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# **SPECTROPHOTOMETRIC DETERMINATION OF COPPER (II)** WITH DITHIOLPHENOLS AND HETEROCYCLIC DIAMINES

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# ABSTRACT

2, 6-dithiol-4-methylphenol (DTMP) and 2, 6-dithiol-4-ethylphenol (DTEP) as a photometric reagent for the extractive spectrophotometric determination of Copper(II) is presented in this paper. The reagent DTMP and DTEP in the presence hydrofobic amins gave instantaneous and stable blue colour with Copper (II) in the pH range 6.5 to 8.1. The Beer's law was applicable in the range of  $0.05 - 3.8 \mu g/ml$  at 629-640 nm. The Limit of Detection (LOD) is found to be 8.5-8.8 ng/mL. The stoichiometry of the complex is established as 1:1:1 (M: L: Am) by equilibrium shift method. The standard deviation and the coefficient of variance are presented. The interference of various cations and anions in the method were studied.

**Keywords:** Copper, spectrophotometric determination, chloroform, 2, 6-dithiol-4-methyl-phenol, 2, 6-dithiol-4-ethylphenol.

# INTRODUCTION

For determination the elements in objects of various compositions commonly used photometric method, characterized by high sensitivity and selectivity, ease of implementation and does not require the determination of expensive equipment. Copper helps provide energy required by biochemical reactions. Although copper is an essential micronutrient and is required by the body in very small amounts, excess copper in the human body can cause stomach and intestinal distress such vomiting, diarrhea, and stomach cramps. The lowest level at which these adverse effects occur has not been well defined. Copper is also a commonly occurring element in natural waters. Most copper contamination in drinking water happens in the water delivery system, as a result of corrosion of the copper pipes or fittings [1].

Copper is available in nature in the free state in the form of sulphides, chlorides and carbonates. Copper is utilised in electrical industries and in industrially useful alloys. Biologically copper is essential in small amounts for the synthesis of haemoglobin.Copper is one of the essential elements in human body. Lack of copper in the body results in health problems such as anemia.



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Copper extensive use as an electrical conductor, heat conductor, building material, and a constituent of various metal alloys. Hence, it is necessary to seek highly, accurate and selective analytical methods for quantitative determination of copper at trace levels.

Various spectrophotometric methods have been proposed for the determination of copper contents of the various samples including natural waters and pharmaceutical samples [2]

For the spectrophotometric determination of copper in various sites(in water, alloys and pharmaceutical samples, synthetic mixtures) suggested naphthazarin (5,8-dihydroxy-1,4-naph-thoquinone) [3], 1-phenyl-1-hydrazonyl-2-oximino propane -1, 2- dion [4], 4-[*N*, *N*-(dimethyl) amino] benzaldehyde thiosemicarbazon [5], 2-(5-bromo-2-oxoindolin-3-ylidene) hydrazine carbothioamide as an analytical reagent [6], o-hydroxyacetophenone isonicotinoylhydrazon [7], 4-(4'-nitrobenzylidene imino)-3-methyl-5-mercapto-1, 2, 4-triazole [8], 2-hydroxy-3-methoxy benzaldehyde thiosemicarbazon [9], 2-acetylthiophene thiosemicarbazone [10].

Oxyphenolate and dithiophenolate complexes of Co(II), Nb(V), V(IV) and Mo(V) insoluble in chloroform, while mixed-ligand complexes with hydrophobic amines and aminophenols easily dissolve in various organic solvents [11-16].

In this respect, a very promising reagent is dithiolphenols (DP), which contains one hydroxyl and two sulphohydryl groups and is a sulfur-containing analogue of mononuclear poly-phenols with two oxygen atoms replaced with sulfur atoms. The real work is devoted to studying of reaction of a complex formation of Copper(II) with 2, 6-dithiol-4-methylphenol (DTMP) and 2, 6-dithiol-4-ethylphenol (DTEP) in the presence of hydrophobic amines (Am). As hydrophobic amine phenantroline (Phen), batophenantroline (BPhen) and dipiridile (Dip) were used.

### Materials and Methods Reagents and Apparatus

The stock solution (1mg / ml) of Copper (II) was prepared by dissolving weighed amount of Copper Sulphate (CuSO<sub>4</sub>) in doubly distilled deionized water [17]. More dilute standard solutions were prepared from this stock solution as and when required. Solutions of DP and Am in chloroform (0.01M) were used.

