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DEVELOPMENT OF A SPECTROPHOTOMETRIC METHOD FOR THE DETERMINATION OF COPPER(II) IONS USING UNSATURATED AMINE ETHERS OF THE AROMATIC SERIES

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The complexation of copper(II) with two ligands (L), 2-methoxy-N-{(1S)-1-phenyl-2-[(prop-2-en-1-yl)oxy]ethyl}aniline (1, MENA) and 2-methoxy-N-{(1S)-1-phenyl-2-[(prop-2-yn-1-yl)oxy]ethyl}aniline (2, MINA), was studied. Organic solvents used for Cu(II) extraction can be ranked by extraction efficiency as follows: $CHCl_3>CCl_4>C_2H_4Cl_2>C_6H_5Cl>C_6H_5CH_3>C_6H_6>CH_3COOC_2H_5>n\text{-}C_4H_9OH>$ iso-$C_5H_{11}OH>C_6H_5CH_2OH$. After a single extraction with chloroform at a 4:1 aqueous-to-organic phase ratio, 97.5–98.3% of Cu(II) is extracted as a complex with the ligand. The optimal acidity range for the Cu(II)–MENA (1) and Cu(II)–MINA (2) complexes is pH_{opt} 3.1–6.2 (pH_{form} 1.2–8.7) and pH_{opt} 3.3–7.4 (pH_{form} 1.3–8.9), respectively. Phase volume ratios from 5:5 to 140:5 did not affect the extraction, allowing simultaneous concentration and extraction-photometric determination of Cu(II). A 28-fold increase in the volume of the aqueous phase relative to the organic phase does not affect the completeness of the extraction. A complex compound of Cu(II) ions with ligands 1 and 2 forms within 10 minutes, during which the absorbance increases from 0.395 to 0.460 and then stabilizes. The yield of the Cu(II) complex was maximal at a ligand concentration of C_L=0.007 M and remained stable for at least 48 hours and more than two months after extraction. Cu(II)–L complexes 1 and 2 exhibit absorption maxima at 445 nm and 450 nm, respectively. The molar absorption coefficients are $\varepsilon_{445}=4.21\cdot10^4$ (for complex 1) and $\varepsilon_{450}=4.37\cdot10^4$ (for complex 2). The composition of the complexes corresponds to a 2:1 ligand-to-metal ratio. The Cu(II) complexes do not polymerize in chloroform (γ=1.13–1.17). Based on the results, a photometric method for the determination of copper in steel from various brands and in food processing has been proposed. This method is characterized by good reproducibility (relative standard deviation not exceeding 0.05) and a low limit of quantitation.

Keywords: copper, ligand, chloroform, complexes, absorption spectra, Beer's law.

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Introduction

Most processes of substance separation and concentration employ methods such as extraction, flotation, and sorption. In many cases, these methods are based on complex formation processes, i.e., the interaction of organic ligands with metal ions in solution. The efficiency of these processes depends on the properties of the ligands. The wide variety of industrial objects and raw material sources, which are complex mixtures, necessitates the development of new reagents for extracting valuable components from them.

Atomic absorption spectrometry [1–3], inductively coupled plasma emission spectrometry [4], potentiometry [5], derivative potentiometric injection analysis [6], flow injection catalytic photometric method [7,8], and inductively coupled plasma mass spectrometry [8] have been used to determine copper content in various compounds.

Many chelating reagents belonging to different classes of compounds and containing N, O, or S as donor atoms are suitable for the photometric determination of copper. Reagents containing hydroxy and carboxy groups, or two hydroxy groups positioned ortho to each other, interact with copper mainly in weakly acidic and neutral media to form colored complex compounds [9]. Copper is one of those metals that have chromophoric properties; therefore, among the numerous photometric methods for its determination, there are those based on colored reagents containing chromophoric groups and others that use colorless reagents [10].

A sensitive, accurate and rapid spectrophotometric method that can be used for the determination of Cu(II) in analytical samples using a new chromogenic reagent azo-Schiff base 1-((4-(1-(2-hydroxyphenylimino)ethyl)-phenyl)diazenyl) naphthalene-2-ol was studied. The obtained complex showed a brown color with maximum absorption at λ_{max}=500 nm at pH 9. Beer's law was obeyed in the concentration range of 1.7 to 5.4 $\mu g \cdot mL^{-1}$. The molar absorption and Sandell's sensitivity values of the Cu(II) complex were found to be $0.5038 \cdot 10^4$ and 0.0039 $\mu g \cdot cm^{-2}$, respectively. The structure of the prepared complex was investigated by using the continuous variation, mole ratio method and slope analysis method. The obtained results showed that the complex has molar ratio: M:L=1:2. This method was applied for the determination of Cu(II) in alloy [11]. Using 4-hydroxybenzaldehyde thiosemicarbazone at pH 6.5, copper(II) was determined spectrophotometrically (370 nm, with an absorption coefficient of $2.85 \cdot 10^4$) [12]. To determine Cu(II), a colorimetric method was used using the chromogenic reagent 2-[(3-chloro-4,6-disulfanamide phenyl)azo]-4,5-diphenylimidazole in a neutral medium at 588 nm with a concentration range of 6–0.25 $\mu g \cdot mL^{-1}$ [13].

