

1, 2- Aminothioly as an Analytical Reagent for Extraction Spectrophotometric Determination of Copper (II)

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Abstract

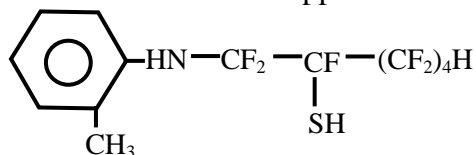
In the present study, the we have synthesized very effective reagent 1- (2'-methylanilino) -1,1,2,3,3,4, 4,5,5,6,6- undekafluorinehexanetriol-2 in the laboratory and this reagent was used for the determination of copper ions in various environmental samples. Copper (II) could be extracted quantitatively (98.92 %) by R into chlorophorm from an aqueous solution of pH 2.8 to 5.3. The chlorophorm extract of Cu - R complex showed intense peak at 450 nm. The composition of the extracted complex was found to be 1:2 (Cu:R) by Job's continuous variation and Mole ratio method. The Komar-Tolmachev method allows calculating the true molar absorptivities (ϵ) of the complexes. The obtained value, $\epsilon = (4.5 \pm 0.6) \times 10^4 \text{ L mol}^{-1} \text{ cm}^{-1}$, agrees well with that obtained from Beer's law (ϵ') and this is an indication for absence of serious side-reactions. The adherence to Beer's law was studied by measuring the absorbance value of the series of solutions containing different concentrations of the metal ion. A linear calibration graph drawn between absorbance and the copper ion concentration indicates that Cu(II) may be determined in the range 0.2-20 $\mu\text{g/ml}$. A straight-line with equation $y=0.0098x+0.0126$ and a correlation coefficient of 0.9994 was obtained. Sandell's sensitivity was estimated to be 1.38 ng cm^{-2} . The limits of detection (LOD) and quantification (LOQ) were calculated as 3 times and 10 times standard deviation of the intercept divided by the slope: $\text{LOD} = 5.0 \text{ ng L}^{-1}$ and $\text{LOQ} = 18.0 \text{ ng L}^{-1}$. The proposed method was applied for the determination of Cu(II) in steel and in soils.

KEYWORDS: Copper, liquid-liquid extraction, Beer's Law, chlorophorm, 1:2 complex.

1. INTRODUCTION

Copper is a very common substance that occurs naturally in the environment. Long-term exposure to copper can cause irritation of the nose, mouth and eyes and it causes headaches, stomachaches, dizziness, vomiting and diarrhea. Chronic copper poisoning results in Wilson's disease, characterized by a hepatic cirrhosis, brain damage, demyelization, renal disease, and copper deposition in the cornea. Because effective methods have been discovered which can control the concentration of copper at a suitable level. Turkoglu et al [1] reported a simple spectrophotometric determination of copper in natural waters and pharmaceutical samples with chloro(phenyl) glyoxime. Copper is quantitatively retained with 1,5- diphenylcarbazone on microcrystalline naphthalene in the pH range 6.5 - 8.0 from a large volume of aqueous solutions of various samples as reported by Shishehborea et al [2]. The liquid-liquid extraction of Cu^{2+} ions with organic solutions containing different chelating agents was reported by Marczenko [3] and Eaton [4]. Spectrophotometric determination of copper in environmental water samples by solvent extraction of an ion association complex of the dichlorocuprate (I) ion with ethylviolet has been developed [5]. Yamamoto [6] reported Spectrophotometric determination of copper in steel, stainless steel and aluminium alloys by the solvent extraction of an ion associate of dichlorocopper (I) ion with ethyl violet. Zalov et al [7] reported a simple spectrophotometric determination of copper in various environmental samples with o-hydroxythiophenol derivative (2-hydroxy-5-chlorothiophenol, 2-hydroxy-5-bromothiophenol and 2-hydroxy-5-iodothiophenol).

In this study of the derivatives of 1,2-aminothiols we synthesized a highly effective reagent 1- (2'-methylanilino) -1,1,2,3,3,4, 4,5,5,6,6-undekafluorinehexanetriol-2 (R). Structural formulae of the reagents used in the present study are shown in Scheme 1. This reagent and the laboratory was used for the determination of copper ion in various environmental samples.



Scheme 1. 1- (2'-methylanilino)-1,1,2,3,3,4,4,5,5,6,6-undekafluorinehexanetriol-2

2. Experimental Procedure

2.1. Reagents and Apparatus

A stock solution (1mg / mL) of copper (II) was prepared by dissolving in water an exact linkage $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$ in water containing 2 ml conc. H_2SO_4 , and diluted with water to 1 liter [8]. The concentration of the copper solution was adjusted gravimetrically [9].