To create the optimal acidity, 0.1M solutions of KOH and HCl or ammonium acetate buffers were applied. Acetate buffer solution, prepared by mixing of 2 mol x  $L^{-1}$  aqueous solutions of CH<sub>3</sub>COOH and NH<sub>4</sub>OH.

The extractant was purified chloroform. All reagents and chemicals used were of analytical or chemically pure grade. The stock solution of various metal ions and anions were prepared by dissolving the appropriate metal salts in distilled water or with suitable dilute acids and making up to a known volume.

The absorbance of the extracts was measured using a Shimadzu UV1240 spectrophotometer and KFK 2 photocolorimeter (USSR). Glass cells with optical path of 5 or 10 mm were used. pH of aqueous phase was measured using an I-120.2 potentiometer with a glass electrode. Muffle furnace was used for dissolution of the samples. The process of thermolysis of the compounds was studied using derivatograph system «Shimadzu TGA-50H». IR spectra were recorded on a spectrophotometer "Bruker" (Germany).



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# General procedure for the determination of Copper

Portions of stock solutions of Copper(II) varying from 0.1 to 1.0 mL with a 0.1-mL step, a 2.0 mL portion of a 0.01 M solution of DP, and a 2.5 mL portion of a 0.01M solution of Am were placed in to calibrated test tubes with ground-glass stoppers (the volume of the organic phase was 5 mL). The required value of pH was adjusted by adding 1M NaOH.

The volume of the aqueous phase was increased to 20 mL using distilled water. In 10 minnute after the complete separation of the phases, the organic layer was separated from the aqueous layer and the absorbance of the extracts was measured on KFK-2 at room temperature and 590 nm (l = 0.5 cm) against a reagent blank.

# **RESULTS AND DISCUSSION**

DP were synthesized according to the procedure [18] Structure of ligand was confirmed by using NMR and IR spectra (table 1, fig.1) [19, 20, 21].

Reagent	IR (KBr, $v_{max}$ , cm <sup>-1</sup> )	<sup>1</sup> H NMR (300,18 MHz, $C_6D_6$ )
DTMP	3460 cm <sup>-1</sup> v (OH), 3050 cm <sup>-1</sup> v(CH),	δ 5.24 (s, 1H- OH), δ 3.32(s, 2H - 2SH), δ
	2570см <sup>-1</sup> v(SH), 2962 и 2872 см <sup>-1</sup> v(-	7.11 (s, 2H Ar-H), δ 2.38 (s, 3H –CH <sub>3</sub> ).
	CH <sub>3</sub> ), 1555cm <sup>-1</sup> $\delta$ (C <sub>6</sub> H <sub>5</sub> ), 1390 cm <sup>-1</sup> $\delta$ <sub>as</sub> (-	
	CH <sub>3</sub> ).	
DTEP	3460 cm <sup>-1</sup> v (OH), 3050 cm <sup>-1</sup> v(CH),	δ 5.29 (s, 1H- OH), δ 3.38(s, 2H - 2SH), δ
	2575см <sup>-1</sup> v(SH), 2965 и 2874 см <sup>-1</sup> v(-	7.15 (s, 2H Ar-H), δ 2.59 (s, 2H –CH <sub>2</sub> -), δ
	CH <sub>3</sub> ), 1555cm <sup>-1</sup> $\delta$ (C <sub>6</sub> H <sub>5</sub> ), 1460 cm <sup>-1</sup> $\delta$ <sub>as</sub> (-	1.22 (s, 3H –CH <sub>3</sub> ).
	CH <sub>2</sub> -CH <sub>3</sub> ).	

Table 1. The research results of IR and NMR spectroscopy

Cu(II) reacts with DP gives a yellow colored complexes. These complexes are insoluble in non-polar solvents. Experiments on electromigration in a U-shaped tube and on sorption on EDE-10P (EDE-ethylenediamine, epichlorohydrin; 10- serial number of the brand: P-means that the matrix has a macroporous structure) anion exchangers have demonstrated the anionic nature of single-ligand complexes, in the electromigration study of the complexes, it was found that the yellow dithiophenolate complexes of Cu(II) moved to the cathode. When the sign of the charge of the single-ligand complexes was determined by ion chromatography, the EDE-10P anion exchanger completely absorbed the colored component of the solution. When hidrophob amins (Am) were introduced into the system, the extraction of these compounds into the organic phase as a mixed-ligand complex (MLC) was observed.



