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Spectroscopic determination of copper(II) with dimercaptophenols and heterocyclic diamines

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ABSTRACT

2,6-Dimercapto-4-methylphenol (DMMP) and 2,6-dimercapto-4-ethylphenol (DMEP), 2,6-dimercapto-4-tert-buthylphenol (DMBP) as a photometric reagent for the extractive spectrophotometric determination of copper(II) is offered in this paper. The component DMMP, DMEP and DMBP in the presence of hydrofobic amines resulted in an immediate and consistent blue colour with copper(II) in the pH range 5.2 to 8.5. The Beer's law was relevant in the range of 0.3 - 20 µg/ml at 585-650 nm. The stint of detection is discovered to be 8.2-9.5 ng/mL. Compounds of several classes were proved as organic solvents. Analysis have shown that the best of those tested is chloroform. The stoichiometry of the complex is determined as 1:1:1(M: L: Am) by the method of equilibrium shift. The standard drift and the factor of variance are presented. The proposed methods is free from interferences from great number of foreign ions. The proposed methods was effectively for separation and determination of copper(II) from various pharmaceutical, food and plant samples. Thus the methods can be employed for the determination of trace amount of copper(II) in pharmaceutical, food and in plant samples are presented.

1. Introduction

Copper helps to consume the energy necessary for biochemical reactions. Despite the fact that copper is the main trace element and is required by the body in very small quantities, an excess of copper in the human body can cause stomach and intestinal disorders, such as vomiting, diarrhea and abdominal pain. Copper is also the most common element in natural waters. Most of the contamination of drinking water with copper occurs in the water supply system due to the degradation of copper pipes or fittings [1].

Copper is one of the leading elements in the human body and is present in all body materials. The liver, brain, heart and kidneys contain the largest amount of copper. Copper is transported, absorbed, stored, distributed and excreted from the body. Copper deficiency contributes to such diseases as anemia, decreased immune function, osteoporosis, wound healing, arthritis and cardiovascular diseases. Excess copper leads to diarrhea, upset stomach, nausea, and also causes jaundice, Wilson's disease, tissue damage, etc.

The daily norm of copper consumption depends on age, gender and individual characteristics. In a healthy person, it is from 1 to 3 mg per day. A child needs up to 2 mg. Babies up to 1 year need to receive up to 1 mg per day. For children up to 3 years, no more than 1.75 mg. For pregnant women, it is especially important to observe the necessary norm. This is up to 2 mg per day of this element. Copper has an effect on the normal formation of the baby's heart and nervous system.

To avoid deficiency, it is necessary to follow a certain diet, take vitamins or food supplements containing copper.

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Specialists recommend that some people increase the daily consumption rate of this element. Basically, it is necessary for those who suffer from: allergies, osteoporosis, anemia, periodontitis, various infections, heart problems, arthritis, intestinal disorders and ulcers.

Pure copper is usually used in electrical engineering for the manufacture of cables, wires and other conductors. Copper wires, in turn, are also used in the windings of electric drives and power transformers. For these ambitions, the metal must be very unmixed: impurities drastically reduce electrical conductivity. For example, the presence of 0.02% aluminum in copper reduces its electrical conductivity by almost 10%. Copper mixtures are widely used in car radiators, heat exchangers, home heating systems and solar batteries. In addition, they are also used for pipes, valves, fittings for drinking water, technical water and other water-based liquids. Copper sulfate is used in the production of pigments, pesticides and medicines. From this point of view, the development of new analytical methods that allow managing its content in various objects has become relevant. As a result of copper deficiency, the development of diseases of respiratory organs, locomotor apparatus, blood, pathologies of the immune system may occur. As a result, environmental protection requires constant analytical control of the environment of the object.

The human body cannot produce copper on its own. You can replenish stocks only with food products or food supplements. It is absorbed in the intestines. It is excreted from the body with bile and urine.

Most copper is found in liver, raw eggs, vegetables, berries and fruits. Also, don't forget about fresh seafood, fish, meat and dairy products. For example, oysters contain up to 7 mg of this element. They can well help fill the daily norm of a person. The concentration of copper in fish and seafood depends on their freshness. People who constantly observe various diets can include potatoes, asparagus, soybeans and wheat germ in their diet. It is best to give preference to pastries and bread made of rye flour. Cabbage, eggplant, olives, beets, peas are also rich in copper.

Copper is the important element in preparation of complexes with oranic ligand [2]. Various analytical methods have been using to removal [3] or detect copper(II) ion including electroanalytical techniques [4], atomic absorption spectrometry [5], atomic emission spectroscopy [6], photoluminescence spectroscopy, dynamic light scattering [7], inductive coupled plasma-optical emission spectrometry [8,9] and inductive coupled plasma-mass spectrometry [10].

In objects of varied compositions, elements are usually defined using the spectrophotometric method. Spectrophotometry is characterized by high sensibility and particularity, are simple to use and does not require high-priced equipment for determination. It is simple, economical and readily available to most laboratories. Therefore, spectrophotometry is a widely used analytical method of analysis. A variety of spectrophotometric methods have been suggested to identify the copper content in different samples, including natural waters and pharmaceutical samples [11].

For the spectrophotometric identifying of copper in various sites recommended naphthazarin (5,8-dihydroxy-1,4-naphthoquinone) [12], 1-phenyl-1-hydrazonyl-2-oximino propane-1,2-dion [13], 4-[*N*, *N*-(dimethyl) amino] benzaldehyde thiosemicarbazon [14], 2-(5-bromo-2-oxoindolin-3-ylidene) hydrazine carbothioamide as an analytical reagent [15], o-hydroxyacetophenone isonicotinoylhydrazon [16], 4-(4’-nitrobenzylidene imino)-3-methyl-5-mercapto-1, 2, 4-triazole [17], 2-hydroxy-3-methoxy benzaldehyde thiosemicarbazon [18], 2-acetylthiophene thiosemicarbazone [19], 5-bromosalicylaldehyde thiosemicarbazone [20], 5-{α–methyl-3-hydroxy benzylidene} rhodanine [21], 4-(2-pyridylazo) resorcinol [22], *o*-methylphenyl thiourea [23], 2-[4-chloro-2-methoxyphenylazo]-4,5-diphenyl imidazole [24]. However, most of these spectrophotometric reagents with draw from various limitations such as more time for color development, heating, narrow Beer’s range, and interferences from many ions.

The spectrophotometric approach we are talking about is basic, affordable and accessible, so it is used to determine metal ions in varied object. Hydroxythiophenolate and dithiolphenolate complexes Co(II), Nb(V), V(IV) and Mo(V), insoluble in nonpolar organic solvents, while mixed ligand complexes with hydrophobic amines and aminophenols readily dissolve in a variety of organic solvents [25-31].

