression[18].

$$q_n = 100 (V_n - V_{io}) / S_n - V_{io}$$

Let n be the water quality parameters and quality ratings or sub index (q_n) corresponding to n^{th} parameter is a number reflecting the relative value of this parameter in the polluted water with respective standard permissible value.

q_n = Quality rating for the n^{th} water quality parameter.

V_n = Estimated value of n^{th} parameter at a given sampling station.

S_n = Standard permissible value of the n^{th} parameter.

V_{io} = Ideal value of n^{th} parameter in pure water.

Unit weight was calculated by a value inversely proportional to the recommended standard value S_n of the corresponding parameters[19].

$$W_n = K / S_n$$

W_n = Unit weight for the Nth parameters.

S_n = Standard value for Nth parameters

K = Constant for proportionality.

The overall water quality index calculated by aggregating for quality rating with the unit weight linearly[20].

$$WQI = \sum q_n \; W_n / \sum W_n$$

Table - 1: Status and Index level (WQI) of water quality:

Water Quality Status	Water Quality of Index level
Excellent water quality	0 - 25
Good water quality	26 - 50
Poor water quality	51 - 75
Very Poor water quality	76 - 100
Unsuitable for drinking	> 100

Result and Discussion:

- The results of physicochemical parameters of bore water at various points are given in Table 3. The PH of the bore well waters in all the stations are acceptable and varies from 6.00 to 8:00. Through, PH has no direct effect on human health; all biochemical reactions are sensitive to the variations of PH. The permissible limits of PH value of drinking water ICMR (1975) is specified as 6.5 to 8.5. If PH is less, algae die, fish cannot reproduced and it cause acidity, corrosion, irritation of mucous membranes, tuberculosis and other health problems in humans [21, 22].
- Electrical conductivity is very important parameters for determining water quality for drinking and agricultural purpose[23]. The value in the study area is from 170 - 400 millimhos. The ideal value of electrical conductivity is < 2.4 Millimhos.

- The total dissolved solids (TDS) in the study area varied from 200 to 550 mg/L. The high value of TDS (above 500 mg/L) recorded at S4, S7 and S10, may be due their proximity to the industrial area. If TDS is more, water cannot be used for drinking as well as construction purpose. TDS affects palatability of food cooked and also causes gastro intestinal irritations[24].
- Total alkalinity of all the sampling stations is high and varied from 60 - 90.mg/L. The large amount alkalinity imparts a bitter taste to water[25].
- Total hardness of water is characterized by contents of calcium and magnesium salts. The total hardness in the study area varied from 160 - 290 mg/L. The within standards value were observed in all the sampling points.
- The total magnesium in the study area varied from 45 to 100 mg/L. The magnesium content is higher than the calcium in the samples indicates the occurrence of magnesium salts in all samples[26].
- Dissolved oxygen (DO), and biochemical oxygen demand (BOD) are very important pollution parameters. The value of DO and BOD in the study area are 3.0 to 4.0 and 2.0 to 16.0 mg/L. Hence the water treatment is required before it sent into the public distribution system[27].
- The sulphate ion concentration in entire study area varied from 90.5 to 145 mg/L. High concentration of sulphate at S5, S7 is might be due to heavy industrial activity and seepage of sewage water[28].
- The chlorides are also corrosive and impart permanent hardness to water. The chloride imparts a salty taste and sometimes high concentrations cause laxative effect in human beings[29]. The chlorides contents in the study area ranged from 20 to 200 (S2 and S4) mg/L. Chloride content observed within the standard value in all samples. The nitrates is used to assess the self purification properties of water bodies and nutrient balance in surface water, soil and also the state of determination of organic matter present in waste waters.
- The nitrate ion concentrations are very important in public water supplies, because it causes methemoglobinemia in children[30]. The nitrates concentrations in the study area varied between 25 to 30 (S2 and S8) mg/L with all the values well below the permissible

levels (ICMR, 1975) except S4. The drinking water standards recommended by several agencies and their unit weight are reported in Table – 2.

- The variations of water quality index (WQI) at various sampling sights are shown in fig.1.
- The variations of water quality rating at various sampling sights are shown in fig.2.

Table - 2: Drinking water standards recommending agencies and unit weight:

Sr. No.	Parameters	Standards	Units	Recommended	Unit weights
1	PH	6.5 – 8.8	-	ICMR / BIS	0.2190
2	Dissolved oxygen	5.0	millimols	ICMR/BIS	0.0037
3	Electrical conductivity	500	Mg/lit	ICMR / BIS	0.0037
4	Total dissolved solid	120	Mg/lit	ICMR / BIS	0.0155
5	Total alkalinity	300	Mg/lit	ICMR / BIS	0.0062
6	Total Hardness	500	Mg/lit	WHO	0.0037
7	Total suspended solids	75	Mg/lit	ICMR / BIS	0.025
8	Calcium	30	Mg/lit	ICMR / BIS	0.061
9	Magnesium	250	Mg/lit	ICMR	0.0074
10	Chlorides	45	Mg/lit	ICMR / BIS	0.0412
11	Nitrates	150	Mg/lit	ICMR / BIS	0.01236
12	Sulphate	150	Mg/lit	ICMR / BIS	0.3723
13	Biological Oxygen Demand	5.00	Mg/lit	ICMR	0.3723

All values except PH and electrical conductivity are in Mg/lit

Table - 3: Physic – Chemical parameters of water bodies in Waluj:

Sr. No.	Parameters	S1	S2	S3	S4	S5	S6	S7	S8	S9	S10
1	PH	6.0	6.5	7.0	6.9	7.3	6.8	7.0	7.6	6.7	6.5
2	Dissolved oxygen (mg / lit)	3.5	4.5	4.0	3.5	4.0	2.5	3.0	2.9	3.1	3.0
3	Electrical conductivity (millimols)	170	380	388	300	250	370	330	200	280	220
4	Total dissolved solid (mg / lit)	220	500	490	450	350	500	400	520	450	400
5	Total alkalinity (mg / lit)	60	85	88	72	86	75	70	60	85	70
6	Total hardness (mg / lit)	280	200	170	165	160	162	275	180	185	187
7	Total suspended solids	335	230	330	400	380	370	300	365	400	340
8	Calcium (mg / lit)	180	130	125	110	115	120	180	90	95	110
9	Magnesium (mg / lit)	100	75	40	55	50	45	85	85	85	70
10	Chlorides(mg / lit)	20	120	130	200	150	180	85	130	170	95
11	Nitrates (mg / lit)	35	30	45	50	40	45	25	30	35	30
12	Sulphate (mg / lit)	130	130	120	140	120	140	90	135	135	100
13	Biological Oxygen Demand(mg / lit)	5	5	10	12	10	15	25	6	2	2.5

Table – 4: water quality index of S1: Waluj KD

Sr. No.	Parameter	Observed values	Standard values (Sn)	Unit weight (Wn)	Quality rating (qn)	Wn qn
1	PH	7.3	6.5 – 8.5	0.2190	60	13.14
2	Dissolved oxygen (mg / lit)	3.5	5.0	0.0037	116	0.4292
3	Electrical conductivity (millimols)	170	500	0.0037	34.00	0.1258
4	Total dissolved solid (mg / lit)	220	120	0.0155	183.33	2.85
5	Total alkalinity (mg / lit)	60	300	0.0062	20.00	0.124
6	Total hardness (mg / lit)	280	500	0.0037	56.00	0.21
7	Total suspended solids	335	75	0.025	447.0	11.18
8	Calcium (mg / lit)	43	30	0.061	143.0	8.72
9	Magnesium (mg / lit)	100	250	0.0074	40.00	0.30
10	Chlorides(mg / lit)	20	45	0.0412	44.44	1.83
11	Nitrates (mg / lit)	35	150	0.01236	23.33	0.29
12	Sulphate (mg / lit)	130	150	0.3723	86.67	32.27
13	Biological Oxygen Demand(mg / lit)	5	5.00	0.3723	100.0	37.23
				∑ **Wn** = 1.15	∑ = **qn** 1353.8	∑ = **Wn qn** 109.20
Water Quality Index = ∑ **Wn qn** / ∑ **Wn** = 94.96						