Solution of R in chloroform (0.01M) were used. R were synthesized according to the procedure [10]. Their purity was verified by melting point determination and paper chromatography. The synthesized compound was identified by IR (Fig.1) and NMR spectroscopy (Fig.2) (table 1). To create the optimal acidity, 0.1M solutions of KOH and HCl or ammonium acetate buffers were applied. The extractant was purified chloroform. The absorbance of the extracts was measured using a SF 26 spectrophotometer (USSR) and KFK 2 photocolimeter (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. IR and NMR - spectra were recorded on a spectrophotometer "Bruker".

Table 1. The research results of IR and NMR spectroscopy

IR (KBr) [11]	^1H NMR (300,18 MHz, C_6D_6)
1120-1110, 1365-1350 cm^{-1} ν (CF); 3360-3340 cm^{-1} ν (NH); 3050 cm^{-1} ν (CH); 2545-2540 cm^{-1} ν (SH); 1460-1445, 1510-1500, 1610-1590 cm^{-1} ν (C_6H_5).	δ 2.9 (s, 1H - CH); δ 7.28 (s, 4H - Ar-H); δ 3.57 (s, 1H - SH); δ 3.12 (s, 1H - NH); δ 1.28 (s, 3H- CH_3).

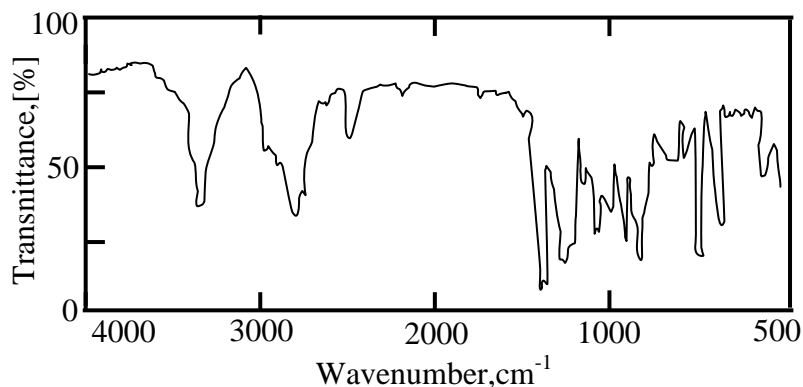


Fig. 1. IR spectrum of R.

2.2. Procedure for Establishing the Optimum Operating Conditions

Aliquots of Cu(II) solution, R solution (up to 3.0 mL) and buffer solution (1.5-5 mL; pH ranging from

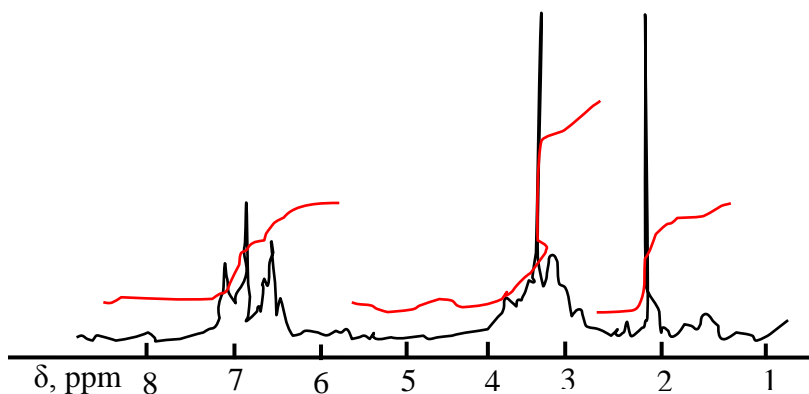


Fig. 2. NMR spectrum of R.

1 to 7) were introduced into 125 mL separatory funnels. The resulting solutions were diluted with distilled water to a total volume of 25 mL. Then 2 mL of chloroform was added and the funnels were shaken for a defined period of time (6 min). A portion of the organic extract was filtered through a filter paper into a cell and the absorbance was read against a blank.

