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

Shashikant R. Kuchekar[a],*, Shivaji D. Pulate[a], Haribhau R. Aher[b], Vishvas B. Gaikwad[c], Sung H. Han[d]

[a]*Principal, Pravara Rural Education Society's, Women's College of Home Science & BCA, Tal-Rahata, Dist-Ahmednagar, (MS), 413713, India*

[b]*P. V. P. College, Pravaranagar, India*

[c]*Principal, K. T. H. M. College, Nashik, India*

[d]*Inorganic Nanomaterial Laboratory, Department of Chemistry, Hanyang University, Seoul, South Korea*

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

*Corresponding author: Shashikant R. Kuchekar
Tel: +91 (9822522004), Fax: N/A
E-mail: shashi17@gmail.com

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 ($\mu g\ mL^{-1}$) 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	Absorbance in UV region	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	Low sensitivity	8
N'',N'''-bis[(E)-(4-fluorophenyl) methylidene] thiocarbonohydrazide	375	1.7–3.4	2–14	4.2546×10^4	1:1:2		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		16
2-Acetylthiophenone thiosemicarbazone	370	5–7	0.2– 6.0	1.83×10^4	1:1	Absorbance in UV region, requires synergent and surfactant	17
4-Vanllideneamino-3-methyl-5-mercapto-1,2,4-triazole	430	8.5	4–32	9.92×10^2	1:2	Requires synergent	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	PM
						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 spectro-photometer (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.
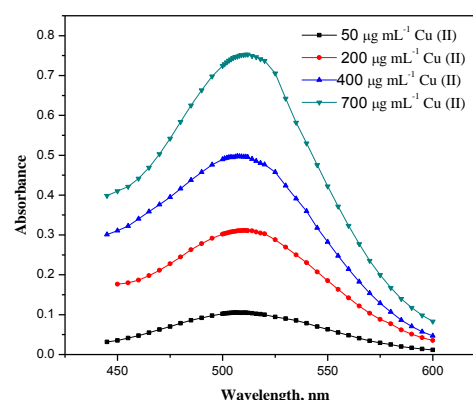

Figure 1. Absorption spectra of Cu (II)-OMPT complex
OMPT: 0.020 mol L^{-1} ; KIO$_3$: 0.075 mol L^{-1},shaking time 1.5 min.

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).
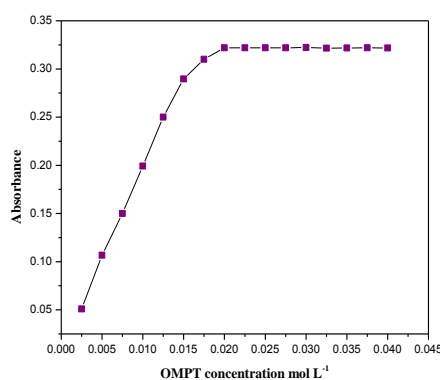

Figure 2. Reagent concentration variation
copper (II): 200 µg mL^{-1}; KIO$_3$: 0.075 mol L^{-1} shaking time 1.5 min.

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).
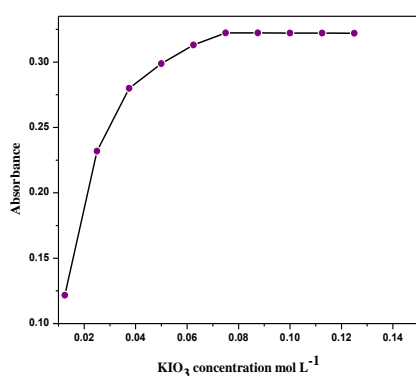

Figure 3. Potassium iodate concentration variation copper (II): 200 µg mL^{-1} ; OMPT: 0. 020 mol L^{-1}; λ_{max}: 510; shaking time 1.5 min.

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).

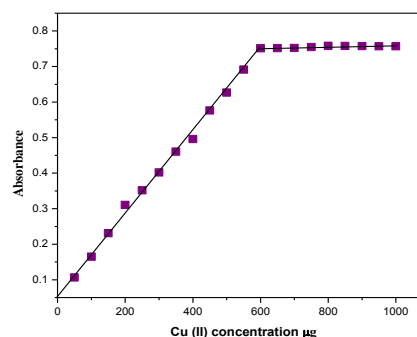**Figure 4.** Beers law OMPT : 0.020 mol L^{-1}; KIO_3: 0.075 mol L^{-1}, λmax: 510 nm; shaking time 1.5 min.
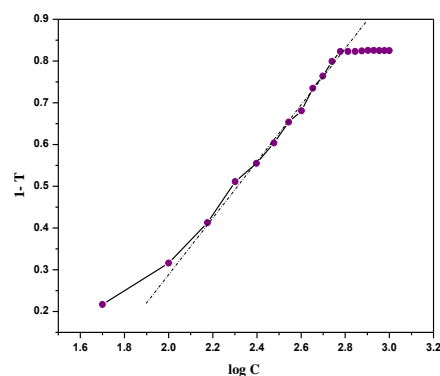
Figure 5. Ringboms plot OMPT : 0 020 mol L^{-1}; KIO_3: 0.075 mol L^{-1}, λ_{max}: 510 nm; shaking time 1.5 min.