Table – 5: water quality index of S2: Dharmapur

Sr. No.	Parameter	Observed values	Standard values (Sn)	Unit weight (Wn)	Quality rating (qn)	Wn qn
1	PH	7.5	6.5 – 8.5	0.2190	100	21.9
2	Dissolved oxygen (mg / lit)	4.5	5.0	0.0037	110	0.407
3	Electrical conductivity (millimols)	380	500	0.0037	76.00	0.0028
4	Total dissolved solid (mg / lit)	500	120	0.0155	416.67	6.46
5	Total alkalinity (mg / lit)	85	300	0.0062	28.33	0.18
6	Total hardness (mg / lit)	200	500	0.0037	40.00	0.15
7	Total suspended solids	230	75	0.025	306.67	7.67
8	Calcium (mg / lit)	130	30	0.061	433.33	26.43
9	Magnesium (mg / lit)	75	250	0.0074	30.00	0.222
10	Chlorides(mg / lit)	120	45	0.0412	266.67	10.99
11	Nitrates (mg / lit)	30	150	0.01236	20.00	0.25
12	Sulphate (mg / lit)	130	150	0.3723	86.67	32.27
13	Biological Oxygen Demand(mg / lit)	5	5.00	0.3723	100	37.23
				∑ **Wn** = 1.15	∑ = **qn** 2014.34	∑= **Wn qn** 144.17
Water Quality Index = ∑ **Wn qn** / ∑ **Wn** = 125.37						

Table - 6 water quality index of S3: Deolali

Sr. No.	Parameter	Observed values	Standard values (Sn)	Unit weight (Wn)	Quality rating (qn)	Wn qn
1	PH	7.9	6.5 – 8.8	0.2190	180	39.42
2	Dissolved oxygen (mg / lit)	4.0	5.0	0.0037	110.0	0.407
3	Electrical conductivity (millimols)	388	500	0.0037	77.60	0.29
4	Total dissolved solid (mg / lit)	490	120	0.0155	408.33	6.33
5	Total alkalinity (mg / lit)	88	300	0.0062	29.33	0.19
6	Total hardness (mg / lit)	170	500	0.0037	34.00	0.13
7	Total suspended solids	330	75	0.025	440.0	11.00
8	Calcium (mg / lit)	125	30	0.061	416.67	25.42
9	Magnesium (mg / lit)	40	250	0.0074	16.00	0.12
10	Chlorides(mg / lit)	130	45	0.0412	288.88	119.0
11	Nitrates (mg / lit)	45	150	0.01236	30.00	0.37
12	Sulphate (mg / lit)	120	150	0.3723	80.00	29.78
13	Biological Oxygen Demand(mg / lit)	10	5.00	0.3723	200.0	74.46
				∑ **Wn** = 1.15	∑ = **qn** 2310.81	∑= **Wn qn** 306.91
Water Quality Index = ∑ **Wn qn** / ∑ **Wn** = 266.88						

Table – 7: water quality index of S4: Pandharpur

Sr. No.	Parameter	Observed values	Standard values (Sn)	Unit weight (Wn)	Quality rating (qn)	Wn qn
1	PH	7.1	6.5 – 8.8	0.2190	20.00	4.38
2	Dissolved oxygen (mg / lit)	3.5	5.0	0.0037	115.62	0.43
3	Electrical conductivity (millimols)	300	500	0.0037	60.00	0.22
4	Total dissolved solid (mg / lit)	450	120	0.0155	375.0	5.81
5	Total alkalinity (mg / lit)	72	300	0.0062	24.00	0.15
6	Total hardness (mg / lit)	165	500	0.0037	33.00	0.12
7	Total suspended solids	400	75	0.025	533.33	13.33
8	Calcium (mg / lit)	110	30	0.061	366.67	22.37
9	Magnesium (mg / lit)	55	250	0.0074	22.00	0.16
10	Chlorides(mg / lit)	200	45	0.0412	444.44	1.83
11	Nitrates (mg / lit)	50	150	0.01236	33.33	0.41
12	Sulphate (mg / lit)	140	150	0.3723	93.33	34.75
13	Biological Oxygen Demand(mg / lit)	12	5.00	0.3723	240	89.35
				∑ **Wn** = 1.15	∑ = **qn** 2360.72	∑= **Wn qn** 126.34
Water Quality Index = ∑ **Wn qn** / ∑ **Wn** = 109.86						

Table – 8: water quality index of S5: Garkheda

Sr. No.	Parameter	Observed values	Standard values (Sn)	Unit weight (Wn)	Quality rating (qn)	Wn qn
1	PH	7.3	6.5 – 8.8	0.2190	60.00	13.14
2	Dissolved oxygen (mg / lit)	4.0	5.0	0.0037	110.41	0.41
3	Electrical conductivity (millimols)	250	500	0.0037	50.00	0.19
4	Total dissolved solid (mg / lit)	350	120	0.0155	291.67	4.52
5	Total alkalinity (mg / lit)	86	300	0.0062	28.67	0.18
6	Total hardness (mg / lit)	160	500	0.0037	32.00	0.12
7	Total suspended solids	380	75	0.025	506.67	12.67
8	Calcium (mg / lit)	115	30	0.061	383.33	23.38
9	Magnesium (mg / lit)	50	250	0.0074	20.00	0.15
10	Chlorides(mg / lit)	150	45	0.0412	333.33	13.73
11	Nitrates (mg / lit)	40	150	0.01236	26.67	0.33
12	Sulphate (mg / lit)	120	150	0.3723	80.00	29.78
13	Biological Oxygen Demand(mg / lit)	10	5.00	0.3723	200.0	74.46
				∑ **Wn** = 1.15	∑ = **qn** 2122.75	∑= **Wn qn** 173.06
Water Quality Index = ∑ **Wn qn** / ∑ **Wn** = 150.49						

Table – 9: water quality index of S6: Naralibag

Sr. No.	Parameter	Observed values	Standard values (Sn)	Unit weight (Wn)	Quality rating (qn)	Wn qn
1	PH	7.8	6.5 – 8.8	0.2190	160.0	35.04
2	Dissolved oxygen (mg / lit)	2.5	5.0	0.0037	126.0	0.47
3	Electrical conductivity (millimols)	370	500	0.0037	74.00	0.27
4	Total dissolved solid (mg / lit)	500	120	0.0155	416.67	6.5
5	Total alkalinity (mg / lit)	75	300	0.0062	25.00	0.155
6	Total hardness (mg / lit)	162	500	0.0037	32.40	0.12
7	Total suspended solids	370	75	0.025	493.33	12.33
8	Calcium (mg / lit)	120	30	0.061	400.0	24.4
9	Magnesium (mg / lit)	45	250	0.0074	18.00	0.13
10	Chlorides(mg / lit)	180	45	0.0412	400.0	16.48
11	Nitrates (mg / lit)	45	150	0.01236	30.00	0.37
12	Sulphate (mg / lit)	140	150	0.3723	93.33	34.75
13	Biological Oxygen Demand(mg / lit)	15	5.00	0.3723	300	111.69
				∑ **Wn** = 1.15	∑ = **qn** 2568.73	∑= **Wn qn** 242.7
Water Quality Index = ∑ **Wn qn** / ∑ **Wn** = 211						

Table - 10: water quality index of S7: Mahmoodpura

Sr. No.	Parameter	Observed values	Standard values (Sn)	Unit weight (Wn)	Quality rating (qn)	Wn qn
1	PH	7.2	6.5 – 8.8	0.2190	40.0	8.76
2	Dissolved oxygen (mg / lit)	3.0	5.0	0.0037	120	0.44
3	Electrical conductivity (millimols)	330	500	0.0037	66.0	0.24
4	Total dissolved solid (mg / lit)	400	120	0.0155	333.33	5.20
5	Total alkalinity (mg / lit)	70	300	0.0062	23.33	0.14
6	Total hardness (mg / lit)	275	500	0.0037	55.0	0.20
7	Total suspended solids	300	75	0.025	400.0	10.0
8	Calcium (mg / lit)	180	30	0.061	600.0	36.6
9	Magnesium (mg / lit)	85	250	0.0074	34.0	0.25
10	Chlorides(mg / lit)	85	45	0.0412	188.9	7.78
11	Nitrates (mg / lit)	25	150	0.01236	16.67	0.20
12	Sulphate (mg / lit)	90	150	0.3723	60.0	22.33
13	Biological Oxygen Demand(mg / lit)	25	5.00	0.3723	500.0	186.15
				∑ **Wn** = 1.15	∑ = **qn** 2437.23	∑= **Wn qn** 278.29
Water Quality Index = ∑ **Wn qn** / ∑ **Wn** = 241.99						

Table - 11: water quality index of S8: Naigaon

Sr. No.	Parameter	Observed values	Standard values (Sn)	Unit weight (Wn)	Quality rating (qn)	Wn qn
1	PH	7.6	6.5 – 8.8	0.2190	120	26.28
2	Dissolved oxygen (mg / lit)	2.9	5.0	0.0037	210	0.78
3	Electrical conductivity (millimols)	200	500	0.0037	40.0	0.148
4	Total dissolved solid (mg / lit)	520	120	0.0155	433.33	6.72
5	Total alkalinity (mg / lit)	60	300	0.0062	20.0	0.124
6	Total hardness (mg / lit)	180	500	0.0037	36.0	0.1332
7	Total suspended solids	365	75	0.025	486.67	12.17
8	Calcium (mg / lit)	90	30	0.061	300.0	18.3
9	Magnesium (mg / lit)	85	250	0.0074	34.0	0.25
10	Chlorides(mg / lit)	130	45	0.0412	288.88	11.90
11	Nitrates (mg / lit)	30	150	0.01236	20.0	0.012
12	Sulphate (mg / lit)	135	150	0.3723	90.0	35.50
13	Biological Oxygen Demand(mg / lit)	6	5.00	0.3723	120.0	44.68
				∑ **Wn** = 1.15	∑ = **qn** 2198.88	∑= **Wn qn** 156.99
Water Quality Index = ∑ **Wn qn** / ∑ **Wn** = 136.51						