In this regard, a particularly promising reagent is dimercaptophenols (DP), which contains one hydroxyl and two sulphohydryl groups and is a sulfur-containing analogue of mononuclear polyphenols with two oxygen atoms replaced with sulfur atoms. The actual work is focused on researching of reaction of a complicated copper formation(II) with 2,6-dimercapto-4-methylphenol (DMMP), 2,6-dimercapto-4-ethylphenol (DMEP) and 2,6-dimercapto-4-*tert*-buthylphenol (DMBP) in the presence of hydrophobic amines (Am).

As hydrophobic amine phenantroline (Phen), batophenantroline (BPhen), dipyridyle (Dip) and pyridine (Py) were used.

The goal of this work was studying the reaction of copper thoroughly with dimercaptophenols in the presence of a slight excess of the reagent and to search for optimal conditions for the direct spectrophotometric determination of copper in complex objects.

The study's objectives included identifying the best conditions for determining microquantities of copper(II) without prior separation and concentration, as well as to establish the range of decisived concentrations and metrological characteristics of the method.

2. Computational details

2.1. Reagents and Apparatus

Preparation stock solution. The stock solution **(**1mg / ml**)** of copper**(**II**)** was prepared by dissolving weighed amount of copper sulphate ($CuSO_4$) in doubly distilled deionized water [32**]**. The working standard of copper solution was prepared by suitable dilutions of this stock solution.

Solutions of complexing reagents (of DP and Am) in chloroform (0.01M) were used.

To create the optimal acidity, 1M solutions of KOH and HCl or ammonium acetate buffers were applied. Acetate buffer solution, prepared by mixing of 2 mol·L^{-1} aqueous solutions of CH_3COOH and NH_4OH.

The extractant was cleaned chloroform. All reagents and chemicals used were of analytical or chemically pure grade. The stock solution (1mg/mL) of several metal ions and anions were prepared by dissolving the appropriate metal salts in double distilled water or with suitable dilute acids and making up to a known volume.

Apparatus: The absorbance of the extracts was calculated using a Shimadzu UV1240 spectrophotometer and KFK 2 photocolorimeter (USSR). Glass cells with optical path of 5 or 10 mm were used. The combination of hydrogen ions was managed by an I-120.2 potentiometer with a glass electrode. Muffle furnace was used for disruption of the samples. The process of thermolysis of the compounds was considered using derivatograph system «Shimadzu TGA-50H». IR spectra were recorded on a spectrophotometer "Bruker" (Germany).

2.3. General procedure

2.3.1. General procedure for the determination of Copper

Portions of copper(II) stock solutions ranging 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 Amhs were put in to calibrated test tubes with ground-glass stoppers (the volume of the organic phase was 5 mL). The necessary value of pH was regulated by adding 1M NaOH.

Using distilled water the volume of the aqueous phase was raised to 20 mL. 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) opposed to a reagent blank after the phases had completely separated within 10 minutes.

2.3.2. Procedure for Determination of Cu (II) in Pharmaceuticals samples

Boiling with 10 ml of aqua regia dissolved 0.5 g of pharmaceuticals samples. The combination was evaporated to dryness and the residue was dispersed in 10 ml of 1M HCl filter. If necessary the resulting solution was subsequently reduced to 100 ml with doubly distilled water. The stock solution was properly diluted to create the working solution. From an aliquot of this solution 1 ml was resolved for Cu(II) by the procedure as described earlier.

2.3.3. Determination of copper in the beans

In a porcelain dish at 105 ºC A portion of beans (10 g) was crushed and dried . A muffle furnace at 500 ºC is used to heat the dry residue. The ash was dissolved in diluted (1:1) HNO3, evaporated to wet salts, and then dissolved in water. The mixture was then filtered into a volumetric flask of 100 ml and diluted to a known volume using double-distilled water. Aliquots of the solutions were analyzed for copper(II), by using the proposed procedure.

2.3.4. Determination of copper in the gelatin

5 grams of gelatin in a porcelain dish soak 50 ml of distilled water for 2-3 hours. By the swollen gelatin was added 25 mL (1: 1) HNO_3 and heated in a bath of boiling water for 2 hours. The solution was filtered and neutralized with NH_4OH (1:1) was quantitatively transferred into a volumetric flask of 50 ml and make up to the mark with distilled water. Suitable volumes of these solutions were taken, 10 mL of ammonium acetate

buffer of pH 7.0 were added, and analyzed as per the proposed procedure.

2.3.5. Determination of copper in wheat bran.

5 g sample of wheat bran was dried in an oven at a temperature porcelain cups 105 ºC. Then, the cup was set to asbestos plate contents burned on an open fire. Charred residue with a cup was transferred into a muffle furnace and calcined at a temperature 800ºC. Mineralized residue was dissolved in 0.1 M HNO_3 and filtered through a medium density filter in a 100 ml flask. The copper content was determined DP and Am, and with diétylditiokarbamate.

3. Results and Discussion

DP were synthesized in accordance with the procedure [33] Structure of ligand was verified by using ^{1}H NMR and IR spectra (table 1, fig.1) [34, 35, 36].

Table 1. The research results of IR and ^{1}H NMR spectroscopy

Reagent	IR (KBr, ν_{max}, cm^{-1})	^{1}H NMR (300,18 MHz, C_6D_6)
DMMP	3460 см$^{-1}$ ν (OH), 3050 см$^{-1}$ ν(CH), 2570см$^{-1}$ ν(SH), 2962 и 2872 см$^{-1}$ ν(-CH_3), 1555см$^{-1}$ δ(C_6H_5), 1390 см$^{-1}$ δ_{as} (-CH_3).	δ 5.24 (s, 1H- OH), δ 3.32(s, 2H - 2SH), δ 7.11 (s, 2H Ar-H), δ 2.38 (s, 3H –CH_3).
DMEP	3460 см$^{-1}$ ν (OH), 3050 см$^{-1}$ ν(CH), 2575см$^{-1}$ ν(SH), 2965 и 2874 см$^{-1}$ ν(-CH_3), 1555см$^{-1}$ δ(C_6H_5), 1460 см$^{-1}$ δ_{as} (-CH_2-CH_3).	δ 5.29 (s, 1H- OH), δ 3.38(s, 2H - 2SH), δ 7.15 (s, 2H Ar-H), δ 2.59 (s, 2H –CH_2-), δ 1.22 (s, 3H –CH_3).
DMBP	3458 - ν(OH), 2568 - ν(SH), 3040 - ν(CH), 1535- ν(C_6H_5), 1395- δ (–$C(CH_3)_3$)	δ 5.2 (s, 1H- OH), δ 3.35(s, 2H- 2SH), δ 7.05 (s, 2H Ar-H), δ 1.42 (s, 9H- -$C(CH_3)_3$)

When Cu(II) and DP react, yellow colored complexes are produced. In non-polar solvents, these complexes cannot be dissolved. When hidrophob amins (Am) were added to the mixture, it was seen that these substances extracted into the organic phase as a mixed-ligand complex (MLC).