2.5. Determination of tungsten in different objects

2.5.1. Determination of tungsten in steels

0.1 g weighed sample of steel [composition steel A 95-4 — (0,180 Al; 0,025 Fe; 0,025 Pb; 0,010 Cd; 0,010 Cu; 0,010 Sb; 0,007 % Sn; and the rest of Zn), A 95-5 — (0,230 Al; 0,040 Fe; 0,040 Pb; 0,015 Cd; 0,015 Cu; 0,015 Sb; 0,010 % Sn; and the rest of Zn), 69б — (0,90 Mn; 12,51Cr; 11,90 Ni; 9,70 Co; 3,03 W; 0,16 V; 2,09 Mo; 0,09 Ti; 4,23 % Cu; and the rest of Fe), 69в — (0,39 Mn; 12,71 Cr; 8,05 Ni; 1,51 V; 1,15 Mo; 0,07 Ti; 4,43 % Cu; and the rest of Fe), A-195-3 — (11,3 Si; 0,3 Mn; 0,6 Fe; 0,23 Zn; 0,14 Cu; 0,08 Ti; 0,17 Mg; and the rest of Al), A-195-4 — (12,3 Si; 0,13 Mn; 0,9 Fe; 0,3 Zn; 0,11 Cu; 0,2 Ti; 0,12 Mg; and the rest of Al), A-195-5 — (13,2 Si; 0,08 Mn; 1,1 Fe; 0,38 Zn; 0,04 Cu; 0,4 Ti; 0,09 Mg; and the rest of Al)] was dissolved under heating in 4 mL of freshly prepared mixture of HCl and HNO₃ (3: 1) in the presence of a few drops of HF. After dissolution, 0.5 mL of HCOOH is added, and the mixture is heated until the decomposition of HNO₃ occurs. After cooling, the mixture is transferred to a 50 mL volumetric flask and diluted up to the mark with water. An aliquot portion of the resulting solution is transferred to a separatory funnel; 3.0 mL of 0.01 M HCl and 0.3-0.5 mL of a 0.01 M R solution were added, and, after thorough mixing, the volume of the organic phase was adjusted to 5 mL with chloroform, and the volume of the aqueous phase was brought to 20 mL with distilled water. The mixture is shaken for 5-8 min. After layering of the phases, the absorbance of extracts is measured using a KFK-2 photocolormeter at 440 nm in cuvettes of 0.5 cm in thickness. The copper concentration is found from the calibration curve. The results of the determination of copper in steel demonstrate the reliability of the proposed procedure.

2.5.2. Determination of tungsten in soils

The proposed procedures for the determination of copper were applied to its determination in light-chestnut soil from the Caspian zone. A 0.5 g weight was finely ground in an agate mortar and calcined in muffle furnace for 3 h. After cooling, the sample was treated and dissolved in a graphite cup in a mixture of 16 mL of HF (conc.), 5 mL of HNO₃ (conc.), and 15 mL of HCl (conc.) at 50-60°C to remove excess hydrogen fluoride. A further 8 mL portion of HNO₃ (conc.) was added triply to the solution that was each time evaporated to 5-6 mL. After that, the solution was transferred into a 100

mL volumetric flask and its volume was brought to the mark with distilled water. Copper was determined in aliquot portions of the solution using the proposed procedures.

2.3. Procedure for determining the distribution constant

The distribution constant K_D was found from the ratio $K_D = A_1/(A_3-A_1)$ where A_1 is the light absorbance measured after a single extraction at the optimum operating conditions (Table 1, 25 ml final volume) and A_3 is the absorbance measured after a triple extraction under the same conditions [12].

Table 1. Optimum conditions and analytical characteristics of the Cu(II)-R-H₂O-CHCl₃ system

Optimum conditions	Analytical Characteristics
Wavelength: 450 nm	Apparent molar absorptivity: $\epsilon=4.3 \times 10^4 \text{ L mol}^{-1} \text{ cm}^{-1}$
$C_R: 2.8 \times 10^{-3} \text{ mol L}^{-1}$	True molar absorptivity: $\epsilon'=4.3 \times 10^4 \text{ L}^3 \text{ mol}^{-1} \text{ cm}^{-1}$
Shaking time: 3 - 4 min	Adherence to Beer's law: 0.2-20 mg ml ⁻¹
The pH range of education and extraction: 0.2 – 8.0	Limit of detection: 5.0 mg L ⁻¹
The pH range of maximum extraction: 2.8 – 5.3	Limit of quantification: 18.0 ng L ⁻¹
Degree of extraction: 98.92 %	Sandell's sensitivity: 1.38 ng cm ⁻²

RESULT AND DISCUSSION

3.1. The Choice of the Extractant

Copper (II) could be extracted quantitatively (98.92 %) by R into chlorophorm from an aqueous solution of pH 2.8 to 5.3. Organic solvents used for extraction of Cu (II) can be arranged on the basis of their extraction coefficient values as (Fig.3).