Table -12: water quality index of S9: Kanchanwadi

Sr. No.	Parameter	Observed values	Standard values (Sn)	Unit weight (Wn)	Quality rating (qn)	Wn qn
1	PH	7.7	6.5 – 8.8	0.2190	140	30.66
2	Dissolved oxygen (mg / lit)	3.1	5.0	0.0037	119.80	0.44
3	Electrical conductivity (millimols)	280	500	0.0037	56.0	0.21
4	Total dissolved solid (mg / lit)	450	120	0.0155	375.0	5.81
5	Total alkalinity (mg / lit)	85	300	0.0062	28.33	0.18
6	Total hardness (mg / lit)	185	500	0.0037	37.0	0.14
7	Total suspended solids	400	75	0.025	533.33	13.33
8	Calcium (mg / lit)	95	30	0.061	316.67	19.31
9	Magnesium (mg / lit)	85	250	0.0074	34.0	0.25
10	Chlorides(mg / lit)	170	45	0.0412	377.78	15.56
11	Nitrates (mg / lit)	35	150	0.01236	23.33	0.29
12	Sulphate (mg / lit)	135	150	0.3723	90.0	33.50
13	Biological Oxygen Demand(mg / lit)	2	5.00	0.3723	40.0	14.90
				∑ **Wn** = 1.15	∑ = **qn** 2171.24	∑= **Wn qn** 136.58
Water Quality Index = ∑ **Wn qn** / ∑ **Wn** = 118.77						

Table – 13: water quality index of S10: Padegaon

Sr. No.	Parameter	Observed values	Standard values (Sn)	Unit weight (Wn)	Quality rating (qn)	Wn qn
1	PH	7.4	6.5 – 8.8	0.2190	80.0	17.52
2	Dissolved oxygen (mg / lit)	3.0	5.0	0.0037	120.83	0.44
3	Electrical conductivity (millimols)	220	500	0.0037	44.0	0.16
4	Total dissolved solid (mg / lit)	400	120	0.0155	333.33	5.16
5	Total alkalinity (mg / lit)	70	300	0.0062	23.33	0.14
6	Total hardness (mg / lit)	187	500	0.0037	37.4	0.14
7	Total suspended solids	340	75	0.025	453.33	11.33
8	Calcium (mg / lit)	110	30	0.061	366.66	22.36
9	Magnesium (mg / lit)	70	250	0.0074	28.0	0.21
10	Chlorides(mg / lit)	95	45	0.0412	211.11	8.70
11	Nitrates (mg / lit)	30	150	0.01236	20.0	0.25
12	Sulphate (mg / lit)	100	150	0.3723	66.66	24.82
13	Biological Oxygen Demand(mg / lit)	2.5	5.00	0.3723	50.0	18.61
				∑ **Wn** = 1.15	∑ = **qn** 1834.65	∑= **Wn qn** 87.84
Water Quality Index = ∑ **Wn qn** / ∑ **Wn** = 76.38						

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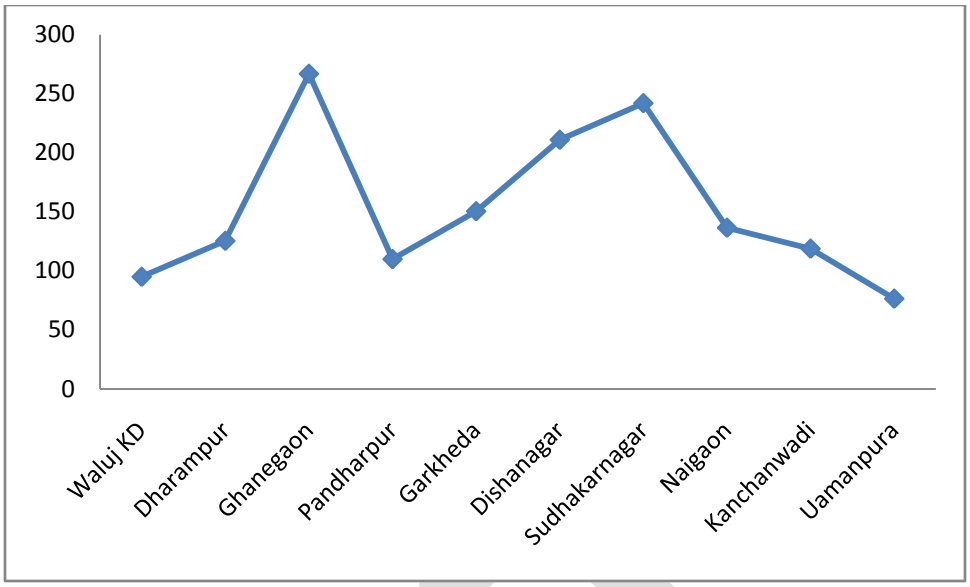

Fig.1. Water Quality Index

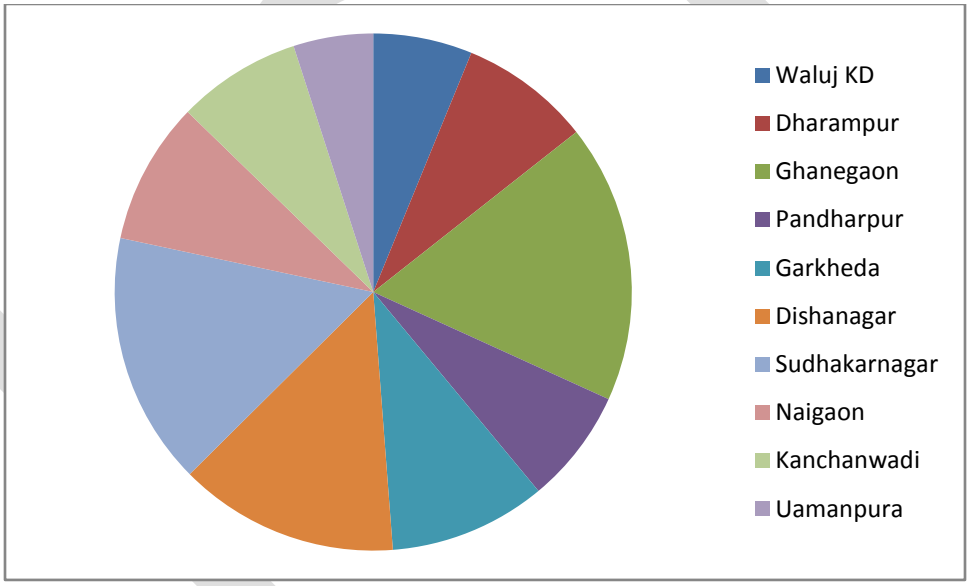

Fig.2. Water Quality Index Rating

Conclusion:

The Water Quality Index (WQI) of waters in industrial areas of Waluj MIDC, is given in Table 4 to 10. The report prepared by the WHO the importance of safe waters supply and sanitation in the control of water borne diseases. The value of WQI in water sampling areas was reported to be less than 100 and greater than 100, indicating that the water is suitable for human use except S3, Deolali, S4, Pandhapur and S6, Naralibag

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STUDIES ON THE STATUS OF AVAILABLE MICRONUTRIENTS FOR PLANT GROWTH IN DIFFERENT SOIL SERIES OF BHIMA RIVER LOWER BASIN AT SIDDHATEK IN AHMEDNAGAR DISTRICT (MAHARASHTRA)

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ABSTRACT

In ten soil samples of sugar cultivating area in Ahmednagar District of Maharashtra, available micronutrients along with other physico-chemical parameters have been studied. All the soil series are free from salinity hazards. Most of the soil samples contain excess available micronutrients like iron and copper. The ratio between iron and other micronutrients has been worked out.

Key words: Soil quality, Physico-chemical parameters, Micronutrients, Micronutrients ratio.

INTRODUCTION

In many part of India, surface as well as ground water has been used extensively for various purposes viz. drinking and agriculture etc. Sometimes water is not suitable for drinking and other purposes because of chemical and biological contaminations[1,2]. Different elements are essential for the healthy growth of plants; these elements are grouped in to macro and micronutrients. The deficiency or excess presence of micronutrients such as iron, manganese, zinc and copper may produce synergetic and antagonistic effects on the plant growth and crops yields[3]. Water is the most important component of the earth. About 99.70% of water found on earth is in the ocean and sea. The people used the water for irrigation as well as house hold applienceses[4]. Now pollution is major problem in developing

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countries. The waste water from manmade activities such as house hold appliances, industrial processes, high use of pesticides and fertilizers creates water pollution as well as soil pollution problems[5]. Bhima River is flowing through the Siddhatek and the people used waters for domestic and irrigation purposes, depending up on quality, quantity and resources available in the region. Knowledge about the water quality would help to decide the treatment, which should be given to water for different purposes[6]. Siddhatek is popular for Siddhivinayak Ganpati, which is one among the Ashtakvinayak in Maharashtra.