In the search for effective reagents for the extraction–spectrophotometric determination of *d*-transition elements, chelating ligands capable of forming soluble complexes in organic solvents are of great interest [14–20]. From this perspective, 2-methoxy-N-{(1S)-1-phenyl-2-(prop-2-en(in)-1-yl)oxy]etnyl}aniline (1, 2) merits attention as these compounds contain nitrogen and oxygen donor atoms capable of forming stable complexes with non-ferrous metal ions [21]. Based on the structure of their functional groups, it can be assumed that these ligands form five-membered chelate rings with metal ions through coordination via nitrogen and oxygen atoms. The synthesis of organic compounds containing such donor atoms opens new prospects for the development of reagents suitable for the extraction-spectrophotometric determination of metal ions. Numerous methods for class identification have been investigated due to the widespread problem of pharmaceutical contamination [22]. Spectrophotometric techniques offer significant advantages for analyzing environmental samples due to their low cost and ease of use [23–26].

In this work, the complexation of copper(II) ions with the ligands (L) – 2-methoxy-N-{(1S)-1-phenyl-2-[(prop-2-en-1-yl)oxy]ethyl}aniline (1, MENA) and 2-methoxy-N-{(1S)-1-phenyl-2-[(prop-2-yn-1-yl)oxy]ethyl}aniline (2, MINA) – was investigated.

Currently, compounds 1 and 2 are regarded as promising chelating ligands. Therefore, it is reasonable to examine their physicochemical and complexation properties to evaluate their potential application in technological processes for the separation and concentration of metal ions.

Materials and methods

Reagents and solutions

In this study, chloroform ($CHCl_3$) was used as the extractant, and 0.01 M solutions of ligands 1 and 2 in chloroform were prepared. To establish the desired acidity of the medium, 1 M solutions of HCl and NaOH were used, as well as ammonium acetate buffer solutions composed of acetic acid (CH_3COOH) and ammonium hydroxide (NH_4OH).

To prepare the stock copper solution (1 $mg \cdot mL^{-1}$), 3.9296 g of freshly recrystallized $CuSO_4 \cdot 5H_2O$ was dissolved in distilled water, followed by the addition of two drops of concentrated sulfuric acid. The resulting solution was diluted to 1 L in a volumetric flask [27]. Working solutions with a concentration of 0.1 $mg \cdot mL^{-1}$ were prepared by diluting the stock solution. The ionic strength (μ=0.1) was kept constant by the addition of KNO_3.

Instrumentation

The absorbance of the extract was measured using KFK-2 and SF-26 spectrophotometers with cuvette path lengths of 0.5 cm and 1.0 cm, respectively. The pH values of solutions of the 1 and 2 complexes with Cu(II) ions were determined using an ANION 4100 pH meter (Infraspak-Analit, Novosibirsk) equipped with an ESC-10603/7 combined electrode. IR spectra were recorded on a Bruker spectrophotometer. Compounds 1 and 2 were analyzed using a Shimadzu LC-10AD liquid chromatograph and a PE SCIEX API 150EX mass spectrometer. The purity of the synthesized compounds was verified by thin-layer chromatography (TLC).

The thermolysis of the compounds was studied using a Shimadzu TGA-50H thermogravimetric analyzer in an air atmosphere over the temperature range of 20–1000^{0}C at a heating rate of 10^{0}C/min. The samples and the reference material were heated in platinum crucibles.

General procedure for the synthesis of ligands A1 and A2

A mixture of benzaldehyde (0.4 mmol), chloromethyl allyl ether (0.2 mmol) or chloromethyl propargyl ether (0.2 mmol, for the synthesis of A2), o-methoxyaniline (0.2 mmol), and pseudoephedrine (0.02 mmol) in 20 mL of MeCN was stirred at 20^{0}C for 48 h. The resulting reaction mixture was filtered, extracted, and dried over Na_2SO_4. After solvent removal under reduced pressure, the residue was purified by column chromatography.

The synthetic routes for ligands A1 and A2 are shown in Scheme 1.

N-[2-(Allyloxy)-1-phenylethyl]-2-methoxyaniline (A1)

IR spectrum (ν, cm^{-1}): 3300; 3090; 3060; 3030; 2100; 1600; 1595; 1505; 1490; 1085; 1010; 855; 820; 750; 725; 690. ^{1}H NMR spectrum ($CDCl_3$), δ, ppm: 2.51 t (1H, ≡CH, ^4J 2.4 Hs), 2.87 d.d (1H, OCH_2, J=15.5, 9.9 Hs); 2.91 d.d (1H, OCH_2, J=15.5, 9.9 Hs); 3.83 d.d (1H, ≡CCH_2O, ^2J 16.2 Hs, ^4J 2.4 Hs), 3.92 s (3H, CH_3O); 4.90 т (1H; J=6.0 Hs); 4.05 d.d (1H, ≡CCH_2O, ^2J 16.2 Hs, ^4J 2.4 Hs), 5.1 m (1H, CH); 6.47 d (1H, Ar, J=7.8 Hs); 6.65–6.83 m (3H, Ar); 7.44–7.22 m (5H, Ar). ^{13}C NMR spectrum ($CDCl_3$), δ, ppm: 43.35; 54.98; 55.61; 56.11 (≡C–CH_2O), 68.35 (≡CH), 79.46 (≡C–CH_2O), 109.58; 111.34; 116.98; 121.24; 126.40; 127.48; 128.81; 136.78; 142.48; 147.03. Found, %: C 76.79; H 6.77; N 4.95. $C_{18}H_{19}O_2N$. Calculated, %: C 76.84; H 6.81; N 4.98. UV spectrum ($CHCl_3$), λ_{max}, nm: 257.