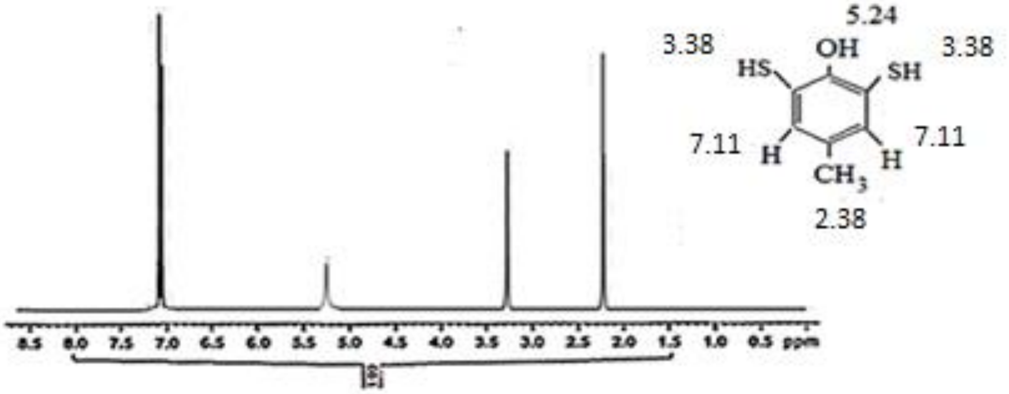

Fig. 1. ^{1}H NMR –spectrum of DMMP

We know that complex compounds are formed by the action of metal ions and organic substances. While studying this process, it’s necessary to know both the state and properties of metal ions in different environments. They are: dissociation and protonization constants, absorption spectra of various forms of the re-agent, etc (table 2). The study of various ionic states of organic reagents is of interest for elucidating the mechanism of their interaction with metal ions, as well as choosing the optimal conditions for the formation of the studied complexes. Knowing the acid-base properties of the reagent is also important for the characterisation of complex compounds.

The DP ionization constants were studied by the method of potentiometric titration. The acidic properties of DP molecules and singly charged anions decrease with decreasing dielectric constant of the solution.

DP exist in solution in four forms - one molecular (H_3R) and three ionic (H_2R^-, HR^{2-} and R^{3-}). At pH 0-6.5 the reagents exist mainly in molecular form, at pH 6-7 in the form - H_2R^-, at pH 8-10 - HR^{2-} and at pH 11-14 - R^{3-}. With an increase in pH, the reagents pass from one form to another, resulting in a slight bathochromic shift in the absorption spectrum and an increase in the molar absorption coefficient.

Table 2. Ionization constants of DP (pK_a) (C_{DP} = 0.1M, $t = 25 \pm 0.5$ °C, $n = 6$, $P = 0.95$ μ=0.1)

DMMP			DMBP		
pK_1	pK_2	pK_3	pK_1	pK_2	pK_3
6.92	8.74	11.15	6.98	8.78	11.26

3.1. The choice of the extractant

Various organic solvents like chloroform, carbon tetrachloride, 1,2-dichloroethane, benzene, toluene, chlorobenzene, benzoyl alcohol, isoamyl alcohol, ethyl acetate, methyl ethyl ketone, *n*-butanol and their mixes were tried for extraction (fig.2). The distribution coefficient and the level of extraction were used to assess the extractability of the complexes. The circumstances and the extraction of the MLC are little affected by the basicity of amines. By extracting the complexes with chloroform, the layers quickly separated and the molar absorption coefficient reached its maximum value. After a single extraction with chloroform at a ratio of aqueous and organic phases of 4:1, 97.6-98.5% of copper is recovered in the form of a mixed-ligand complex with a mixed coordination sphere (in the case of dichloroethane and carbochloranhydride, 95.5-96.6% of copper was removed).The degree of extraction of mixed ligand complexes was calculated by the formula R=100D/(D+1), where D is the distribution coefficient. Until the phase volume ratio reaches a 20:1 , the extent of extraction remains constant.

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 > chlorobenzene > toluene > benzene > ethyl acetate > *n*-butanol > isoamyl alcohol > benzyl alcohol (table 3, 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. Photometric measurements afterback extraction with rubeanic acid were used to measure the concentration of copper in the organic phase, while in the aqueous phase was used to measure by the difference.

Table 3. Influence of the nature of the organic solvent on the optical density of extracts of the mixed ligand complex
$C_{Cu(II)}$= 1.875 ×10^{-5} M; C_{DP}=(0.80-0.88)×10^{-3}M, C_{Am}= 1.0×10^{-3}M, КФК-2, λ=590 nm, l = 0.5 см.

Solvent	A	Phase color	
		organic	aqueous
Chloroform	0.83	blue-green	colorless
Chloroform + isoamyl alcohol (1:1)	0.72	blue-green	colorless
Chloroform + isoamyl alcohol (1:1)	0.73	blue-green	colorless
Carbon tetrachloride	0.82	blue-green	colorless
Cyclohexanol	0.13	greenish	bluish
Tributyl Phosphate	0.41	greenish	colorless
Benzene	0.42	blue-green	bluish
Chlorobenzene	0.67	blue-green	colorless
Methyl ethyl ketone	0.05	colorless	bluish
Benzoyl alcohol	0.23	greenish	bluish
n-Butanol	0.32	greenish	bluish
Isobutyl alcohol	0.30	greenish	bluish
Isoamyl alcohol	0.23	greenish	bluish
Ethyl acetate	0.35	blue-green	bluish
1,2-dichloroethane	0.81	blue-green	colorless

3.2. Effect of pH

The optimal pH value of the maximum yield was defined as the maximum pH value at which the light absorption is still constant. A change in pH will significantly affect the complex formation of Cu(II) with DP and Am. To study the effect of pH on the maximum development of color, as well as on the quantitative extraction of colored complexes into chloroform, the color reaction and 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 process . The absorbance values of each of the extracted solutions were measured. It is seen from that the area of existence of complex compounds is within pH 5.2-8.5. The observed absorbance values were lower beyond this pH range. At pH > 9 complexes are practically not extractable, which is apparently due to increasing concentration of not extractable complexes in aqueous solution $[Cu(DP)_2]^{4-}$ and $[Cu(DP)_3]^{7-}$ since DP for the second dissociation 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. These results showed that optimum pH for extraction was pH_{ex} 9 for both ions.

