

The use of o-methylphenyl thiourea as a new reagent for solvent extraction and spectrophotometric measurement of copper (II) from environmental samples

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Abstract

Using o-methylphenyl thiourea (OMPT) as a sensitive reagent, a quick and easy way to determine copper (II) by spectrophotometry has been devised. The procedure is based on the idea of creating a copper (II)-OMPT complex. From an aqueous solution in 0.075 mol L⁻¹ potassium iodate, copper (II) was extracted using chloroform and 0.020 mol L⁻¹ OMPT. At 510 nm, the complex's absorbance was recorded. Up to 600 µg mL⁻¹ of copper (II), Beer's law was followed. The complex has a molar absorptivity of 1.0167×10³ L mol⁻¹ cm⁻¹ and a Sandell's sensitivity of 0.0625 µg cm⁻². There was a 0.93 correlation coefficient for the approach. Using slope ratio, mole ratio, and job's continuous variation techniques, the stoichiometry of the copper (II)-OMPT complex was determined to be 1:1. Over twenty-four hours, the copper (II)-OMPT combination remained stable. There are no outside ions that might potentially disrupt the suggested approach. Copper (II) was effectively separated and determined using the suggested approach from both natural (vegetable and environmental) samples and manufactured (binary and ternary) combinations. The method's accuracy was verified by determining a relative standard deviation of 0.23% for eight separate results.

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

Introduction

Copper, which is found all throughout the environment, is the body's third most important trace element, behind zinc and iron [1]. While copper is found in every bodily tissue, it is most abundant in the kidneys, liver, brain, and heart. Copper goes through the following bodily processes: absorption, storage, distribution, and excretion. Ensuring a consistent and appropriate supply of micronutrients while simultaneously avoiding excess levels is a difficult homeostatic process [2]. Anemia, impaired immunological function, osteoporosis, slow wound healing, arthritis, and cardiovascular disease are all brought on by a lack of copper. Poisoning, nausea, vomiting, jaundice, Wilson disease, tissue damage, and other gastrointestinal issues may result from consuming too much copper [3]. Electric contacts, cables, wires, and a myriad of other conducting components all make extensive use of pure copper. Copper alloys are extensively used in many applications such as vehicle radiators, heat exchangers, residential heating systems, and solar energy panels. Additionally, they find employment in systems that transport process water, potable water, and other types of aqueous fluids via pipelines, valves, and fittings. Many different kinds of pigments, insecticides, and medicinal products include cupric sulfate. According to the reviewed literature, the solvent extraction

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-
undekafluorinehexanetriol-2 [8], N,N- bis [(E)-(4-fluorophenyl) methylidene]
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], morpholine-4-carbodithiote [15], 1-(2', 4'-dinitro amino phenyl)-4,4,6-trimethyl-14-dihydropyrimidine-2-thiol [16], 2-acetyl-thiophenone thiosemicarbazone [17], 4-vanillideneamino-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 (nm)	$\lambda_{\max}$	Condition / pH	Beer's Law ($\mu\text{g mL}^{-1}$) validity range	Molar Absorptivity ($\text{L mol}^{-1} \text{cm}^{-1}$)	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°C	6
1-Phenyl-1-hydrazone-2-oximinopropane-1,2-dione	345	9.4	0.1–1.0	0.35×10^3	1:2		7
1-(2'-methylanylino)-1,1,2,3,3,4,4,5,5,6,6-undekafluorinehexanethiol-2 N'',N'''-bis[(E)-(4-fluorophenyl) methylidene] thiocarbonohydrazide	450	2.8-5.3	0.2-20	4.5×10^4	1:2	Absorbance in UV region	8
2-[4-Chloro-2-methoxyphenylazo]-4,5-diphenyl imidazole	375	1.7–3.4	2–14	4.2546×10^4	1:1:2	Low sensitivity	9
Isonitrosopropiophenone thiosemicarbazone	519	8.0	0.5–30	8.459×10^3	1:2	Absorbance in UV region, requires synergent	10
3-Methoxy-4-hydroxybenzaldehyde-4-bromophenylhydrazone	390	10.0	0.5–6.0	5.8×10^3	1:2	Separation requires 10 minutes	11
2-Hydroxy-5methyl acetophenone	462	4.0	0.2–4.0	2.05×10^4	1:1	Absorbance near UV region	12
Isonicotinoyl hydrazone α -(2-Benzimidazolyl)- α' , α'' -(N-5-nitro-2-pyridylhydrazone)-toluene	440	3.4	0.5–4.0	9.3×10^4	1:1		13
Morpholine-4-carbodithiote	410	6.0	0–2.5	3.81×10^4	1:2	Requires surfactant	14
1-(2',4'-Dinitro amino phenyl)-4,4,6-trimethyl-14, dihydropyrimidine-2-thiol						Applications not studied	

2-Acetylthiophenone thiosemicarbazone	320	4–7	0.2–15	2.46×10^4	1:2:1	Shaking time 5 minutes, requires surfactant	15
4-Vanillideneamino-3-methyl-5- mercapto-1,2,4-triazole	445	8.7–10	100–600	8.7×10^4	1:2:2	Absorbance in UV region, requires	16
Hydrazinecarboxymide2-[(2- hydroxyphenyl) methylene (HC22HPM)	370	5–7	0.2– 6.0	1.83×10^4	1:1	synergent and surfactant	17
O-methylphenyl thiourea	430	8.5	4–32	9.92×10^2	1:2	Requires synergent	18
	359	6.80	1–10	0.33×10^5	1:2	Absorbance in UV region	19
	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, sensitive 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 $\lambda_{\max}$ 510 nm against reagent blank.

Results and discussion

Absorption spectra

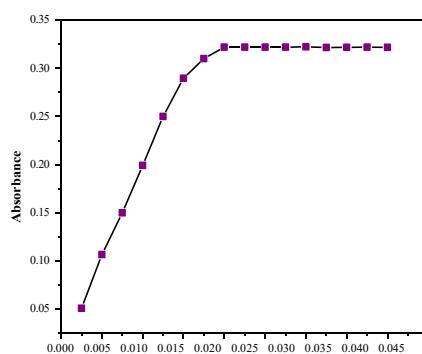
Copper (II)-OMPT complex shows absorbance in the range of 450 nm to 600 nm. The wavelength of maximum absorbance ($\lambda_{\max}$) is 510 nm. The reagent blank shows no absorption at the wavelength 510 nm (Figure 1). Physico-chemical characteristics of the copper (II)-OMPT complex are reported in Table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

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

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



OMPT concentration mol L⁻¹

Figure 2. Reagent concentration variation
copper (II): 200 $\mu\text{g mL}^{-1}$; 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).

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

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 $1.0167 \times 10^3 \text{ L mol}^{-1} \text{ cm}^{-1}$ and $0.0625 \mu\text{g cm}^{-2}$ respectively. The correlation coefficient values of complex with an independent variable as concentration in $\mu\text{g mL}^{-1}$ 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 (Figure 7) and Job's continuous variation method (Figure 8). **Table 3.** Effect of foreign ions

Foreign Ions	Added as	Tolerance limit
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) ₃ 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

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; KIO₃: 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; KIO₃: 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

Vegetable sample

The vegetable samples (Cauliflower

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 $\mu\text{g mL}^{-1}$; KIO_3 : 0.075 mol L^{-1} ; OMPT: 0.020 mol L^{-1} ; λ_{max} : 510 nm; shaking time 1.5 min.

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

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 $\mu\text{g mL}^{-1}$), lower limit of detection at microgram level (0.08 $\mu\text{g mL}^{-1}$), 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 $\mu\text{g cm}^{-2}$ 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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