2-Methoxy-N-[1-phenyl-2-(prop-2-yn-1-yloxy)etyl]aniline (A2)

Yield 86%. IR spectrum (ν, cm^{-1}): 3120; 3090; 3060; 3030; 2100; 1600; 1595; 1505; 1490; 1085; 1010; 855; 820; 750; 725; 690. ^{1}H NMR spectrum ($CDCl_3$), δ, ppm: 2.88 d.d (1H, OCH_2, J=15.6, 9.9 Hs); 2.92 d.d (1H, OCH_2, J=15.6, 9.9 Hs); 3.91 c (3H, CH_3O); 4.17 d.d.d (1H, OCH_2, J=12.15, 1.61, 1.23 Hs), 4.61 d.d (1H, OCH_2, J=12.15, 5.34 Hs), 4.88–4.83 m (1H); 5.11 m (1H, CH); 5.17 d.d.d (1H, H_2C=, J=9.15, 1.57, 1.23 Hs), 5.31 d.d.d (1H, H_2C=, J=17.21, 1.57, 1.61 Hs), 5.85 d.d.d (1H, OCH=, J=17.21, 9.15, 5.34 Hs), 6.50–6.54 m (1H, CH); 6.61–6.80 m (3H, Ar); 7.38–7.31 m (4H, Ar). ^{13}C NMR spectrum ($CDCl_3$), δ, ppm: 31.63; 34.73; 43.45; 54.71; 55.76; 72.32 (=C–CH_2O), 109.71; 111.38; 116.97; 117.67 (H_2C=), 121.41; 125.85; 126.18; 134.63 (–HC=), 137.08; 138.51; 147.16; 150.39. Found, %: C 77.79; H 8.64; N 4.17. $C_{22}H_{29}O_2N$. Calculated, %: C 77.84; H 8.61; N 4.13. UV spectrum ($CHCl_3$), λ_{max}, nm: 259.

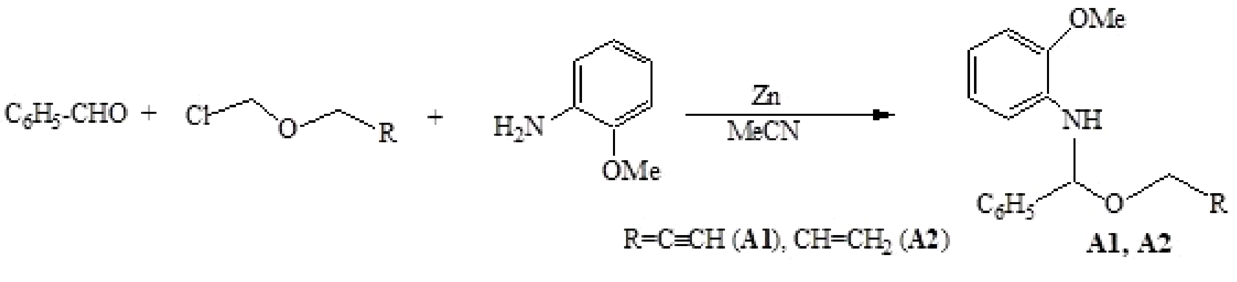
General procedure for absorbance measurement

The copper solution (0.1–1.0 mL), 0.01 M ligand solution (2.5 ml) and 1.0 M HCl solution (2.6 ml) were added to the test tubes. The volume of the organic phase was adjusted to 5 mL with CH_3Cl, and the total volume was brought to 25 mL with distilled water. After 5 minutes, the phases were separated, and the light absorbance of the organic phase was measured at 440 nm using a KFK-2 spectrophotometer with a 0.5 cm cuvette path length.

Results and discussion

Selection of extractant

A range of non-polar and polar solvents of both proton-donor and proton-acceptor nature, as well as aprotic aromatic and aliphatic hydrocarbons was used to extract copper in the form of complexes. The selection of solvents with differing chemical natures was guided by the presence of various donor atoms within the ligand molecules.



Scheme 1

The efficiency of Cu(II) extraction by the organic solvents used can be ranked in the following order: $CHCl_3$>CCl_4>$C_2H_4Cl_2$>C_6H_5Cl>$C_6H_5CH_3$>C_6H_6>$CH_3COOC_2H_5$>n-C_4H_9OH>iso-$C_5H_{11}OH$>$C_6H_5CH_2OH$. Among them, chloroform exhibited the highest extraction efficiency and was therefore selected as the extractant for all further experiments.

Extraction with chloroform resulted in rapid phase separation and a maximal molar absorption coefficient. A single extraction using a 4:1 aqueous-to-organic phase ratio allowed for the extraction of 97.5–98.3% of Cu(II) in complexed form. The degree of extraction of the complexes was calculated using the formula R=100D/(D+1), where D is the distribution coefficient. The extraction degree remained stable up to a phase volume ratio of 20:1.