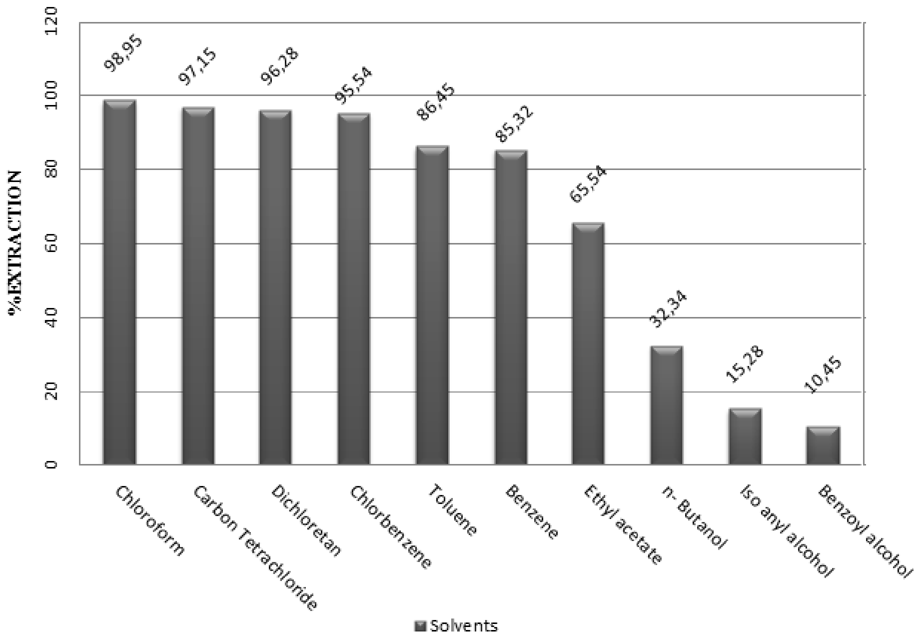

Fig. 2. Effect of solvents on extraction of Cu(II) –DMEP-Dip

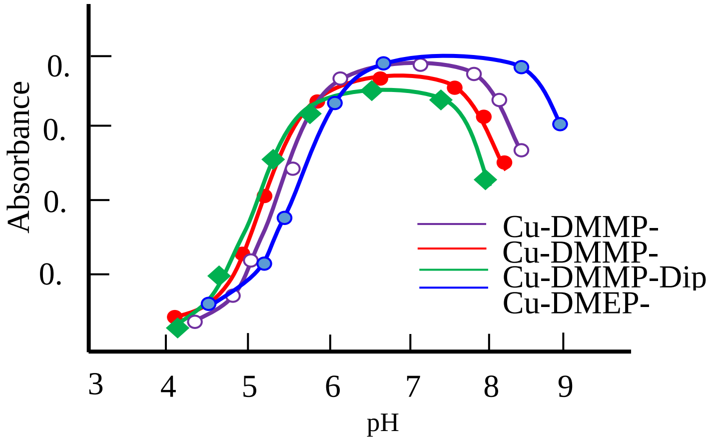

Fig. 3. Absorbance of mixed-ligand complexes as a function of the pH of the aqueous phase $C_{Cu(II)}$= 1.875 ×10^{-5} M; C_{DP}=(0.80-0.88)×10^{-3}M, C_{Am}= 1.0×10^{-3}M, КФК-2, λ=590 nm, *l* = 0.5 sm.

3.3. Absorption spectrum

The absorption spectrum of the Cu-DP-Am complexes in chloroform solution was studied over the range of 400-800 nm (Fig.4). Absorption spectra were recorded for extracts obtained under optimal complexation and extraction conditions. Maximum absorbance of MLC is observed at 585-650 nm. The absorption of mercaptophenols and hydrophobic amines under these conditions is negligible. Thus, further absorbance measurements of the complexes were made at 590 nm. The absorption spectrum of the Cu(II) - DP complexes demonstrates the maximum absorption at 475-480 nm. . The contrast between the reactions was high: the initial reagents are colorless, whereas the complexes are heavily painted. The molar absorption coefficients of mixed ligand complexes are (3.28-4.92) ×10^4 dm$^{3.}$ mol^{-1}· cm^{-1}. It is clearly seen here that the light absorption maxima of chloroform extracts are shifted to a longer wavelength region and the light absorption of extracts is much more intense, which leads to higher molar absorption coefficients, and to greater detection sensitivity.

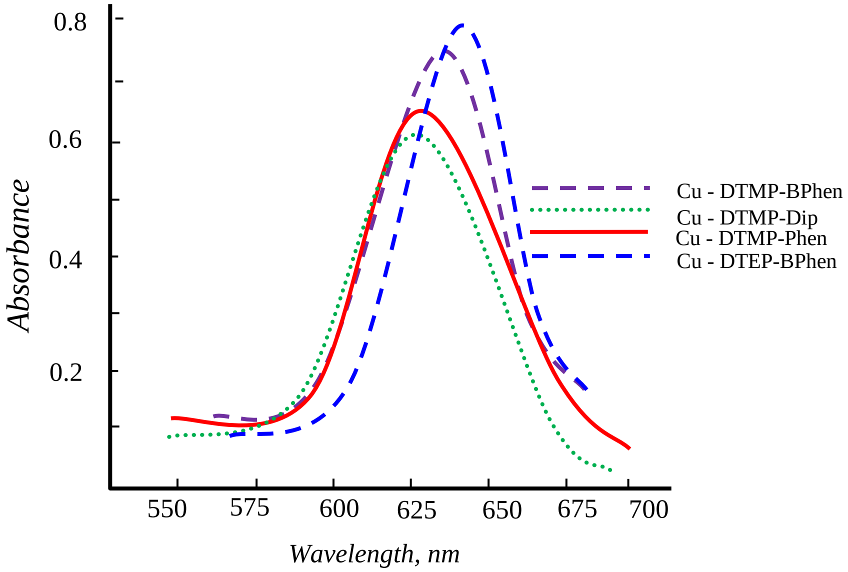

Fig. 4. Absorption spectrum of mixed-ligand complexes Cu - DP -Am.
$C_{Cu(II)}$= 1.875 ×10^{-5} M; C_{DP}=(8.0-8.8)×10^{-4}M, C_{Am}= 1.0×10^{-3}M, Shimadzu UV1240, *l* = 1sm.