Molar absorptivity, Sandell's sensitivity and correlation coefficient

The molar absorptivity and Sandell's sensitivity of the complex are 1.0167×10^3 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).
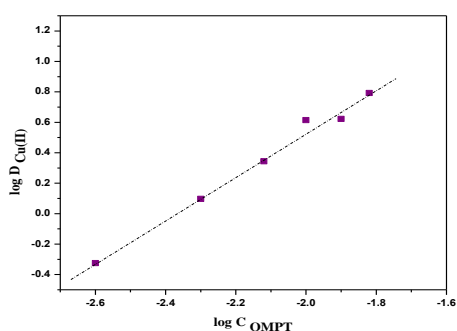

Figure 6. Log – log plot copper (II); 200 µg mL^{-1}; KIO$_3$: 0.075mol L^{-1}; λ_{max}: 510 nm; shaking time1.5 min.
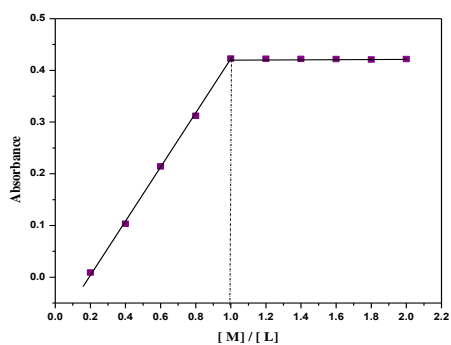

Figure 7. Mole ratio plot for Cu (II)-OMPT complex
KIO$_3$: 0.075 mol L^{-1}, λmax: 510 nm, shaking time: 1.5 min.

Table 3. Effect of foreign ions

| Foreign Ions	Added as	Tolerance limit mg
Mn(II)	MnCl$_2$.6H$_2$O	0. 10
Cd(II)	CdCl$_2$.2H$_2$O	1. 00
Fe(III)	(NH$_4$)Fe(SO$_4$)$_2$..12H$_2$O	0. 025
Hg(II)	HgCl$_2$	0. 50
Ni(II)	NiCl$_2$.6H$_2$O	0. 25
Ce(IV)	Ce (SO$_4$)$_2$.4H$_2$O	0. 50
Al(III)	AlCl$_3$. 6H$_2$O	0. 50
Cr(III)	CrCl$_3$	0. 10
Zn(II)	ZnSO$_4$.7H$_2$O	0. 25
La(III)	LaCl$_3$.7H$_2$O	0. 15
Li(I)	LiCl	0. 50
Ti(III)	(Ti$_2$SO$_4$) $_3$	0. 10
Mg(II)	MgCl$_2$.6H$_2$O	0. 50
Ga(III)	GaCl$_3$	0. 005
Mo(VI)	(NH$_4$)$_5$MO$_7$.2H$_2$O	0. 10
W(VI)	Na$_2$WO$_4$2H$_2$O	0. 25
Zr(IV)	ZrOCl$_2$ .8H$_2$O	0. 10
Pb(II)	PbCl$_2$	0. 25
V(V)	V$_2$O$_5$	1. 0
Co(II)	CoCl$_2$.6H$_2$O	0. 10
Ba(II)	BaCl$_2$ .6H$_2$O	0. 01
Ca(II)	CaCl$_2$.2H$_2$O	0. 25
Tl(III)	Tl$_2$O$_3$	0. 20
Se(IV)	SeO$_2$	0. 96
U(VI)	UO$_2$(CH$_3$COO)$_2$	0. 05
Fluoride	NaF	5. 00
Sulphate	K$_2$SO$_4$	5. 00
Tartarate	(CHOH. H$_2$O)	5. 00
Citrate	(C$_6$H$_8$O$_7$. H$_2$O)	5. 00
Succinate	(CH$_3$COONa)$_2$.6H$_2$O	5. 00
Acetate	(CH$_3$COONa).3H$_2$O	5. 00
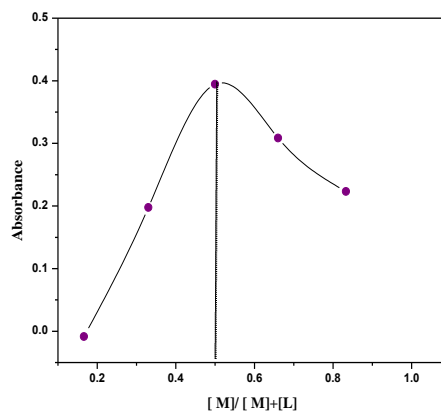
Figure 8. Job's continuous variation method KIO$_3$: 0.075 mol L^{-1}, λmax: 510 nm, shaking time: 1.5 min.

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 $\pm$ 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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