Influence of the pH value of the aqueous phase

The study of the dependence of complexation on pH shows that the extraction efficiency strongly depends on the pH of the solution. A change in pH significantly affects the complexation of Cu(II) with L. The optimal pH range for the formation of Cu(II)–MENA (1) and Cu(II)–MINA (2) complexes is pH_{opt} 3.1–6.2 (pH_{form} 1.2–8.7) and pH_{opt} 3.3–7.4 (pH_{form} 1.3–8.9), respectively (Fig. 1, Table 1). At pH values above 8.9, no extraction of the complexes is observed, which can be attributed to the formation of hydrolyzed species of Cu(II).

To determine the optimal pH range, 0.2 mL of a $1.0 \cdot 10^{-2}$ mol·L^{-1} Cu(II) salt solution was placed into a 25.0 mL volumetric flask. Various volumes of ammonium acetate buffer solution were then added to achieve the desired pH. Subsequently, 5.0 mL of a $11.0 \cdot 10^{-2}$ mol·L^{-1} solution of ligand 1 or 2 was added. The solution was diluted to the mark with distilled water and thoroughly mixed. Absorbance was measured using a KFK-2 photoelectric colorimeter at a wavelength of 440 nm in a quartz cuvette with a path length of 0.5 cm.

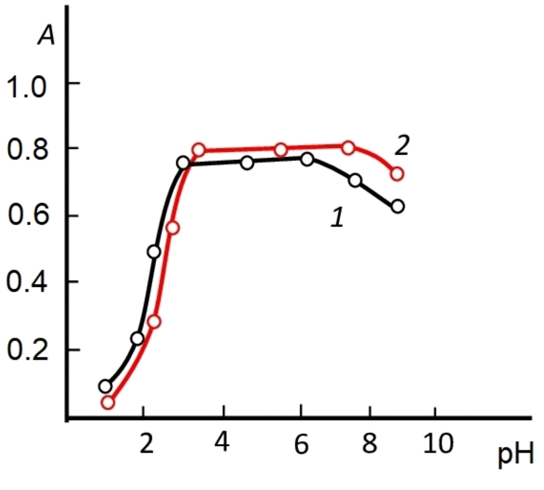


Fig. 1. Effect of aqueous phase pH on the formation of Cu(II)–L complexes: 1 – Cu(II)–1; 2 – Cu(II)–2. $C_{Cu(II)}=1.81 \cdot 10^{-5}$ M; $C_L=8.0 \cdot 10^{-3}$ M; l=0.5 cm

Effect of phase volume ratio, holding time, and ligand concentration

Phase volume ratios ranging from 5:5 to 140:5 had no effect on the extraction efficiency. This enables simultaneous concentration and extraction-photometric determination of Cu(II). A 28-fold increase in the volume of the aqueous phase relative to the organic phase did not reduce the completeness of extraction. The Cu(II)–1,2 complex is formed within 10 minutes, during which the absorbance of the solution increases from 0.395 to 0.460 and then remains nearly unchanged. The maximum yield of Cu(II) was observed at a ligand concentration of C_L=0.007 M, and the complex remained stable for at least 48 hours and even after more than two months after extraction.

The calibration equations are calculated as: $y=0.290x+0.025$ (for complex 1) and $y=0.297x+0.031$ (for complex 2). Based on these equations, the photometric detection limit (LOD) and limit of quantification (LOQ) for copper in the form of its complexes were determined. The system follows the fundamental law of light absorption in the concentration range of $C_{Cu(II)}$=0.20–24 μg·mL^{-1}.

The analytical characteristics of the Cu(II)–L complexes are summarized in Table 1.

Absorption spectra

The Cu(II)–L complexes 1 and 2 exhibit maximum absorbance at 445 nm and 450 nm, respectively (Fig. 2), whereas the ligands MENA and MINA show absorption maxima at 256 nm and 258 nm. The bathochromic shifts, calculated using the formula $\Delta=\lambda_{Cu(II)-L}-\lambda_L$, are 189 nm and 192 nm

Table 1

Analytical characteristics of Cu(II)–L complexes

Parameter		Value	
		1	2
pH	formation	1.2–8.7	1.3–8.9
	optimal	3.1–6.2	3.3–7.4
λ, nm		445	450
$\varepsilon \cdot 10^{-4}$		4.21	4.37
lgK_{eq}		10.14	11.37
lg_{Kex}		14.27	16.82
Beer's law execution interval, μg·mL^{-1}		0.20–24	0.23–22
$y=ax+b$		$0.290x+0.025$	$0.297x+0.031$
LOD, ng·mL^{-1}		8.9	31.5
LOQ, ng·mL^{-1}		8.5	30.6

for complex 1 and 2, respectively. The molar absorption coefficients are ε_{445}=4.21·10^4 and ε_{450}=4.37·10^4 for complex 1 and 2, respectively.

Composition of the complexes

The stoichiometry of the studied complexes was established by equilibrium shift and relative yield methods [28]. The complexes have a stoichiometric ratio of 2 moles of ligand (1 or 2) per mole of copper(II). Chloroform molecules are not coordinated in the extracted complexes; the solvation number, determined from the slope of the extraction data, is zero.

To clarify the chemistry of the complexation process, information regarding the ionic forms of Cu(II) and the number of protons displaced during the formation of one complex molecule is required. For this purpose, the degree of complexation of Cu(II) ions with HL was determined as a function of the solution pH [29]. If the graphical dependence of −lg B on pH is plotted, assuming that two ionic species exist in the solution (Cu^{2+} and $CuOH^+$), then the correct graph will be linear, and the slope of the line (qn) is an integer. The results showed that the complex-forming copper ion is the divalent cation Cu^{2+} [29]. In this case, the number of protons displaced from one molecule of HL was one. The Cu^{2+} complex does not polymerize in chloroform (γ=1.13–1.17) [30].