Reagent concentrations were consistently modified in order to determine the best concentrations, and the optical density change was tracked over time. It was observed that as the reagent concentration increased percent extraction increased. There must be a 10-15-fold excess of complexing agents for the production and extraction of MLC. In all cases considered, a complex is formed in the systems we are looking at. This process is accompanied by a change in the pH of the solution. But the nature of light absorption spectra remains unchanged. As the concentration of DP and Am increases, the nature of the spectra does not change, but the intensity of light absorption increases, reaching a maximum constant value at a concentration of (8.0-8.8)·10^{-4} M mol/l DP and 1.0 ·10^{-3} M Am. In all cases, in the studied systems, one complex is formed, and with a change in the pH of the solution, the nature of the light absorption spectra remains unchanged. As the concentration of DP increases, the nature of the spectra does not change, but the intensity of light absorption increases, reaching a maximum constant value at a concentration of 1•10^{-3} M mol/l. The determination is interfered by a significant overabundance of hydrophobic amino acids. However, it was discovered that the excess of the reagent solution did not affect the color reaction's absorbance.For the quantitative extraction of copper, a 3.0 minute equilibration period is sufficient. The stability of complex was studied with the absorbance value measurement at regular time intervals of 1.0 h each at room temperature (fig.5). It is established that the complexes copper with DP and Am is labile and forms rapidly . The study of the dependence of extraction on the phase contact time showed that the optimal mixing time required to extract the copper dimercaptophenolate-amine complex is 5 min. The nature of the amine, the organic solvent, and the acidity of the aqueous phase have practically no effect on the rate at which equilibrium is reached. The Cu(II)-DP-Am complex's color stability over time reveals that the extracted species' absorbance is steady for the first 36 hours before observing a minor decline.Various salts are used to adjust the ionic strength. They are similar to natural water samples. The ionic strength of the medium has not markedly affected the complexation process.

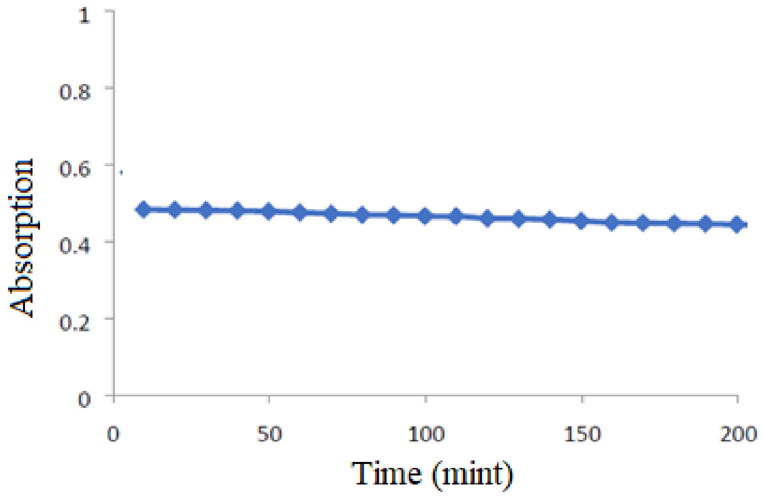

Fig. 5. Effect of time on the absorbance of Cu-DMEP-Phen

3.4. Effect of temperature

The impact of temperature on the absorption of Cu(II)-DMEP-Phen complex has been studied in the range of 25-80 ºC. MLC attained maximum and constant absorbance at 15-70 ºC (fig 6). All subsequent measurements were done at room temperature (25±1 ºC).

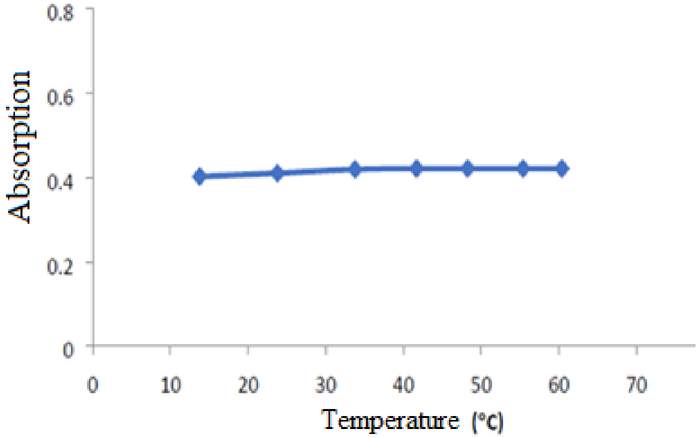

Fig. 6. Effect of temperature on the absorbance of Cu-DMEP-Phen

3.5. Determination of the stoichiometry of the complex and the mechanism of complexation

To clarify the composition of the complex, the Starik-Barbanel relative yield method, equilibrium shift method, crossed lines method, and Asmus' methods were all used [37]. It shows that the composition of Cu(II) : DP: Am complex is 1:1:1 (Fig.7). In the case of Py - 1: 1: 2. At pH 4-9, in all cases, copper dimercaptophenolate is extracted with chloroform only in the presence of an amine, which is part of the extractable compound with a Cu:Am ratio of 1:1.

The disappearance of the pronounced absorption bands in the 3620-3250 cm^{-1} with a maximum at 3475 sm^{-1} observed in the spectrum of DMMP, 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^{-1} 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^{-1} indicates the presence of a coordinated phenantroline [35, 36].

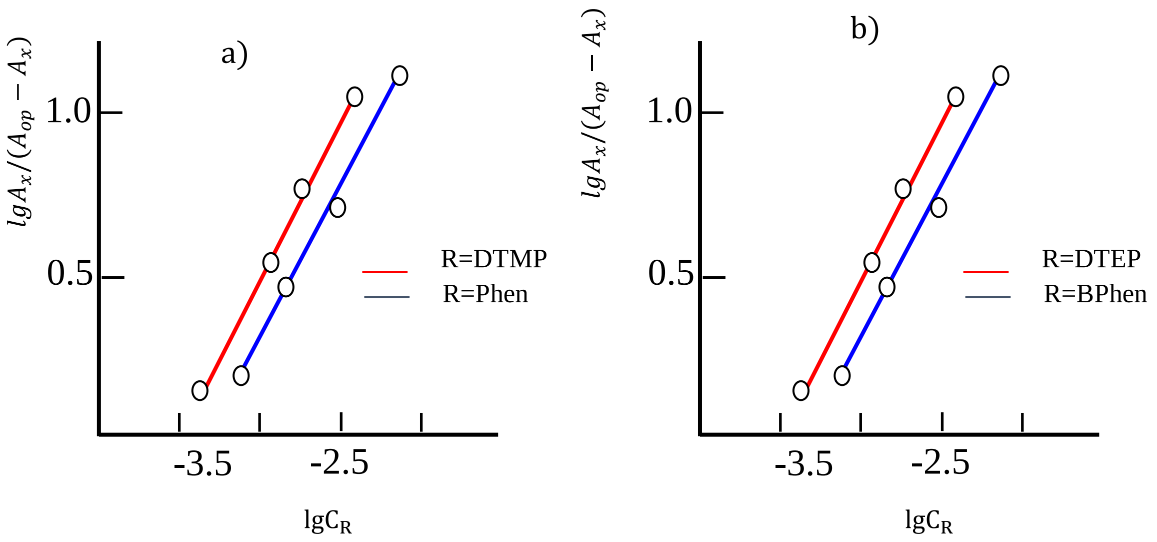

Fig. 7. Determination of the ratio of components by equilibrium shift method for Cu-DMMP-Phen (a) and Cu -DMEP-BPhen (b).
$C_{Cu(II)}$= 1.875 ×10^{-5} M; C_{DP} = (8.0-8.8)×10^{-4}M, C_{Am}= 1.0×10^{-3}M, pH=7, λ = 590 nm, KFK-2. ℓ=1 sm.