Hence, many people and many foreigners visit at this village, which is responsible for creates pollution of river basin. At Siddhatek sugarcane, wheat and sorghum are cultivated as main crops but from last few years the crop yields per acre are found to be decreasing in many parts of the Bhima river basin. The present study deals with the measurements of the pH, electrical conductance and estimation of available iron, zinc and copper in different soil samples.

EXPERIMENTAL

Soil samples were collected from ten villages studied on the bank of Bhima River around Siddhatek in Ahmednagar district. The collection of soil samples and brings to laboratory for analysis according to standard method prescribed in APHA[7]. The pH and electrical conductivity of the soil were determined with 1:2 soil water suspension (Instrument Ilico Pvt. Ltd. P. E. 130) are used. The available micronutrients like copper, zinc and iron were estimated for different soils using atomic absorption spectrophotometer. All the chemicals used were of AR grade.

RESULTS AND DISCUSSION

Soil with pH greater than 8.5 are generally called as sodic soils, hence only two soil samples are sodic in nature and remaining soil series are free from sodicity hazzards[8]. The increasing in pH due to the increased amount of carbonates and bi-carbonates. Conductivity is a measure of the total conductance of the ionized substances. The mobility of the ions, valences, actual and relative concentrations affects conductivity. The electrical conductivity is in the range of 0.200 to 380 µmho/cm as against the critical limits of 4 µmho/cm for saline soils. Thus all the soil series can be considered as free from salinity hazzards[9]. Iron is one of the micronutrients for plant and it is present as complexes in plant tissues[10]. The status of available iron varies from 7.0 to 12.0 ppm (critical limits 2.0 ppm). The status of available

copper for different soil samples in the range 2.50 to 7.50 ppm (critical limit1.0 ppm). The results are reported in Table 1.

Table 1: Concentration of physico-chemical parameters and micronutrients ratio

S. No.	pH	E. C. µmho	% Organic carbon	Available micronutrients (ppm)			Ratio Fe/Zn	Ratio Fe/Cu
				Copper	Zinc	Iron		
1	7.5	0.290	0.45	5.00	1.0	8.5	8.50	1.7
2	8.0	0.380	0.50	4.50	1.05	9.0	8.57	2.0
3	8.5	0.300	0.60	2.50	0.80	10.20	12.75	4.08
4	8.7	0.280	0.55	3.50	0.55	7.5	13.63	2.14
5	8.9	0.350	0.80	3.60	0.50	9.5	19	2.63
6	8.5	0.280	0.35	4.00	1.50	9.25	6.16	2.31
7	7.5	0.354	0.28	7.5	0.90	10.0	11.11	1.33
8	8.0	0.240	0.75	5.50	0.95	12.0	12.63	2.18
9	8.4	0.360	0.20	5.80	0.43	7.0	16.27	1.20
10	8.01	0.200	0.30	6.00	1.65	10.15	6.15	1.69

The results shows that all the soil samples are rich in available copper, hence it is very toxic to the plants. The germination percentage of the seeds generally decreases with the increase of copper concentration[11]. Zinc deficiency leads to widespread nutritional disorder in various crops. The available zinc supply to the plant may be diluted by the increased concentration of phosphorous. The available zinc for the plant is found to vary from 0.43 to 1.65 ppm (critical limits 0.80 to1.00 ppm). The soil from Birdi, Bhambora and Siddhatek (BK) are found to certain excess of zinc. It must be diluted by adding phosphatic fertilizes for increased up take by plant roots. Since other three soil samples have low zinc content, they need zinc fertilization for the growth of crop and better yield. In the physiology of plants, the relative amounts of iron, manganese and zinc present are essential for photosynthesis and biological reactions. Hence, the relative availability of the micronutrient is examined and results are reported in Table 2. The iron zinc ratio varies from 6.15 to 19.0 ppm[12]. The lower ratio affects the availability of iron to the plants, the higher ratio produces the mutual antagonistic effect of iron and zinc (critical limit 2.5 to 2.0 ppm).

Table 2: Relation of iron to other micronutrients

Name of village	Iron : Zinc	Iron : Copper
Siddhatek (KD)	12.75	4.08
Birdi	16.27	1.20
Deulgoan	19.00	2.63
Hingni	6.16	2.31
Pedgoan	13.63	2.14
Bhambora	6.15	1.69
Jalalpur	12.63	2.18
Baradgoan	8.57	2.0
Shirapur	11.11	1.33
Siddhatek (BK)	8.50	1.7

CONCLUSION

This study reveals that the lower basin of Bhima River at Siddhatek is rich content of iron and copper than the limits given in WHO and ISI. Sampling stations show pollution of Bhima River water and not suitable for irrigation as well as domestic use. Mainly, the biomass was affected because of excess use of fertilizer and water for irrigation. There is a need for proper management to achieve sustainable agriculture progress. By all means, the natural quality of water as well soil got contaminated in this area by anthropogenic activities.

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Highly Nutritious Designed Soyaladoo Supplementation to Malnourished Preschool Children and it's Benefits on their Nutrient Intake

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Abstract

Malnutrition among preschool children is now a global problem. Formulation of the food products of low cost and highly nutritiuon is only the solution to overcome the problem hence the visionary design of the soyaladoo is done. Organoleptically high scored soyaladoo was taken for supplementation. The nutritional qualities likes major nutrients such as energy(470.0kcal), proteins (20.1 g) and fats (22.0 g) content found more in soyaladoo. The micro nutrients such as iron (6.3 mg), zinc (3.8 mg) and calcium (286.5 mg) were also observed higher range in soyaladoo. It also noted, very less antinutrtional factors like phytate phosphorous (160mg), tannin (0.34 mg), tryspin inhibitor activity (5.5ml), acid detergent fiber (1.31g), cellulose (1.00g) and lignin (0.3ml) etc. Soyaladoo has also shown very low production cost. Hence, it found very cheap and affordable to the below poverty line group of malnourished children. Significant improvements in nutrients intake were seen after supplementation of soyaladoo for six months to preschool malnourished children. The supplementation was given at the @ 50gm/child/day.

Keywords: Nutrition intake, soyladoo and supplementary feeding.

Introduction

Soyabean has high quality of amino acid, better protein digestibility. It also contents a better lipoxidase activity, lecithin and lipid profile. Due to these qualities in soybean and soya products are used in the dietary treatment of various deficiencies diseases[1].

However, the processing techniques used in the preparation of these innovative soya products are tedious, complicated, high costing and require skill personals. Generally home based treatment has been recommended during the rehabilitation phase of treatment for malnutrition in areas where follow up is possible[2]. The traditional foods are most familiar in the community. It requires less skill for their preparations. Hence, such traditional and homemade based foods are chosen after the value addition and planned to use as a dietary treatment for the malnutrition in preschool children. Soyabean is referred as vegetarian meat due to its high quality amino acid profile. It is less expensive legume as well as oil seed crop locally available. Due to excellence source of macro and micro and other biological properties this can be use food formulation of high nutri mix weaning and supplementary foods to combat malnutrition and maintain good health and nutritional status of preschoolers. By keeping this view present research study has been designed.

Material and Methods

The local varieties of soybean ie. MACH-58 and Bengal gram ie. pragati phule were procured from the market. It was cleaned, washed, dried, coarsely grind, dehulled and make into flour separately by use of grinding machine. Soyladoo was prepared.

Sensory evolution: By the use of three different combination soychakali was prepared and evaluation by organoleptically with the help of trained panel of judges on a nine point Hedonic scale[3].

Chemical Analysis of Soyproducts: High scored soyladoo in sensory evaluation was selected for chemical analyses. Such as moisture content, total ash, major nutrient like crude protein, fat, carbohydrates, B complex vitamins, minerals such as iron, calcium, zinc and crude fiber with the use of method described in [4].

Statical Analysis: The organoleptical qualities of soyladoo was carried out after it storage for 0 to 1 month and 1 to 2 month packed in polythene and high gauge packaging materials at room temperature. The differences noticed among this were calculated by statically and also nutrient intake before and after feeding with one month interval. data was analyzed statically procedure[5].

Results and Discussion

Biochemical compositions and storage stability of soyladoo: The data given in table 1 reveal the storage changes in proximate, biochemical compositions and sensory qualities in soyladoo kept in different packages for 0 to 1 and 1 to 2 months at room temperature. The changes in per cent of moisture and the content of B complex vitamins and β carotene in soyladoo were noticed at significant level after two months of storage.