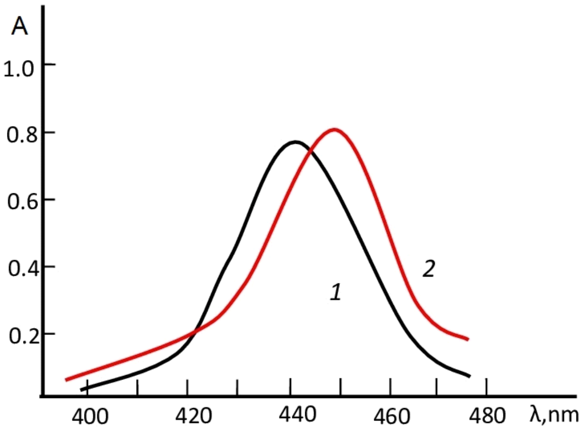


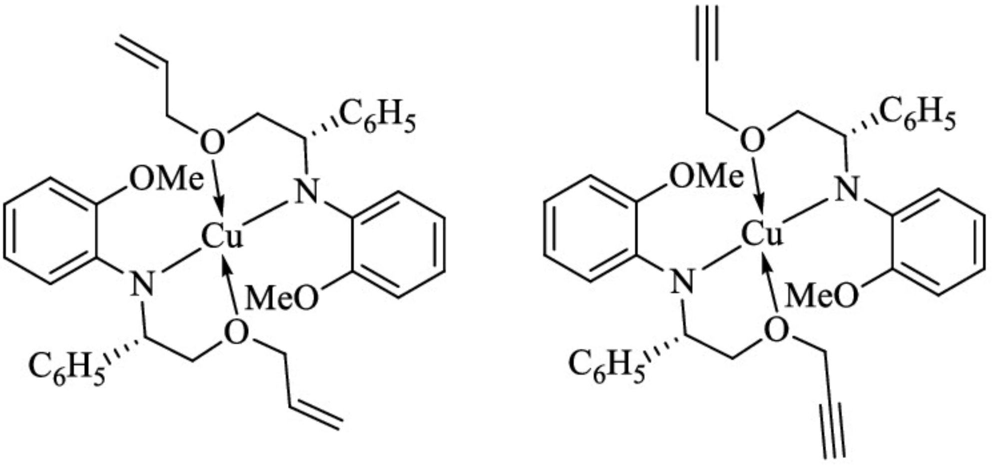
Fig. 2. Electronic absorption spectra of the Cu(II)–L complexes in $CHCl_3$: 1 – Cu(II)–1; 2 – Cu(II)–2. $C_{Cu(II)}$=3.34·10^{-5} M; C_L=8.0·10^{-3} M

It is known that copper exhibits intermediate behavior between "hard" and «soft» acids. Therefore, copper has a low affinity for oxygen atoms. It is assumed that copper is connected to the nitrogen atom by a basic bond, and to oxygen by a coordination bond. The composition of the complexes can be represented by the formula CuL_2 (Scheme 2).

Thermal decomposition of the Cu(II) complexes occurs in two stages: at 62–128^0C, water evaporates (weight loss being 5.15% and 5.13% for 1 and 2, respectively), and at 350–395^0C, the ligands decompose (weight loss being 87.43% and 87.41% for 1 and 2, respectively). The final product of thermolysis is CuO.

General procedure for the synthesis of Cu(II) complexes

The Cu(II) complexes were obtained via an exchange reaction between a copper(II) salt and compounds 1 or 2. To this end, an ethanolic solution of 1 was added to 15 mL of an ethanol solution of $CuSO_4·5H_2O$ (0.250 g, 0.626 mmol). The reaction mixture was stirred at 65^0C for 20 minutes. Dark red crystals began to precipitate after 24 hours. The crystals were filtered, washed with ethanol, and dried in a vacuum desiccator to constant weight. The yields were



1 **2**

Scheme 2

0.028 g for complex 1 and 0.023 g for complex 2.

Cu(II)–1. Yield 86.5%. IR spectrum, ν, cm^{-1}: 730 (CH_{arom}); 1054 (C–O); 1102 (–C–C_{aliph}); 1229 (CH_{arom}); 1297 (=C–H); 1496 (C–H); 1499 (C_6H_5–); 1567 (C–C_{arom}); 1619 (–C_{arom}=C_{arom}); 1657 (C=C); 2938 (CH_{aliph}); 3109 (CH_{arom}); 3358 (–NH). Found, %: C 70.68; H 7.81; O 8.62; N 3.77; 8.62 Cu. $C_{44}H_{58}O_4N_2Cu$. Calculated, %: C 69.34; H 7.48; O 7.90; N 4.05; 8.33 Cu. UV spectrum ($CHCl_3$): λ_{max}=445 nm.