It was found using the Nazarenko method that Cu(II) in the complexes was present in the form of Cu^{2+}. Regardless of the nature of the amine during extraction, one hydrogen ion is replaced in the reagent molecule, and the ratio of copper and DP in the complex is always 1:1 [38, 39].

The thermogravimetric study of the complexes Cu-DMMP-Phen and Cu-DMEP-Phen showed that they are stable up to 180 ^{0}C. Thermal decomposition of the complexes occurs in three stages: at 180-220 °C water evaporates (weight loss - 4.035-4.16%), at 425-500 °C- decomposed Phen and Dip (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 DMMP and complexes is given in Table 4.

Table 4. Elemental analysis of DMMP and Cu-DMMP-Phen

Ligand / complex	Mr	Gross formula	Found / Calculated %		
			C	O	S
DMMP	172.28	$C_7H_8OS_2$	48.84	9.30	37.21
			48.92	9.35	37.13
Cu-DMMP-Phen	432.06	$C_{19}H_{16}CuN_2O_2S_2$	52.82	7.41	14.84
			53.02	7.48	14.73
Cu-DMMP-Dip	408.06	$C_{17}H_{16}CuN_2O_2S_2$	50.13	7.74	15.79
			50.04	7.84	15.69

Study of the Cu(I)-DTMP-Phen complex by ^{1}H NMR spectroscopy

The singlet observed in the spectrum of the DTMP ligand at 5.48 ppm, associated with the phenol group -OH, disappears in the spectrum of the complex. This shows that the -OH group is involved in the complex formation. The intensity of the signal observed at 3.28 ppm, associated with the thiol group –SH decreases by a factor of two and slightly shifts to a weaker field (3.43 ppm). This confirms that one thiol group is involved in the complex formation. The presence of water molecules in the complexes is confirmed by the appearance of a new signal at 3.55 ppm associated with H_2O protons (Fig. 8).

Elemental analysis of isolated compounds is consistent with the Cu-DP-Am formula established by the aforementioned techniques. Proceeding from the obtained data, we propose the following structure for the extracted mixed ligand complex (Fig.9).

The curve-crossing method was determined using to calculate the stability constant of the Cu(II)-DP-Am complexes, which was found to be lgβ = 9.90-12.26 at room temperature. The sizes of equilibrium constant K ecalculated on a formula lgK$_e$ = lg D - lg [Am] were presented in Table 4.

According to the experiments the complexes exist in monomeric form in the organic phase, polymerization ratios are 1.03 - 1.15. [40].

The extraction constants of the resulting complexes with chloroform in the presence of amines at a concentration of $1\cdot10^{-3}$M were determined. A comparison of the extraction constants shows that, regardless of the nature of the amine, the extraction constants are practically the same. But with an increase in the ionic strength of an aqueous solution, the extraction constant decreases.

In conclusion, Table 5 provides the analytical parameters related to the suggested approach.

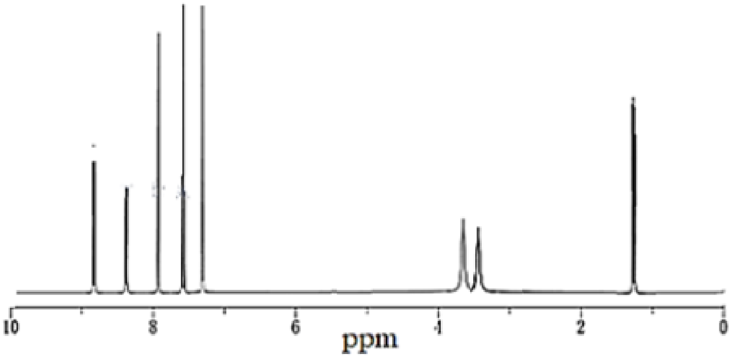

Fig. 8. ^{1}H NMR spectrum of the mixed-ligand complex Cu(I)-DTMP-Phen

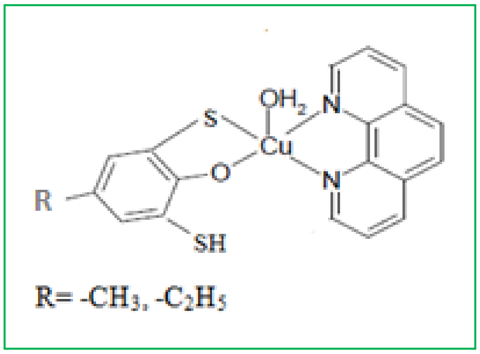

Fig. 9. Structure of complex Cu(DP)(H_2O)Phen

Table 5. Precision and accuracy of the spectrophotometric measurement of Cu(II) with DP and Am, as well as its optical properties

Compound	pH	λ, nm	Δλ, nm	ε×10^{-4}	lgβ	lgK$_p$	lgK$_{эк}$
Cu -DMMP-Dip	6.5-7.9	629	355	3.28	11.47	6.64	13.21
Cu-DMMP-Phen	6.7-7.9	630	356	3.45	11.62	6.70	13.25
Cu-DMMP-BPhen	6.6-8.1	635	361	4.37	11.94	6.79	13.32
Cu -DMEP-Dip	6.2-7.4	634	360	3.61	10.52	6.73	12.29
Cu-DMEP-Phen	6.3-7.5	635	359	3.70	10.82	6.71	12.33
Cu-DMEP-BPhen	6.4-7.7	640	364	4.82	10.96	6.81	12.47
Cu-DMBP-Py	5.2-6.3	585	305	3.42	9.90	6.40	10.87
Cu-DMBP-Dip	6.8-8.1	642	362	3.75	11.85	6.79	11.03
Cu-DMBP-Phen	6.9-8.2	644	364	3.91	11.95	6.75	11,04
Cu-DMBP-BPhen	7.1-8.5	650	370	4.92	12.26	6.84	11.18

3.6. Effect of interference ion

Various methods are proposed for the determination of copper in anhydrous solutions. In order to evaluate the selectivity of those methods, we studied the effect of many foreign cations, as well as some complexing anions, on the results of determination of copper by Dp and Am. The experiments were carried out according to the recipe, according to which the calibration curves were established, with the only difference that a certain amount of the corresponding ions was introduced into the solution other than Cu(II). The tolerance limit was set for ions that do not cause a deviation of more than +2% in the value of optical density for Cu(II)-DP-Am complexes.