The per cent of proximate compositions such as fat and protein were found decreased at highly significant level i.e. 31.34 to 28.15 and 27.89 to 25.02 respectively in the ladoo stored up to 2 months of period. Whereas the value of B complex vitamins such as vitamins B_1 (0.50 to 0.31 mg) vitamin B_2 (0.38 to 0.29 mg) and vitamin B_3 (2.51 to 2.09mg) were observed reduced significantly in the soyladoo for 2 months. Non significant effect was noticed in the changes of mineral and crude fiber contents in the soyladoo after 2 months of storage.

Average major nutrient like calorie, protein, fats and minor nutrients such as vitamins and minerals intake by experimental groups were expressed in table 2. The mean calorie intake by soyaladoo supplemented group of children was noted as 1144 ±11.4 Kcal (78.4per cent). The control group had lower calorie intake i.e. 634.2 ±5.3 Kcal (43.4per cent)[6].

The protein intake by soyaladoo was noted as 17.4±4.3 g. (66.9per cent), The control group reported the protein intake only 10.0±2.7g (38.5per cent), The mean fat intake by soyaladoo was found more 21.1±4.3g. (84.5per cent). Only 10.3±2.1g. average fat intake was found in control group of children which noted as poorly adequate i.e. (41.3per cent). Average intake of vitamin B_1 (thiamine) by group I recorded as highest i.e.0.65±0.1mg which was recorded as 78.7per cent. Control group found consumed vitamin B_1 as 0.31± 0.06mg which was reported only 41.3 per cent. Vitamin B_2 or riboflavin consumption recorded more i.e. 0.63±0.14mg (73.9per cent) in group I. The control group consumed only 0.33±0.1mg (38.8per cent) intake of riboflavin which reported as poorly adequate level. The mean intake of vitamin B_3 or niacin by group I again found in highest score i.e. 0.62±0.1mg. Minimum average intake of niacin was observed in control group 0.40±0.9mg. A similar average intake of vitamin C was noted by group I i.e. 27.2±1.7 mg and it was noticed below the moderate adequate level (68.0per cent) of each group.

Table-1
Proximate And Composition In Soyladoo (Per 100g) With Its Storage Stability

Sr.No.	Bio-Chemical Compositions	Proximate and storage period		
		Up to 1 Month	1 to 2 Months	't' test
1	Moisture (%)	14.60	13.92	2.278*
2	Ash (%)	3.11	3.05	0.912 NS
3	Fat (%)	31.34	28.15	2.6.11**
4	Protein (%)	27.89	25.02	2.659**
5	Vitamins B_1 (mg)	0.50	0.31	2.155*
6	Vitamins B_2 (mg)	0.38	0.29	1.981*
7	Vitamins B_3 (mg)	2.51	2.09	1.920*
8	B. carotene (μ g)	239.00	237.10	1.992*
9	Iron (mg)	7.23	7.09	0.790 NS
10	Calcium (mg)	168.80	168.21	0.915 NS
11	Zinc (mg)	4.65	4.25	0.875 NS
12	Crude fiber (g).	1.85	1.82	0.048 NS

** - significant at 1 % level , * - Significant at 5% level, Non Significant

Table-2
Average Nutrients Intake of Experimental Groups

Sr. No.	Nutrients	Group I Mean ± S.D.	Group II Mean ± S.D.
1	Calories (K.cal)	1144 ±11.6(78.4)	634.2± 5.3(43.4)
2	Protein (g)	17.4±4.3(66.9)	10.0±2.7(38.5)
3	Fat (g)	21.1±4.3(84.5)	10.3±2.1(41.3)
4	Vitamin B_1 (mg)	0.65±0.1(78.7)	0.31±0.1(41.3)
5	Vitamin B_2(mg)	0.63 ±0.1(73.9)	0.33±0.07(38.8)
6	Vitamin B_3 (mg)	0.62±0.1(65.3)	0.40±0.9(42.0)
7	Vitamin C(mg)	27.2±1.7(68.0)	22.4±1.4(56.0)
8	β Carotene (µg)	1128±14.1(70.5)	757.1±7.9(47.3)
9	Iron (mg)	7.6 ±1.2(76.4)	5.6±2.2(56.1)
10	Calcium (mg)	262.8±7.6(65.0)	168.6±5.5(42.0)
11	Zinc (mg)	4.6±0.7(46.1)	3.8±0.6(38.0)

Group I - Experimental group supplemented with soyaladoo. Group II - No supplementation i.e. control group. Figures in parantheses indicate percentage. *significant at 5 per cent level, **significant at 1 per cent level, NS Non Significant, BS – Before supplementation, AS – After supplementation.

Intake of vitamin C (i.e.22.4±1.4mg) was noticed in control group. In case of fat soluble vitamin like β carotene intake by The intake of β carotene in Group I, 1176± 8.5 µg and Very poor intake of β carotene was noted by control group i.e. 757.1±7.9 µg.

The average intake of calcium by the children who supplemented with soyaladoo i.e. group I was recorded as more i.e. 262.8±7.6 mg. None the control group consumed only 168.6±5.5 mg calcium, which was reported as poorly adequate.

The average iron intake by soyaladoo group I was found as 7.6± 1.20 mg (76.4per cent). The intake of iron by control group shown as 5.6±2.2 mg (56.1 per cent). They found as 46.1, zinc intake in group I, Very poor intake of zinc by control group was noticed as 3.8±0.6 mg (38.0per cent).

Average major nutrients intake like calories, protein and fat by experimental group was compared with their before supplementation intake level. The relevant data was presented in tables 3 to 5. Table 3 gives an idea about the comparison in average major nutrient intake like calorie, protein and fats before and after supplementation among experimental groups. Average calorie intake in group I was significantly increased after supplementation. It was found increased from 724±8.9 kcal to 1144±11.6 kcal after six months of experiment. Per cent calorie (78.4) intake of this i.e. group I found nearby moderate adequate level after supplementation. There was no significant change noticed in average calorie intake of control group. Group I found highly significant increased protein intake (17.4 g) after supplementation. Whereas the average intake of protein after supplementation was slightly found decreased in control group as compared with their intake before supplementation.

Table-3
Average Major Nutrients Intake of Experimental Groups with their before and after Supplementation

Sr.No.	Nutrients	Group I Mean ± S.D.			Group II Mean ± S.D.		
Major nutrients		BS	AS	't' value	BS	After 6months	't'value
1	CaloriesK.cal)	724±9 (49.4)	1144±11.6 (78).	14.1**	634±86.6 (43.8)	635±86.5 (43.4)	0.15NS
2	Protein (g)	8.4±1.1 (32.2)	17.4±4.3 (66.9)	8.0*	9.0±1.3 (34.3)	10.0±2.7 (38.5)	0.70NS
3	Fat (g)	6.1± (24.5)	21.1±4.3 (84.5)	8.3**	10.00±1.3 (40.0)	10.3±2.1 (41.3)	1.10NS

Group I - Experimental group supplemented with soyaladoo. Group II - No supplementation i.e. control group. Figures in parantheses indicate percentage. *significant at 5 per cent level, **significant at 1 per cent level, NS Non Significant, BS – Before supplementation, AS – After supplementation.

Table-4
Average Vitamins Intake of Experimental Groups with their before and after Supplementation

Sr. No.	Vitamins	Group I Mean ± S.D.			Group II Mean ± S.D.		
		BS	AS	't'value	BS	After 6months	't'value
1	VitamiB_1(mg)	0.4±0.1 (58.7)	0.65±0.1 (78.7)	3.8**	0.30±0.0 (40.0)	0.31±0.1 (41.3)	1.7NS
2	VitaminB_2(mg)	0.6±0.1 (64.7)	0.63±0.1 (73.9)	3.1**	0.30±0.1 (36.8)	0.33±0.07 (38.8)	1.3 NS
3	VitaminB_3(mg)	0.4±0.1 (44.2)	0.63±0.1 (65.3)	2.7*	0.40±0.1 (42.0)	0.40±0.9 (42.0)	0.0 NS
4	Vitamin C(mg)	27.2±1.7 (68.1)	27.2±1.7 (68.1)	0.0NS	22.0±3.0 (55.0)	22.14±1.4 (56.0)	0.10NS
5	βCarotene (µg)	500±3.7 (31.3)	1128±14.1 (70.5)	6.1**	326±4.5 (20.4)	757.1±7.9 (47.3)	2.8**

Group I - Experimental group supplemented with soyaladoo. Group II - No supplementation i.e. control group. Figures in parantheses indicate percentage. *significant at 5 per cent level, **significant at 1 per cent level, NS Non Significant, BS – Before supplementation, AS – After supplementation

Table-5
Average Minerals Intake of Experimental Groups with their before and after Supplementation

Sr No	Minerals	Group I Mean ± S.D.			Group IIMean ± S.D.		
		BS	AS	't'value	BS	After 6months	't'value
1	Calcium(mg)	82.0±1.220.5)	262.8±7.6(65.0)	6.7**	157.0±1.4(39.3)	168.6±5.5(42.0)	0.7 NS
2	Iron(mg)	5.1±0.7(51.1)	7.6±1.2(76.4)	3.8 **	5.6±2.2(56.1)	5.6±2.2(56.1)	0.2 NS
3	Zinc(mg)	1.3±0.2(12.9)	4.6±0.7(46.1)	4.1**	3.8±0.5(38.0)	3.8±0.6(38.0)	0.2 NS

Group I - Experimental group supplemented with soyaladoo. Group II - No supplementation i.e. control group. Figures in paran theses indicate percentage. *significant at 5 per cent level, ** significant at 1 per cent level, NS Non Significant, BS – Before supplementation, AS – After supplementation.