Cu(II)–2. Yield 82.8%. IR spectrum, ν, cm^{-1}: 654 (–C≡C–H); 738 (CH_{arom}); 1068 (C–O); 1100 (–C–C_{aliph}); 1227 (CH_{arom}); 1293 (=C–H); 1497 (C_6H_5–); 1498 (C–H); 1579 (C–C_{arom}); 1613 (–C_{arom}=C_{arom}); 1652 (C=C); 2021 (–C≡C–); 2932 (CH_{aliph}); 3100 (CH_{arom}); 3291 (–C≡C–H); 3357 (–NH). Found, %: C 71.15; H 7.27; O 8.67; N 4.25; 8.67 Cu. $C_{44}H_{54}O_4N_2Cu$. Calculated, %: C 69.12; H 7.78; O 7.19; N 3.68; 7.57 Cu. UV spectrum ($CHCl_3$): λ_{max}=450 nm.

The singlet observed in the spectrum of the 1 and 2 ligands at 4.87–4.84 ppm, attributed to the phenolic –NH group, disappears in the spectrum of the complex. This indicates that the –NH group is involved in complex formation.

The complexation reaction can be represented as follows:

$$Cu^{2+} + 2HL \rightleftarrows [CuL_2] + 2H^+ .$$

The equilibrium constants (K_{eq}) and extraction constants (K_{ex}) of the reaction, calculated using the formulae $\lg K_{eq} = \lg D - 2\lg[HL]$ and $\lg K_{ex} = \lg D - 2pH - \lg[HL]$, are presented in Table 1.

Table 2 presents data that enable a comparison of the analytical characteristics of the proposed copper determination method with several previously reported methods [31–36]. In all cases, the molar absorption coefficients are high [31–36], the colored extracts exhibit absorption at longer wavelengths [31–35], the Beer's law range is broader [31–34], and the reactions occur in relatively acidic media [31–34,36].

Effect of foreign ions

To evaluate the applicability of the ion-association method for the separation and determination of copper, the influence of foreign ions was investigated. The selectivity of the spectrophotometric determination of copper in the form of the studied complexes is presented in Table 3 (50 μg of Cu^{2+} was used). It was found that large excesses of alkali and alkaline earth metals, rare earth elements, F^-, Cl^-, Br^-, SO_3^{2-}, SO_4^{2-}, NO_3^-, and $C_2O_4^{2-}$ do not interfere with copper determination. However, citrates, tartrates, I^-, CN^-, $S_2O_3^{2-}$, and thiourea were found to interfere.

The interfering effects of Fe^{3+}, Nb^{5+}, and Ta^{5+} were eliminated using oxalic acid; Ti^{4+} – with sodium fluoride or tiron; Hg^{2+} – with sulfite ion; and Mo^{6+} and W^{6+} – with both sodium fluoride and oxalic acid. When a 1% ascorbic acid solution was used, Mn^{7+}, V^{4+}, Nb^{5+}, Cr^{6+}, Mo^{6+}, and Fe^{3+} no longer interfered with the determination. Similarly, the use of a 0.01 M oxalic acid solution suppressed the interference from V^{4+}, Nb^{5+}, Ta^{5+}, Cr^{3+}, Mo^{6+}, W^{6+}, and Fe^{3+}.

Determination of copper in steels

A weighed steel sample (approximately 1 g) was dissolved in 10 mL of a mixture of concentrated HCl and HNO_3 in a 3:1 ratio. After complete dissolution, 5 mL of 1:1 H_2SO_4 were added, and the solution was evaporated until the emission of SO_3 vapors ceased. Then, 30 mL of water and 2–3 mL of a 30% H_2O_2 solution were added, and the mixture was heated to

Table 2

Comparative characteristics of the methods for the determination of copper

Reagent*	pH	Beer's law range (μg·mL^{-1})	λ, nm	ε·10^{-4}	Ref.
DETK	4–11	0.3–2.5	436	1.4	[31,32]
Cuproin	4–7	0.2–24.6	546	0.63	[31,32]
Neokuproin	3–10		454	0.78	[31,32]
Dithizone	1		550	4.4	[31,32]
BSTC	5–6	4–9.6	378	1.08	[33]
ECTC	3	0.4–3.6	374	2.2	[34]
DBTS	4.4–5.4		420	1.7	[35]
CMDI	8	0.5–3.0	518	0.90	[36]
1	3.1–6.2	0.20–24	445	4.21	this work
2	3.3–7.4	0.23–22	450	4.37	

Note: * – DETK – dietylditiokarbamat; BSTC – 5-bromosalicylaldehyde thiosemicarbazone;
ECTC – N-ethyl-3-carbazolecarboxaldehyde-3-thiosemicarbazone;
DBTS – 4-[N,N-(dimethyl)amino]benzaldehyde thiosemicarbazone;
CMDI – 2-[4-chloro-2-methoxyphenyl azo]-4,5-diphenylimidazole.

boiling. The resulting insoluble residue was filtered through a dry paper filter and washed twice with distilled water. The filtrate and washings were collected in a 100 mL volumetric flask, cooled, and diluted to the mark with distilled water. An aliquot of the resulting solution was transferred to a separatory funnel. The pH was adjusted to 5 with 0.1 M KOH, and 2.2 mL of 0.01 M L were added. The volume of the organic phase was adjusted to 5 mL with chloroform, and the total volume was brought to 25 mL with distilled water. The mixture was shaken for 5 minutes. After phase separation, the absorbance of the extract was measured at 440 nm in a 0.5 cm cuvette using a KFK-2 spectrophotometer (Table 4).