Certain masking agents are used in this process. Thus, the interference of various cations is stopped. Such a situation is also observed in the spectrophotometric determination of copper. The results are summarized in the Table 6.

Table 6. Influence of interfering ions on the determination of copper(II) as MLC with DMEP and Dip (30.0 µg Cu added)

Ion	Molar excess of the ion	Masking agent	Found Cu, µg	**S_r**
Fe(II)	40		29.8	0.043
Co(II)	50		30.2	0.053
Ni(II)	50	NaCN	29.7	0.026
Cd(II)	200		29.6	0.054
Al(III)	200		29.5	0.034
Fe(III)	40	NaF	29.9	0.045
Zr(IV)	50		30.4	0.033
W(VI)	25		29.6	0.053
Hg(II)	38	$Na_2S_2O_3$	30.1	0.058
Ti(IV)	30	NaF	29.6	0.043
V(IV)	20		30.3	0.056
Mo(VI)	10	Citrate	29.8	0.054
Cr(III)	120		29.6	0.064
Nb(V)	50	NaF	30.6	0.055
Ta(V)	50	NaF	30.3	0.045
Pb (II)	25		30.3	0.034
Pd (II)	5		29.4	0.035
Pt(II)	8		30.5	0.050
Ag (I)	15	KI	30.2	0.045
UO_2^{2+}	50		29.2	0.042
Bi(III)	40		30.6	0.051
Acetate	100		30.2	0.050
Tartarate	120		30.3	0.054
Sulphate	125		29.6	0.023
Thiourea	25		29.8	0.044
Fluoride	110		30.2	0.053
Thiosulphate	36		29.8	0.048

The proposed extraction-spectrophotometric approach is exceedingly sensitive, easy to use, and reasonably priced. (Table 7).

It can be assumed that large amounts of alkaline ions, alkaline-earth ions, Cl^-, Br^-, SO_3^{2-}, SO_4^{2-}, NO_2^-, NO_3^- and $C_2O_4^{2-}$. Tartrate, citrate, F^- , I^-, CN^-, thiourea interfere determination of Cu(II). Co(II), Ni(II), Fe(II, III), V(IV,V), W(VI), Mo(VI), Ti(IV) and Mn(II) interfere determination of Cu(II). However, the interfering effect of some of these ions can be reduced by masking with oxalate, citrate or EDTA.

Interference of Fe(III) eliminated oxalic acid; Ti(IV) - tiron or sodium fluoride; Hg(II) ion -sulfit; Nb(V) and Ta(V) - oxalic acid, and Mo(VI) and W(VI) - sodium fluoride and oxalic acid. When using a 1% solution of ascorbic acid does not interfere with determination Mn(VII), V(IV), Nb(V), Cr(VI), Mo(VI) и Fe(III). When using 0.01M oxalic acid definition not interfere V(IV), Nb(V), Ta(V), Cr(III), Mo(VI) , W(VI) и Fe(III). A slight reduction in absorbance is produced by the majority of the tested ions.

Table 7. Comparative features of the methods for detecting copper

Reagent	pH	Solvent	Beer's law range (μg· ml^{-1})	λ, nm	ε·10^{-4}	Ref
Diétylditiokarbamat	4-11	carbon tetrachloride		436	1.40	[41, 42]
Cuproin	4-7	isoamyl alcohol		546	0.64	[41, 42]
Neokuproin	3-10	isoamyl alcohol		454	0.79	[41, 42]
Dithizone	<1			550	4.50	[41, 42]
5-bromosalicylaldehyde thiosemicarbazone	5-6		4.0 - 9.6	378	1.09	[20]
N-Ethyl-3-carbazole carboxaldehyde-3 thiosemicarbazone	3		0.4–3.6	380	2.243	[43]
4-[*N*,*N*-(Dimethyl)amino] benzaldehyde thiosemicarbazone	4.4–5.4	Chloroform		420	1.72	[14]
2-[4-Chloro-2-methoxy phenyl azo]-4,5-diphenyl imidazole	8.0	Chloroform	0.5-30	519	0.85	[24]
O-methylphenyl thiourea	0.075 mol L^{-1} KIO$_3$	Chloroform	up to 600	510	1. 0	[23]
DMMP+Phen	6.7-7.9	Chloroform	0.5-16	630	3.45	this work
DMMP +BPhen	6.6-8.1	Chloroform	0.5-19	635	4.37	
DMMP +Dip	6.5-7.7	Chloroform	0.5-16	629	3.28	
DMEP+Phen	6.3-7.5	Chloroform	0.6-17	635	3.72	
DMEP +BPhen	6.4-7.7	Chloroform	0.5-19	640	4.82	
DMEP +Dip	6.2-7.4	Chloroform	0.5-17	634	3.61	
DMBP +BPhen	7.1-8.5	Chloroform	0.3-20	650	4.92	

3.7. 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. According to a linear calibration graph between absorbance and the concentration of metal ions, Cu(II) can be determined between 0.3 and 20 g/ml [44]. Table 8 contains the equations for the straight lines that were obtained and other significant characteristics pertaining to the use of mixed-ligand complexes for extractive-spectrophotometric measurement of Cu(II).While using extraction, it is possible to boost selectivity and lowering the detection limit.