Average fat consumption in group I noticed increased at highly significant level. It shown that, fat intake before supplementation 6.1g increased upto 21.1 g after supplementation. This fat intake was noted as moderately adequate (84.5 per cent) level in group I after supplementation. Whereas control group noted a non significant fat intake as compared between their before and after six months of experimental period.

The data about average vitamin intake including vitamin B_1, B_2, B_3, vitamin c and β carotene by different experimental groups was recorded in table 4. It indicated that, highly significant increase in per cent intake of Vitamin B_1 (thiamin) was noticed in Group I. Control group was noted as non significant increase in consumption of vitamin B_1 (from 0.30 to 0.31 mg) after 6 months of experimental period. Average intake of vitamin B_2 or riboflavin was noted increases at highly significant level only in Group I. No significant difference was noticed in control group regarding intake vitamin B_2 before and after supplementation.

This increase in the intake of vitamin B_3 noted as highly significant level among group I. However, these increases level of vitamin B_3 intake in group I 41.0 before supplementation to 62.0 per cent after supplementation. Control group did not found any change in the intake of vitamin B3 after 6 months experimental period.

β carotene intake was highly significant increased in a group I, after supplementation. I reported increased intake of β carotene from 1128 ±14.1 (70.5) Control group was also noted increase in β carotene intake at significant level (from 20.4 to 47.3 per cent) after experimental period.

The data about average intake of minerals namely calcium, iron and zinc by different experimental groups before and after supplementation was given in table 5. It revealed that, calcium intake was found increased at highly significant level groups i.e. group I. Group I scored highest intake of calcium (65.0 per cent), They reported near by fifity per cent deficient in calcium intake. No significant difference was reported in the intake of calcium after experimental period in control group.

Iron intake was noticed increased at highly significant level only in Group I. It was noted as increased from 51.1 to 76.4 per cent after supplementation. Whereas there was no significant difference noted in the intake of iron and control group after supplementation.

The average zinc intake in Group I reported as highest score experimental group. It found as increase in the intake of zinc level from 12.9 to 46.1 per cent after supplementation. Though it was highly significant, but noted as at below adequacy level. No significant change was noticed in control group regarding intake of zinc after experiment.

Conclusion

On whole it can be concluded that the consumption of soyaladoo has positive and highly significant impact on nutrient intake of preschool malnourished children. The soyaladoo can be recommended for the treatment of malnutrition.

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Study on Nutritional Analysis of Soya by products before and after Processing

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Abstract

Formulation (developing a formula for a preparation) is carried out to achieve desired characteristics that make it suitable for a specific action or application. Formulation means making all possible combinations. The formulation of food products had done with its varying amounts in different food products. The most traditional and familiar foods in the family and among the children are purposefully selected. These products are ladoo, chakali and chiwada are the most traditional and familiar products in India particular in Maharashtra, these products are selected for the formulation with Soybean. The principle of nutrition such as carbohydrates, fats, proteins, vitamins and minerals were analyzed from the high scored selected soya by products. The vitamins such as thiamin, riboflavin, niacin, ascorbic acid and β carotene were estimated from soya products as well as minerals like iron, calcium and zinc were analyzed before and after processing. It has been seen that no significant changes in all nutrients have been seen after processing of these soya products, except β complex vitamins.

Keywords: Soya products, nutrients and malnourished preschool children.

Introduction

Soybean is an important legume and oil seed crop in Maharashtra. It is one of the natures wonder and nutritional gift which provides good quality protein with minimum saturated fat and high calorie value. Soybean has endowed with apithel functional food of the country as beyond traditional basic nutrition[1]. Soybean also contain the nutraceutical properties like isoflavones, phytoestrogen, soluble phosphate and potassium sulphate in which these properties are mostly used to prevent the risk of dreaded diseases like breast cancer, osteoporosis, cardiovascular disease, kidney stone and help in beating menopausal blue[2].

Material and Methods

Formulation: Formulation and preparation of soyaladoo, soyachakali and soyaflakes chiwada was done by using standard method by Thangamms[3].

Evaluation of soya products: Sensory Evaluation: Soya products were prepared and evaluated by organoleptically with the help of trained panel of judges on a nine point "Hedonic scale"[4].

Nutritional Evaluation: High scored soyflakes chiwada in sensory evaluation was selected for the nutritional quality analysis. Moisture content, total ash, major nutrient like crude protein, fat, carbohydrates, B complex vitamins including vitamin B_1,B_2 and B_3 , minerals such as iron, calcium, zinc and crude fiber were analyzed by use of methods described in Official methods of analysis, Annual Laboratory techniques [5and6]

Statistical analysis: Soya products food intake were carried out. The obtained data was analyzed by statistical significant at $p < 0.05$ level, S. E. and CD. at 5 per cent level by the procedure given by, Statistical Procedures for Agricultural Research[7].

Results and Discussion

Major Nutrients Content in Soya by product: The data presented in table-1 highlights the major nutrients content in soya doo. It revealed that, per cent of moisture and ash content in raw ingredients of soyaladoo was 13.2 and 4.8 respectively. It was non significantly decreased in per cent of moisture as 11.6 and ash as 3.1 after processing in finished product. Carbohydrate content in the ingredients of soyaladoo noticed as 96.9 (g) before processing. When it was prepared in soyaladoo, decreased non significant level as 95.4 (g). The energy (k.cal) was obtained from raw ingredients of soyaladoo as 1073.7 and as in finished product as 1070.0. Reduction of energy level in the preparation of soyaladoo was found at non significant level. Total protein (g) content in prepared soyaladoo was slightly noted as reduced (32.1) as compared with its raw ingredients (33.5). Similar observations were obtained in case of crude fat. It was found as 26.7 g in the raw ingredients of soyaladoo. Whereas it decreased non significantly as 24.0 in prepared soyaladoo. A non significant reduction were reported in content of moisture, ash, Carbohydrate, energy, total protein, crude fat after processing treatment in the preparation of soyaladoo as compared with its raw ingredients[8]. The ingredients and finished product i.e. soyachakali was given in table 2 It explained that, moisture content in raw ingredients used for the preparation of soyachakali was 12.6 per cent. It was found decreased non

significantly as 11.4 per cent in finished product. Per cent of ash content in raw material and soya chakali as a finished product was obtained as 3.4 and 2.9 respectively. 94.7 g carbohydrates were noted in raw ingredients of soyachakli. Whereas it was recorded as 93.1 in finished product. Total protein (g) content in raw ingredients of soyachakali reported as 32.6. It was slightly decreased in final product i.e. (30.8). 24.3 and 22.8 g crude fat was found respectively in ingredients used for soyachakali and its final product after processing. A non remarkable reduction was observed in all the major nutrients in final product i.e. soyachakali. The major nutrients in raw ingredients of soya flakes chiwda and its content in final product. Percent of moisture recorded as 12.6 in the raw material of soyaflakes chiwada. It was noted as 11.8 per cent in final product as soyaflakes chiwada. 3.8 and 3.6 per cent ash content were observed in raw ingredients from which the soyaflakes chiwada prepared. Whereas 826.6 (k.cal) energy had recorded from its final product. The values of total protein (g) were slightly found lower (28.0) in final product of soyaflakes chiwada than their raw ingredients (29.2). Whereas 23.6 and 22.9 (g) of crude fat were measured from raw material and final preparation of soyaflakes chiwada respectively. A non significant reduction was observed in all the major nutrients after the application of processing techniques.