Determination of copper in beans

A sample of beans (approximately 10 g) was ground and dried in a porcelain crucible, initially at 65–75^{0}C, and then at 110^{0}C. The dried residue was ashed in a muffle furnace at 550^{0}C. The resulting ash was dissolved in diluted (1:1) HNO_3 and evaporated to wet salts, which were then dissolved in water and filtered into a 100/ mL volumetric flask. The copper content was determined using 1 and 2 ligands, as well as the DETK-based methods (Table 5).

Determination of copper in gelatin

A 4–5 g portion of gelatin was placed in a porcelain crucible with 50/ mL of distilled water and allowed to swell for 3–4 hours. Then, 25/ mL of diluted HNO_3 (1:1) was added, and the mixture was heated in a boiling water bath for 2.5 hours. The resulting solution was filtered, neutralized with NH_4OH (1:1), and transferred to a 50/ mL volumetric flask. The copper content in the solution was determined using both the 1 and 2 ligands, as well as the DETK-based methods (Table 5).

Determination of copper in wheat bran

A 4–5 g sample of wheat bran was dried in porcelain crucibles in a drying oven at 110^{0}C to a constant (air-dry) weight. The crucibles were then placed on an asbestos plate, and the contents were

Table 3

Influence of foreign ions on the determination of copper using 1 and 2 (*n*=6, *P*=0.95; 50 μg of Cu^{2+} taken)

Ion,	Molar excess of ion	Masking reagent	Found, μg (S_r)	
			1	2
Co^{2+}	50		49.7 (0.02)	50.2 (0.03)
Ni^{2+}	50		50.0 (0.04)	50.1 (0.07)
Fe^{2+}	200	HOOC–COOH	50.5 (0.08)	50.0 (0.04)
Cd^{2+}	180		50.3 (0.05)	50.3 (0.06)
Al^{3+}	60		49.4 (0.02)	50.1 (0.02)
Fe^{3+}	50		49.8 (0.04)	49.7 (0.02)
Zr^{2+}	25		50.3 (0.03)	50.0 (0.02)
W^{6+}	40	HOOC–COOH	50.0 (0.06)	49.5 (0.03)
Hg^{2+}	30		49.7 (0.08)	50.0 (0.02)
Ti^{4+}	20	tyrone	50.0 (0.05)	49.9 (0.04)
V^{4+}	10	tyrone	50.4 (0.02)	50.3 (0.06)
Mo^{6+}	60	NaF	49.5 (0.02)	50.2 (0.08)
Cr^{3+}	120		49.9 (0.03)	49.7 (0.02)
$Nb5^{+}$	60	NaF	50.2 (0.05)	49.6 (0.05)
Ta^{5+}	50	HOOC–COOH	50.1 (0.02)	50.0 (0.02)
U^{6+}	40		50.0 (0.02)	49.6 (0.04)

Table 4

Results of copper determination in steels (*n*=6, *P*=0.95)

Method	$\overline{X}$, %	Found, Cu, %	S	S_r	Correctness of the methodology, ΔC/C·100%	$\overline{X \pm \frac{t_p \cdot S}{\sqrt{n}}}$, %
Steel s16, (Cu – 0.219%)						
L	0.216	99.0	0.0045	0.021	1.12	0.216±0.004
L	0.221	100.91	0.0043	0.024	0.46	0.221±0.003
Steel s19, (Cu – 0.176%)						
L	0.179	102.0	0.0044	0.026	1.7	0.179±0.004
L	0.172	97.73	0.0037	0.021	2.27	0.172±0.007

incinerated over an open flame. The charred residue, together with the crucible, was transferred to a muffle furnace and calcined at 750–800°C. The resulting mineralized residue was dissolved in 0.1 M HNO_3 and filtered through a medium-porosity filter into a 100 mL volumetric flask. The copper content was determined using the L-based method, as well as the lead-DETK method (Table 5).

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Table 5

Results of copper determination in food products, mg/kg (n=6, P=0.95)

Method	$\overline{X}$, mg/kg	Convergence, %	S	S_r	$X \pm \frac{t_p \cdot S}{\sqrt{n}}$, %
Determination of copper in beans					
DETK	6.07	98.0	0.273	0.046	6.07±0.003
L	5.74	99.2	0.160	0.027	5.74±0.007
L	5.81	101.9	0.153	0.035	5.81±0.005
Determination of copper in gelatin					
DETK	12.13	98.2	0.476	0.040	12.13±0.34
L	11.84	101.5	0.298	0.028	11.84±0.28
L	11.76	99.8	0.283	0.026	11.76±0.46
Determination of copper in wheat bran					
DETK	5.71	97.9	0.197	0.038	12.13±0.08
L	5.58	101.1	0.145	0.047	11.84±0.06
L	5.29	98.9	0.176	0.050	11.76±0.09

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РОЗРОБКА СПЕКТРОФОТОМЕТРИЧНОГО МЕТОДУ ВИЗНАЧЕННЯ ІОНІВ МІДІ(II) З ВИКОРИСТАННЯМ НЕНАСИЧЕНИХ АМІНОЕФІРІВ АРОМАТИЧНОГО РЯДУ