Figure 1. <sup>1</sup>H NMR –spectrum of DTMP



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### The choice of the extractant

Different organic solvents like chloroform, 1,2-dichloroethane, carbon tetrachloride, benzene, chlorobenzene, toluene, isoamyl alcohol, benzoyl alcohol, ethyl acetate, *n*-butanol and their mixes were tried for extraction (fig.2). Extractibility of complexes was estimated in coefficient of distribution and extent of extraction. Thus basicity of amines has no noticeable impact on conditions and extraction of complexes. Fast division of layers and the maximum value of molar coefficient of absorption were received at extraction of complexes by chloroform. After a single extraction with chloroform, 97.6-98.5 % of copper was extracted as an mixed-ligand complex (in a case the dichloroethane and carbontetrachloride was removed 95.5 – 96.6 % of Copper). Chloroform was found to be the best extracting solvent; hence, it was selected for extraction throughout the work. Organic solvents used for extraction of Cu (II) can be arranged on the basis of their extraction coefficient values as chloroform > carbon tetrachloride >1,2-dichloroethane > toluene > benzene > ethyl acetate > *n*-butanol > iso amyl alcohol > benzyl alcohol (fig. 2). The concentration of Copper in the organic phase was determined with rubeanic asid [1] by photometric measurements afterback extraction, while in the aqueous phase it was determined by the difference.



Figure 2. Effect of solvents on extraction of Cu(II)-DTEP-Dip

#### Extraction as a function of pH

Change in pH affected the complexation of Cu (II) - DP - Am. To study the effect of pH on maximum color development and also on quantitative extraction of the colored complexes into chloroform, the color reaction and the extraction were carried out at different pH values. A series of buffer solutions, each differing by 0.2 pH units were prepared and in the presence of these buffers, the color was developed and then the complexes was extracted into chloroform layer as per the procedure. The absorbance values of each of the extracted solutions were measured. It is seen from that the extraction of the complex into chloroform is quantitative and the complex shows maximum absorbance in the pH range 6.2 to 8.1. Beyond this pH range, the observed absorbance values were lower. At pH > 9 complexes are practically not extractable, which is apparently due to increasing concentration of not extractable complexes in aqueous solution [Cu(DP)<sub>2</sub>]<sup>4-</sup> and [Cu (DP)<sub>3</sub>]<sup>7-</sup> since DF for the second dissociation



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sulfhydryl group ( $pK_2 = 8.36-8.72$ ) continues to increase. For all subsequent studies, therefore, the pH is maintained at an optimum level of 7.0.



**Figure 3.** Absorbance of mixed-ligand complexes as a function of the pH of the aqueous phase

 $C_{Cu(II)}$ = 1.875 ×10<sup>-5</sup> M;  $C_{DP}$ =(0.80-0.88)×10<sup>-3</sup>M,  $C_{AM}$ = 1.0×10<sup>-3</sup>M, K $\Phi$ K-2,  $\lambda$ =590 nm, l = 0.5 cm.

#### Absorption spectrum

Spectra of the extracted in chloroform ternary Cu(II)-DP-Am complexes are shown in Figure 4. Maximum absorbance of MLC is observed at 629-640 nm. The reagents has a negligibly small absorbance at the  $\lambda_{max}$  of the complex and, hence, does not interfere with the determination of copper. Thus, further absorbance measurements of the complexes were made at 590 nm. The absorption spectrum of Cu (II)-DP in chloroform shows the maximum absorption at 475-480 nm. Contrast of reactions was high: initial reagents - are colourless, and complexes – are intensively painted. Molar coefficients of absorption make  $(3.28-4.82) \times 10^4$  dm<sup>3</sup> · mol<sup>-1</sup> · cm<sup>-1</sup>.



Figure 4. Absorption spectrum of mixed-ligand complexes Cu - DP - Am.