Table 8. Analytical characteristics of some ternary complexes of Cu with dimercaptophenols and Hydrophobic Amine

Compound	Beer's law range (µg· ml^{-1})	The equation Of calibration curves	Limit of detection (LOD): ng ·mL^{-1}	Limit of quantification (LOQ): ng ·mL^{-1}	Sandell's sensitivity (µg· cm^{-2})
Cu- DMMP+Phen	0.5-16	0.019+0.0502x	8,8	29.0	1.86
Cu-DMMP +BPhen	0.5-19	0.042+0.0596x	8.6	28.4	1.46
Cu-DMMP +Dip	0.5-16	0.046+0.0440x	8.7	28.7	1.95
Cu-DMEP+Phen	0.6-17	0.011+0.0565x	8.7	28.7	1.73
Cu-DMEP +BPhen	0.5-19	0.021+0.0715x	8.5	28.0	1.33
Cu-DMEP +Dip	0.5-17	0.049+0.0485x	8.6	28.4	1.77
Cu-DMBP-Phen	0.4-18	0.024+0.0577x	8.5	28.4	1.64
Cu-DMBP-BPhen	0.3-20	0.052+0.0678x	8.2	27.0	1.38
Cu- DMBP-Dip	0.4-18	0.050+0,0504x	8.6	28.4	1.80
Cu- DMBP-Py	0.5-16	0.019+0.0502x	9.5	32.0	1.90

4. Application of the proposed work and its validation

This method has been researched and tested on various samples in many areas. Determination of copper in pharmaceutical, food and plant samples was carried out photometric method with rubeanic acid. (Table 9 and Table 10)

Table 9. Determination of Cu(II) in Pharmaceuticals samples (n=3,P=0.95)

Sample	Method	$\overline{X}$(mg/tablet)	RSD (%)	$\overline{X} \pm \frac{t_P \cdot S}{\sqrt{n}}$
Zincovit(Apex)	rubeanic acid	0.53	1.24	0.53 ± 0.0068
	DMMP+BPhen	0.51	1.21	0.51 ± 0.0065
Multi vitamin capsule (A-Z)	rubeanic acid	0.89	0.95	0.89 ± 0.0090
	DMMP+Phen	0.91	0.79	0.91 ± 0.0072
	DMEP+BPen	0.91	0.76	0.91 ± 0.0073
Revital (Ranbaxy)	rubeanic acid	0.49	1.27	0.49 ± 0.0064
	DMMP+BPhen	0.52	1.17	0.51 ± 0.0063
	DMEP+BPen	0.51	1.08	0.51 ± 0.0058
Supradyn	rubeanic acid	0.97	0.96	0.97 ± 0.0095
	DMMP+Phen	1.02	0.85	1.01 ± 0.0091
	DMMP+Dip	0.99	0.95	0.99 ± 0.0090
	DMEP+Phen	1.01	0.85	1.01 ± 0.0091

Supradyn: calcium (phosphate Pantothenate) 51.3 mg, magnesium (phosphate, stearate, oxide) 21.2 mg, iron (carbonate, sulfate) 10 mg, manganese (sulphate) 0.5 mg, phosphorus (phosphate) 23.8 mg, Copper (Sulfate) 1 mg, Zinc (Sulfate) 0.5 mg, molybdenum 0.1 mg.

Multi vitamin capsule A to Z ns (alkem): elemental copper 0.9 mg, elemental manganese 2 mg, elemental selenium 55 mcg, elemental zinc 10 mg.

Revital(Ranbaxy): zinc - 10 mg, ferrous fumarate - 17 mg, iodine - 0.1 mg, magnesium - 3 mg, manganese - 0.5 mg, calcium - 75 mg, copper - 0.5 mg, potassium - 2 mg.

Zincovit(Apex): selenium (50 mcg).manganese (0.9 mg), zinc (22 mg), copper (0.5 mg), chromium (chromic) (25 mcg), molybdenum (25 mcg).

Table 10. Determination of copper in food (mg / kg). n = 6, P = 0.95

Sample	Method	$\overline{X}$ μg/kg	SD	RSD (%)	$\overline{X} \pm \frac{t_P \cdot S}{\sqrt{n}}$
Beans	rubeanic acid	6.09	0.304	5.0	6.09 ± 0.31
	DMMP+BPen	5.82	0.186	3.2	5.82 ± 0.19
	DMMP+Dip	5.85	0.164	2.8	5.85 ± 0.17
	DMEP+BPen	5.82	0.185	3.2	5.82 ± 0.20
	DMEP+Dip	5,86	0.166	2.9	5.86 ± 0.17
Gelatin	rubeanic acid	12,10	0.508	4.2	12.10 ± 0,53
	DMMP+Phen	11,80	0.295	2.5	11.80 ± 0,31
	DMMP+Dip	11.74	0.305	2.6	11.74 ± 0.32
	DMEP+Phen	11.78	0.293	2.5	11.78 ± 0.30
Wheat bran	rubeanic acid	5.65	0.198	3.5	5.65 ± 0.21
	DMMP +Dip	5.35	0.165	3.1	5.35 ± 0.17
	DMMP +BPhen	5.28	0.137	2.6	5.28 ± 0.15
Rye	rubeanic acid	4.30	0.189	4.4	4.30 ± 0.198
	DMMP +BPhen	4.15	0.162	3.9	4.15 ± 0.170
Barley	rubeanic acid	0.48	0.0134	2.8	0.48 ± 0.014
	DMEP +BPhen	0.47	0.0113	2.4	0.47 ± 0.012
Buckwheat	rubeanic acid	11.05	0.376	3.4	11.05 ± 0.39
	DMEP +BPhen	10.86	0.423	3.9	10.86 ± 0.44
Oats	rubeanic acid	5.02	0.147	2.8	5.02 ± 0.17
	DMBP+Phen	5.06	0.177	3.5	5.06 ± 0.19
Corn leaf	DMBP+Phen	8.56	0.265	3.2	8.56 ± 0.28
	DMBP+BPhen	8.64	0.302	3.5	8.64 ± 0.32

The relative standard deviations (RSD) are for copper (Table 7 and 8) proving the high precision of the proposed method for the routine application in the analysis of copper. Therefore, the suggested approaches for the photometric determination of copper(II) in objects of various origins have a suitable detection limit, good indicators of correctness, and repeatability.

5. Conclusion

Mixed-ligand complexes of copper (II) with 2,6-dimercapto-4-methylphenol (DMMP), 2, 6-dimercapto-4-ethylphenol (DMEP) and 2, 6-dimercapto-4-tert-buthylphenol (DMBP) in the presence of hydrophobic amines have been investigated by spectrophotometric method. The results obtained show that the newly developed method in which the reagent DMMP, DMEP and DMBP was used, can be effectively used for quantitative extraction and estimation of Cu(II) from aqueous media. Extraction of mixed ligand complexes occurs maximal at pH 5.2-8.5. The suggested technique is rapid and uses a smaller amount of organic solvent. The ratios of the components in the complexes were established, and the best conditions for the formation and extraction of mixed-ligand compounds were discovered.

This method captures the conversion of the colored complex to chloroform, due to which the method tolerant to a number of metal ions related to copper. Beer's law is obeyed for copper concentrations in the range of 0.3-20 μg/ml.

An easy, quick and tactful methods proposed for the determination of trace amounts of Copper. The technique is very accurate, quick and easier than other methods.

İn short, the methods we present have precision and standard values. For these reasons those methods are used in the measurement of copper in various samples in pharmaceutical, food and botanical fields. Experimental findings have shown that the reagents is a potential application for the sensitive, rapid and selective perception of Cu(II).

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