А.З. Залов, Г.М. Талибов, К.А. Кулієв

Досліджено комплексоутворення міді(II) з двома лігандами (L) – 2-метокси-N-{(1S)-1-феніл-2-[(проп-2-ен-1-іл)окси]етил}аніліном (1, MENA) та 2-метокси-N-{(1S)-1-феніл-2-[(проп-2-ін-1-іл)окси]етил}аніліном (2, MINA). Органічні розчинники, які застосовувалися для екстракції Cu(II), за ефективністю можна ранжувати у такому порядку: $CHCl_3>CCl_4>C_2H_4Cl_2>C_6H_5Cl>C_6H_5CH_3>C_6H_6>CH_3COOC_2H_5>n\text{-}C_4H_9OH>iso\text{-}C_5H_{11}OH>C_6H_5CH_2OH$. Після одноразової екстракції хлороформом при співвідношенні об'ємів водної та органічної фаз 4:1, 97,5–98,3% міді(II) екстрагується у вигляді комплексу з лігандом. Оптимальний діапазон кислотності для комплексів Cu(II)–MENA (1) та Cu(II)–MINA (2) становить pH_{opt} 3,1–6,2 (pH_{form} 1,2–8,7) та pH_{opt} 3,3–7,4 (pH_{form} 1,3–8,9), відповідно. Співвідношення об'ємів фаз від 5:5 до 140:5 не впливало на ефективність екстракції, що дозволяє одночасно концентрувати та фотометрично визначати Cu(II). Збільшення об'єму водної фази у 28 разів відносно органічної не впливає на повноту екстракції. Комплексна сполука іонів Cu(II) з лігандами 1 і 2 утворюється протягом 10 хвилин, протягом яких поглинання зростає від 0,395 до 0,460, після чого стабілізується. Вихід комплексу Cu(II) був максимальним при концентрації ліганду $C_L=0{,}007$ M і залишався стабільним щонайменше 48 годин та більше ніж два місяці після екстракції. Комплекси Cu(II)–L 1 і 2 мають максимуми поглинання при 445 нм і 450 нм, відповідно. Молярні коефіцієнти поглинання становлять $\varepsilon_{445}=4{,}21\cdot10^4$ (для комплексу 1) та $\varepsilon_{450}=4{,}37\cdot10^4$ (для комплексу 2). Склад комплексів відповідає співвідношенню ліганд:метал=2:1. Комплекси Cu(II) не полімеризуються в хлороформі ($\gamma=1{,}13–1{,}17$). На основі отриманих результатів запропоновано фотометричний метод визначення міді у сталях різних марок та в процесах харчового перероблення. Метод характеризується хорошою відтворюваністю (відносне стандартне відхилення не перевищує 0,05) та низькою межею кількісного визначення.

Ключові слова: мідь, ліганд, хлороформ, комплекси, спектри поглинання, закон Бера.

DEVELOPMENT OF A SPECTROPHOTOMETRIC METHOD FOR THE DETERMINATION OF COPPER(II) IONS USING UNSATURATED AMINE ETHERS OF THE AROMATIC SERIES

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The complexation of copper(II) with two ligands (L), 2-methoxy-N-{(1S)-1-phenyl-2-[(prop-2-en-1-yl)oxy]ethyl}aniline (1, MENA) and 2-methoxy-N-{(1S)-1-phenyl-2-[(prop-2-yn-1-yl)oxy]ethyl}aniline (2, MINA), was studied. Organic solvents used for Cu(II) extraction can be ranked by extraction efficiency as follows: $CHC_3>CCl_4>C_2H_4Cl_2>C_6H_5Cl>C_6H_5CH_3>C_6H_6>CH_3COOC_2H_5>n\text{-}C_4H_9OH>iso\text{-}C_5H_{11}OH>C_6H_5CH_2OH$. After a single extraction with chloroform at a 4:1 aqueous-to-organic phase ratio, 97.5–98.3% of Cu(II) is extracted as a complex with the ligand. The optimal acidity range for the Cu(II)–MENA (1) and Cu(II)–MINA (2) complexes is pH_{opt} 3.1–6.2 (pH_{form} 1.2–8.7) and pH_{opt} 3.3–7.4 (pH_{form} 1.3–8.9), respectively. Phase volume ratios from 5:5 to 140:5 did not affect the extraction, allowing simultaneous concentration and extraction-photometric determination of Cu(II). A 28-fold increase in the volume of the aqueous phase relative to the organic phase does not affect the completeness of the extraction. A complex compound of Cu(II) ions with ligands 1 and 2 forms within 10 minutes, during which the absorbance increases from 0.395 to 0.460 and then stabilizes. The yield of the Cu(II) complex was maximal at a ligand concentration of $C_L=0.007$ M and remained stable for at least 48 hours and more than two months after extraction. Cu(II)–L complexes 1 and 2 exhibit absorption maxima at 445 nm and 450 nm, respectively. The molar absorption coefficients are $\varepsilon_{445}=4.21\cdot10^4$ (for complex 1) and $\varepsilon_{450}=4.37\cdot10^4$ (for complex 2). The composition of the complexes corresponds to a 2:1 ligand-to-metal ratio. The Cu(II) complexes do not polymerize in chloroform ($\gamma=1.13–1.17$). Based on the results, a photometric method for the determination of copper in steel from various brands and in food processing has been proposed. This method is characterized by good reproducibility (relative standard deviation not exceeding 0.05) and a low limit of quantitation.

Keywords: copper; ligand; chloroform; complexes; absorption spectra; Beer's law.

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