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 $C_{Cu(II)} = 1.875 \times 10^{-5} \text{ M}; C_{DP} = (0.80 - 0.88) \times 10^{-3} \text{ M}, C_{AM} = 1.0 \times 10^{-3} \text{ M}, \text{ Shimadzu UV1240}, l = 1 \text{ cm}.$ 

### Influence of ligand concentration and incubation time

It was observed that as the reagent concentration increased percent extraction increased. For the formation and extraction of MLC, a 10-15-fold excess of complexing reagents is required; for example, the optimal conditions for formation and extraction of these compounds are provided by  $(0.80-0.88)\times10^{-3}$  M DP and  $1.0\times10^{-3}$  M Am. A large excess of hydrophob amin interferers with the determination. However it was found that the presence of excess of the reagent solution does not alter the absorbance of the color reaction. The equilibration time of 3.0 minute is sufficient for the quantitative extraction of Copper. The stability of colour of the Cu(II)- DP-Am complex with respect to time shows that the absorbance is observed. The salts used in adjusting the ionic strength generally similar natural water samples. the ionic strength of the medium has not markedly affected the complexation process.

### Stoichiometry of the complexes and the mechanism of complexation

Starik-Barbanel relative yield method, equilibrium shift method, crossed lines method and Asmus' methods were employed to elucidate the composition of the complex [22]. It shows that the composition of Cu(II): DP: Am complex is 1:1:1 (Fig.4).

The disappearance of the pronounced absorption bands in the 3620-3250cm<sup>-1</sup> with a maximum at 3475 sm<sup>-1</sup> observed in the spectrum of DTMP, says that the -OH group is involved in the formation of the complex. The observed decrease in the intensity, absorption bands in the area 2570 sm<sup>-1</sup> shows that one of the -SH groups involved in the formation of coordination bond in the ionized state. Detection of the absorption bands at 1380 cm<sup>-1</sup> indicates the presence of a coordinated phenantroline [20, 21].



**Figure 5.** Determination of the ratio of components by equilibrium shift method for Cu - DTMP-Phen (a)  $\mu$  Cu -DTEP-BPhen (b). C<sub>Cu(II)</sub>= 1.875 ×10<sup>-5</sup> M; C<sub>DP</sub> = (0.80-0.88)×10<sup>-3</sup>M, C<sub>Am</sub>= 1.0×10<sup>-3</sup>M, pH=7,  $\lambda$  = 590 nm, KFK-2.  $\ell$ =1.sm.

It was found using the Nazarenko method that Cu(II) in the complexes was present in the form of Cu<sup>2+.</sup> The number of protons replaced by cobalt in one DP molecule appeared to be one [23, 24]. The calculations were carried out based on the hydrolysis of copper ions ( $K_{h1}$ = 1×10<sup>-8</sup>,  $K_{h2}$  =1.9×10<sup>-7</sup>), dissociation constant of DTMP ( $K_0$  =1.2×10<sup>-7</sup>,  $K_1$  =1.78×10<sup>-9</sup>) and protonation constants An ( $K_{pr}$  = 3.0×10<sup>-5</sup>).



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Interaction of copper with DP and Am can be represented as follows:

$$Cu^{2+} + qH_2R^+ + pAm \rightarrow [Cu(H_{2-n}R)_q](Am)_p + qnH^+$$
(1)

Calculations were carried out according to the equation:

$$-\lg B = qnpH + \lg \frac{\kappa_{H}}{(\kappa_{n}...\kappa_{n})^{q}}$$
(2)

Where

$$B = \frac{[Cu](C_R - qC_k)^q (C_{Am} - pC_k)^p}{C_{\kappa} \left(1 + \frac{[H^+]}{K_0} + \frac{\kappa_1}{[H^+]}\right)^q \left(\frac{\kappa_{np}}{[H^+]}\right)^p}$$
(3)

The equilibrium concentration of the complex (C<sub>c</sub>) found spectrophotometrically by the following relationship:

 $C_{\kappa} = C_{Cu} \frac{A_{\chi}}{A_{np}}$ (4)

Where  $C_{Cu}$ - the total concentration of Cu(II), mol/l,  $A_x$  - optical density at a specific pH,  $A_{max}$  optical density at full binding copper(II) a colored complex.