Vitamins Nutrients Content in Soya by product: The data about average vitamins content in raw ingredients of soyaladoo and its final preparation is presented in table no 1It describes that, thiamine content (mg) in raw ingredient noticed as 0.38, where it was found as 0.36 in final product. Very low content of riboflavin (mg) and niacin (mg) were obtained as 0.18 and 3.35 in soyaladoo respectively. The values of vitamin B_2 and B_3 found decreased slightly in its processing. Whereas content of β Carotene (µg) in soyaladoo was measured as 1186.6. The values of all vitamins were decreased non significantly in the process of soyaladoo preparation. The vitamin content in raw ingredients used for soyachakali preparation and final product of soyachakali was explains that, thiamin content (mg) in raw material and final prepared soyachakali was recorded as 037 and 0.32 respectively. In comparison of thiamin values between raw ingredients and final product, it found decreased significantly after processing. The content of riboflavin (mg) was as 0.21 in raw ingredients and 0.19 in its final prepared product. The values of niacin (mg) showed significantly reduced in the finally prepared product (5.27) than their raw ingredients (5.89). The β Carotene (µg) values were also noted lowered due to processing in soyachakali (968.5) than that of its raw material (1084.6). It was clearly observed that expect riboflavin, all vitamins levels were reduced during processing of soyachakali. It might be due the deep frying cooking affected on water soluble as well as fat soluble vitamins[9]. The highlights the average vitamin content in soyaflakes chiwada. Vitamin content in raw ingredients of soyaflakes chiwada found as 0.30 mg thiamin, 0.29 mg riboflavin, 7.21 mg niacin and 1129.6 µg β carotene. These values of vitamin were noted as 0.29 mg, 0.27 mg, 7.11 mg and 1127.8 µg as thiamin, riboflavin, niacin and β carotene respectively in final prepared soyaflakes chiwada. Slight changes were observed in the values of vitamins content in raw material and final product. But these changes were noted as non significant.

Minerals Nutrients Content in Soya by product: The soya by products were also evaluated for their mineral contents. The data about minerals such as calcium iron and zinc content in different soy by products was presented in table-3.

Table-1
Major Nutrients Content in Soya by product

Sr. No.	Major nutrients (per 100g)	Soyaladoo Mean ± SD		't' Test	Soyachakali Mean ± SD		't' Test	Soyaflakes chiwada Mean ± SD		't' Test
		Before processing (raw ingredients)	After processing (final product)		Before processing (raw ingredients)	After processing (final product)		Before processing (raw ingredients)	After processing (final product)	
1	Moisture (per cent)	13.2±2.61	11.6±2.19	0.26 NS	12.6±2.04	11.4±1.22	0.21 NS	12.6±2.8	11.8±1.7	0.65 NS
2	Ash (per cent)	4.8±4.90	3.1±1.72	0.21 NS	3.4±1.31	2.9±0.94	0.62 NS	3.8±1.4	3.6±1.5	0.08 NS
3	Carbohydrate (g)	96.9±2.06	95.4±1.91	0.04 NS	94.7±2.75	93.1±0.68	0.04 NS	88.2±2.3	86.7±3.1	1.27 NS
4	Energy (kcal)	1073.7±2.11	1070.0±1.76	0.90 NS	1069±1.36	1065±1.41	0.65 NS	827.8±4.4	826.0±3.6	1.08 NS
5	Total protein (g)	32.1±1.87	28.5±1.65	0.53 NS	32.6±1.28	30.8±1.50	0.41 NS	29.2±1.8	28.0±0.6	0.91 NS
6	Crude fat (g)	26.7±1.69	24.0±1.25	0.41 NS	24.3±1.80	22.8±1.73	0.63 NS	23.6±0.9	22.9±0.7	0.05 NS

NS – Non Significant, *Significant at 5 per cent level. NS – Non Significant

Table-2
Vitamins Nutrients Content in Soya by product

Sr. No.	Minor Nutrients (per 100g)	Soyaladoo Mean ± SD		't' Test	Soyachakali Mean ± SD		't' Test	Soyaflakes chiwada Mean ± SD		't' Test
		Before processing (raw ingredients)	After processing (final product)		Before processing (raw ingredients)	After processing (final product)		Before processing (raw ingredients)	After processing (final product)	
1	Thiamine (mg)	0.38±0.04	0.36± 0.01	0.24 NS	0.37±0.52	0.32± 0.39	2.88 *	0.37±0.52	0.32± 0.39	2.88 *
2	Riboflavin (mg)	0.20±0.06	0.18±0.03	0.18 NS	0.21±0.04	0.19±0.01	1.38 NS	0.21±0.04	0.19±0.01	1.38 NS
3	Niacin (mg)	4.65±0.19	3.35±0.15	0.28 NS	5.89±1.23	5.27±0.98	2.94*	5.89±1.23	5.27±0.98	2.94*
4	B Carotene (µg)	1190.6± 5.65	1186.6±4.49	1.37 NS	1084.6± 4.09	968.5±3.11	2.97*	1084.6± 4.09	968.5±3.11	2.97*

*Significant at 5 per cent level. NS – Non Significant

Table-3
Minerals Nutrients Content in Soya by product

Sr. No.	Major nutrients (per 100g)	Soyaladoo Mean ± SD		't' Test	Soyachakali Mean ± SD		't' Test	Soyaflakes chiwada Mean ± SD		't' Test
		Before processing (raw ingredients)	After processing (final product)		Before processing (raw ingredients)	After processing (final product)		Before processing (raw ingredients)	After processing (final product)	
1	Calcium (mg)	288.4±11.5	286.9±8.6	0.14 NS	247.6±8.2	245.5±4.1	0.16 NS	275.4±4.8	273.8±3.5	0.29 NS
2	Iron (mg)	6.4±1.2	6.3±0.90	0.07 NS	5.3±2.5	4.9±1.4	0.08 NS	6.2± 1.3	5.8 ± 0.6	0.15 NS
3	Zinc (mg)	4.1±0.6	3.8±0.70	0.17 NS	2.3±1.7	2.1±0.6	0.11 NS	2.8 ± 0.7	2.5 ± 0.1	0.08 NS

*Significant at 5 per cent level. NS – Non Significant

It indicated that the raw ingredients of content 288.4 mg calcium, 6.4 mg iron and 4.1 mg zinc. Whereas these values were slightly reduced as 286.9, 6.3 and 3.8 mg of calcium, iron and zinc respectively after the processing and preparation of soyaladoo.

It describes that, calcium (mg) was obtained as 247.6 in raw ingredients of soyachakali. It was slightly noted lower i.e. 245.5 mg in final product of soyachakali. Iron contents (mg) in raw material and its final product of soyachakali were noticed as 5.3 and 4.9 respectively. Zinc (mg) appeared as 2.3 in raw ingredients and 2.1 in the final product of soyachakali[10] mineral content in soyaflakes chiwada calcium (mg) found 275.4 in the raw materials of soyaflakes chiwada. Whereas it was noted as 273.8 mg in final product of soyaflakes chiwada. Iron and zinc were noticed as 6.2 and 2.8 mg in the raw ingredients of soyaflakes chiwada where as it these values were observed as 5.8 and 2.5 mg in final product. All these mineral values were found non significantly decreased after processing in the preparation of soya flakes chiwada[11].

Conclusion

It has to be seen that all formulated soy byproducts; there were no significant change in all nutrients seen after processing of these soya products, except β complex vitamins. In soya chakali and soya flakes chiwada significant changes were seen in thiamine, niacin and ascorbic acid. The major nutrients content in different soya by products were not found significantly different. Similar picture was noticed regarding evaluation of major and minor nutrients like energy, protein, fats vitamins and mineral in all these soy byproducts. These soya products can be utilized to overcome malnutrition among the preschool children.

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Research Paper | Home science

Breastfeeding Practices Among Rural Mothers-Case Study Of Loni Village.

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ABSTRACT

Background: - Breast milk is a natural food for infant. Breast milk is the only insurance for the security of the new born. Inadequate nutrition is an underlying cause of death of more than 2.6 Million children. Keeping in view important of breast feeding, the present study was conducted with 100 rural mother of infant Loni village.

Objective:-To assess the breastfeeding practices among rural mother.

Materials & methods: -An interview schedule was developed before collection of data. Background information about the family was recorded for each mother.

Result:- The study findings revealed that 60% of the mothers had feed colostrums of their babies on the first day. Prelacteal feed were given up to 42% infant. The majority of the mother (43%) started breast feeding their infant within1hour after the child birth.

Exclusively breast feeding practices was followed by 60%mothers but 40% mothers were nonexistent of exclusive breast feeding due to various reason. Most of the mothers (92%) were fed Supplementary feed to infant along with breast milk between 6 months to 1year age. Maximum mother (42%) told reason for starting supplementary-milk as "Inadequate breast milk".

Conclusion: This study finding revealed that there is need to educate or inform to mothers for the benefits of the colostrums feeding and efforts should be enhance to increase the percentage of breast feeding within 1 hours of delivery and also need to create awareness about exclusively breastfeeding

KEYWORDS : colostrums, prelacteal feeding, exclusive breastfeeding, supplementary feeding

INTRODUCTION

Breastfeeding is the normal way of providing young infants with the nutrients they need for healthy growth and development. Virtually all mothers can breastfeed, provided they have accurate information, and the support of their family, the health care system and society at large. Colostrums, the yellowish, sticky breast milk produced at the end of pregnancy, is recommended by WHO as the perfect food for the newborn, and feeding should be initiated within the first hour after birth. Exclusive breastfeeding is recommended up to 6 months of age, with continued breastfeeding along with appropriate complementary foods up to two years of age or beyond [(1)].