Unbound concentration of copper (II) in the colored complex is expressed:

 $C_{Cu} - C_k = [Cu^{2+}] + [CuOH^+]$ (7)

Hence the equilibrium concentrations of ions and hydroxocomplexes are:

$$[Cu^{2+}] = \frac{C_{Cu(II)} - C_k}{1 + \frac{K_r}{[H^+]}}; \qquad [CuOH^+] = \frac{C_{Cu(II)} - C_k}{1 + \frac{[H^+]}{K_r}}$$
(8)

Thermogravimetric study of the complexes Cu-DTMP-Phen and Cu-DTEP-Phen shown that thermal decomposition of the complexes takes place in three stages: at 60-120 °C water evaporates (weight loss – 4.035-4.16%), at 425-500 °C-decomposed Phen (weight loss -40.36-41.66%), and at 495-540 °C- DP (weight loss -39.35-41.25%). In both cases the final product of the termolysis of the complex is CuO.

Elemental analysis of DTMP and Cu(DTMP)Phen is given in Table. 2

Ligand / complex	Mr	Gross formula	Found / Calculated %		
			С	0	S
	172.28	$C_7H_8OS_2$	48.84	9.30	37.21
DIMP			48.92	9.35	37.13
Cu DTMR Phon	432.06	$C_{19}H_{16}CuN_2O_2S_2$	52.82	7.41	14.84
Cu-DT WIF-Fliell			53.02	7.48	14.73

**Table 2.** Elemental analysis of DTMP and Cu-DTMP-Phen

Proceeding from the obtained data, we propose the following structure for the extracted mixed ligand complex (Fig. 6).

The stability constant of Cu(II)-DP-Am complexes was calculated and found to be  $lg\beta = 10.52-11.94$  at room temperature. The sizes of equilibrium constant K ecalculated on a formula  $lgK_e = lg D - lg[Am]$  were presented in Table 3.

Additional experiments by the Akhmedly's method [25] showed that the complex exists in monomeric form in the organic phase (the obtained coefficient of polymerization  $\gamma$  was equal to 1.03 - 1.15).



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**Figure 6.** Structure of complex Cu(DP)(H<sub>2</sub>O)Phen

In conclusion the analytical parameters pertaining to the proposed method are given in Table 3

**Table 3.** Optical characteristics, precision and accuracy of the spectrophotometric determination of Cu(II) with DP and Am

Compound	рН	λ, nm	Δλ, nm	ε×10 <sup>-4</sup>	lgβ	lgKe	lgK <sub>эк</sub>
Cu-DTMP-Phen	6.7-7.9	630	356	3.45	11.62	6.70	13.25
Cu-DTMP-BPhen	6.6-8.1	635	361	4.37	11.94	6.79	13.32
Cu -DTMP-Dip	6.5-7.9	629	355	3.28	11.47	6.64	13.21
Cu-DTEP-Phen	6.3-7.5	635	359	3.70	10.82	6.71	12.33
Cu-DTEP-BPhen	6.4-7.7	640	364	4.82	10.96	6.81	12.47
Cu -DTEP-Dip	6.2-7.4	634	360	3.61	10.52	6.73	12.29

# Beer's law and analytical characteristics

In order to determine the concentration range in which Beer's law is valid, absorbance values were measured at various concentrations of Cu(II) in the solution. A linear calibration graph drawn between absorbance and the metal ion concentration indicates that Cu(II) may be determined in the range 0.05-3.8  $\mu$ g/ml [28].

# CONCLUSIONS

- 1. Mixed-ligand complexes of Copper (II) with 2, 6-dithiol-4-methylphenol (DTMP) and 2, 6dithiol-4-ethylphenol (DTEP) in the presence of hydrophobic amines have been investigated by spectrophotometric method.
- 2. The results obtained show that the newly developed method in which the reagent DTMP and DTEP was used, can be effectively used for quantitative extraction and estimation of Cu (II) from aqueous media.
- 3. Extraction of mixed ligand complexes is maximal at pH 6.2-8.1. The proposed method is quick and requires less volume of organic solvent.
- 4. The optimal conditions for the formation and extraction of mixed-ligand compounds have been found and the ratios of components I the complexes have been determined.
- 5. Since the method tolerates a number of metal ions commonly associated with copper, though the method involves extraction of the colored complex into chloroform.
- 6. The Beer's law was applicable in the range of 0.05-3.8µg/ml.

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