Early and exclusive breastfeeding helps children survive, but it also supports healthy brain development, improves cognitive performance and is associated with better educational achievement at age 5. Breastfeeding is the foundation of good nutrition and protects children against disease[(2)].

Malnutrition is an underlying cause of death for 2.6 million children each year, and it leaves millions more with lifelong physical and mental impairments. Worldwide, more than 170 million children do not have the opportunity to reach their full potential because of poor nutrition in the earliest months of life [(3)].

The beneficial effects of breastfeeding depend upon correct breastfeeding practices. Initiation of breastfeeding after birth is considerably delayed in India, and in most cases the valuable colostrums is discarded before putting to breast [(4)].

Prelacteal feeds such as honey, sugar-water, jaggery water, castor oil, goat's milk are commonly given in many developing countries including India which carries potential risk of infection and aspiration[(5)]

Child mortality is that closely linked with malnutrition and inappropriate infant feeding. No substitute has even been developed that matches the numerous advantages of breastfeeding.

Keeping in view important of breast feeding the present study has been undertaken to assess the breastfeeding practices followed by lactating mother in the rural area of Loni village.

OBJECTIVES

The objectives of the project are as follows-

To assess the breastfeeding practices among rural mother.
To assess the awareness of colostrums feeding.
To ascertain time of initiation of breastfeeding.
To assess the prevalence of exclusive breastfeeding practices.
To find out the practice of prelacteal feeding.
To evaluate the practice of supplementary feeding.

MATERIAL AND METHODS

The study was conducted in Loni village Ta-Rahata Dist- Ahmednagar Maharashtra. 100 rural lactation women were select for purpose study. For collection of data interview technique was used. Data were collected with the help of structured interview schedule and questions were asked to the lactating mother.

RESEARCH AND DISCUSSION

Table no.1 Distribution of mothers according to colostrums feeding.

Particulars	Infant (no. 100)
Colostrums fed to infant on the first day	
Yes	60
No	40

Table no.1 showed that 60 %of mother had fed colostrums to their babies. The rest had discarded it as they thought it to be immature dirty milk and harmful for their infant. Here is the need to educate or inform to mothers for the benefits of the colostrums feeding.

The present study findings were comparable with WaddeS.K, Vedpathak V.L.Yadav V[(6)], Lalita Bahl and R. K. Kaushal [(7)] , Rathore A. S. and Ramesh P.[(8)] observed prevalence of colostrums feeding as 91.18%,91.7%,91.33% respectively. The healthy practice of colostrums feeding was followed as comparable with our study findings.

Table no.2 Distribution of mothers according to prelacteal feeding practices.

Particulars	Infant (no. 100)
Prelacteal feeds	
Given	42
Not given	58

Table no.2 showed that prelacteal feed were given up to 42% infant. Prelacteal feed include plain water, sugar and honey water, ajwain water, jaggery water castor oil, cow milk etc. The present study observations were comparable with WaddeS.K., Vedpathak V.L., Yadav V[6]. B.Purnima,Bhale and Shikhar Jain[9]. Kishor and B. S. Garg [10]and V. R. Parmar et al [11] who found prevalence of prelacteal feeding as 40.2%,43.96%, 45% and 42% respectively.

Table no.3 Distribution of mothers according to time of initiation of breastfeeding

Particulars	Infant(no.100)
Time of initiation of breast feeding	
Within 1 hours	43
Bet 1 hours to 12 hours	21
Bet 12 hours to 24 hours	17
After 24 hours	19

Table no.3 showed that 43% of mother started breast feeding their infant within 1 hour after delivery. 21% of mother breast fed their infant between 1 hour to 12 hours. 17 % mother breast fed between 12 hours to 24 hours and rest of after 24 hours.

Wadde SK,VedpathakVL, Yadav VB.[6] observed 24.84% initiated breastfeeding within half hour. But 85.95% mothers initiated breastfeeding within 24 hours.

S. k. Bandopadhyay[12] observed that 89.4% mothers initiated breast feeding within24 hours while K.Madhu et al[13] found 19% mothers initiated breastfeeding after 24 hours which was comparable with the present study.

Table no.4-Distribution of mothers according to Exclusive Breast Feeding.

Particulars	Infant(no.100)
Exclusive breast feeding	
Followed	60
Not followed	40

Table no.4 showed that Exclusively breast feeding practices was followed by 60%mothers but 40% mothers were nonexistent of exclusive breast feeding due to various reason i.e. misconception, negative advice coming mostly from elder, lactation failure in early day of breast feeding ,mothers goes out to work. however other researcher Wadde SK, Vedpathak VL, Yadav VB[6] observed Only 28.43% mothers exclusively breast fed their babies upto 4 months. While D. K. Taneja et al [14] and A. A.Kameshwrarao [15] observed prevalence of exclusive breast feeding as 26.4% and 37% respectively. Exclusive breast feeding practice was found more in our study findings as comparable.

Tableno.5 Distribution of mothers according to Supplementary feeding to the infant along with breast milk

Particulars	Infant (no.100)
Supplementary milk /semi solid Given to infant along with breast milk	
Yes	92
No	08
Reason for starting supplementary-milk/semi solid	
Inadequate breast milk	42
Next Pregnancy	06
Mother sickness	07
Mother goes to work	30
No specific reason	15
When the mother or child is ill	
Yes	66
No	34
Age of introducing supplementary milk /semi solid	
less than 6 month age	22
6 month to 1 year age	92
Type of supplementary milk/semi solid given	
Cow milk	36
Buffalo milk	21
Goat milk	05
Semi solid(dal water, rice soup etc)	89

Table no.5 showed that 92% mothers were fed Supplementary milk/ semi solid to infant along with breast milk .Top milk and liquids like dal water or rice soup was used by mother along with breast milk. The main reason given for starting top milk/semi solid were inadequate breast milk (42%) , Mother goes to work out side(30%),and followed by next pregnancy and mother /child sickness.

The present study also shows that 22% mother started only supplementary milk to infant before 6 months of age in addition to continuing breast feeding. while 92% were started supplementary milk and semi solid to infant between 6 months to 1year age. The findings of present study also showed that the practice of semisolid like dal water, rice soup etc,(89%) was more common than giving top milks. These findings are in contrast with the findings of Dr. Arun Gupta, Dr.Y.P.Gupta[16] observed 70 % of mothers were giving solid/semi-solid food to the children aged 6-9 months. 53% of mothers also gave cow/goat/ buffalo milk to children. Sweetened water, fruit juice, Tea/Coffee Powder milk, others were given23.3%,12.2%,14.5%,13.4%,14.2% respectively.

D.K. Taneja etal,[14] who reported that in 40.6% infants top milk or semisolids were started before 4 months of age in addition to continuing breast feeding. Most commonly (36.8%) they received diluted animal milk. The reasons for starting top milk in these infants were insufficient breast milk (66.7%), mother ill (15.4%), child ill (5.1%), normal to start at this age (2.6%) and others (10.3%).

The findings of Study D.K. Taneja et al, [14] also showed that the practice of giving top milk (animal milk 73.6%, milk powder 10.4%) or liquids like dal water, fruit juice or soup (55.7%) was more common than giving semisolids which were being given only to 50.0% infants at 6 months of age. Semisolids were not being given to 23.6% infants even at 9 months of age. Breast milk plus semisolids were being given to 65.1 % infants 6-9 months of age. Homemade semisolids were more popular (72.6%) than commercial ones (24.5%).

CONCLUSION&RECOMMENDATION

Only 60 % of mother had fed colostrums to their babies .Here is the need to educate or inform to mothers for the benefits of the colostrums feeding.

Most of mother initiated breast feeding after 1 hour of delivery but efforts should be enhance to increase the percentage of breast feeding within 1 hours of delivery through counseling during pregnancy and support and assistance at the time of birth.

Majority of mothers (60%) were given exclusively breast feeding but 40% mothers were nonexistent of exclusive breast feeding due to various reason. Efforts are needed in this direction to ensure and maintain exclusive breastfeeding for the first six months. These include information during pregnancy and early post-partum period and interpersonal counseling support by skilled healthcare providers or peer counselors.

It is encouraging to note that 92% mothers were started supplementary milk and semi solid to infant between 6 months to 1year. But most of liquid milk or other products provided during this period should be hygienic, solid mushy, homemade/ indigenous /family foods, to help prevent under nutrition in children.

Above points to the need to focus for health education and awareness creating

programmes about the importance of colostrums & exclusive breastfeeding, hazards of prelacteal feeds and appropriate weaning messages infiltrate in the rural area.

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