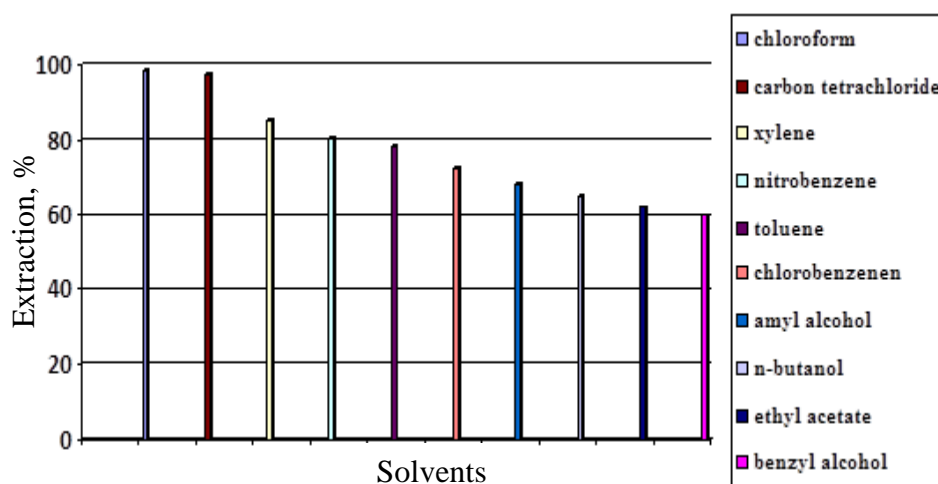


Fig. 3. Percentage extraction coefficient of Cu (II) Into various organic Solvents.

Chlorophorm was found to be the best extracting solvent; hence, it was selected for extraction throughout the work. The chlorophorm extract of Cu - R complex showed intense peak at 450 nm (Fig. 4). Colour reactions were very contrast since the initial solutions are colourless ($\lambda_{\text{max}}(\text{R})=300 \text{ nm}$). Thus, bathochromic shift makes 150 nm. Contrast of reactions was high: initial reagents - are colourless, and complexes - are intensively painted.

3.2. Influence of the pH of the aqueous phase

Studying of dependence of a complex formation from pH showed that, the exit of complexes of copper is maximum at pH 2.8 – 5.3. Extraction of Cu(II) enhanced with the increase in the acidity of the initial solution; the further increase in acidity lead to the gradual decrease of recovery, which was obviously associated with a decrease in the concentration of the ionized form of dithiolphenols. Probably, it is present in the solution in the non-dissociated state. The effect of pH on the intensity of the color reaction is shown in the Fig. 5. Existence of one maximum of absorbance in the specified limits pH confirms the assumption of formation of one complex connection. The nature of acids (HCl, H₂SO₄) almost does not influence a complex formation of copper with R.

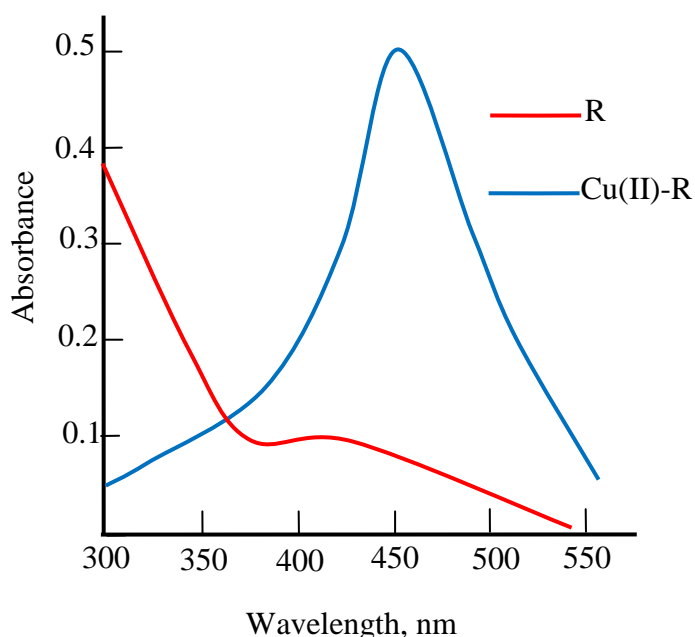


Fig. 4. Absorption of binary complex.

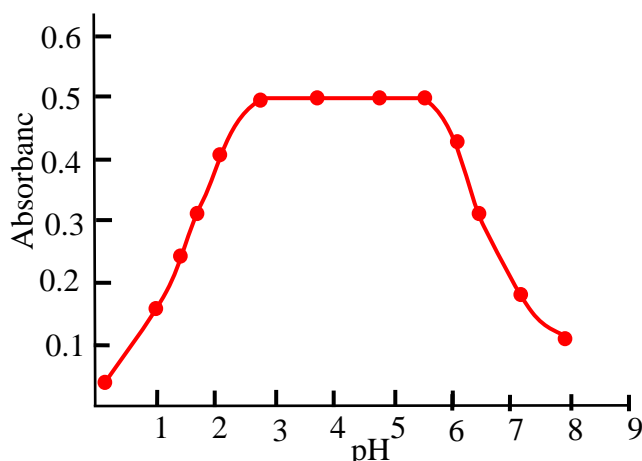


Fig. 5. Absorbance of Cu(II)-R complex in chloroform vs. pH of the aqueous phase. $C_{Cu(II)} = 1.87 \times 10^{-5} \text{ mol L}^{-1}$, $C_R = 2.8 \times 10^{-3} \text{ mol L}^{-1}$, $\lambda=440 \text{ nm}$.

3.3. Effect of Reagents Concentrations and Order of Their Addition

A yellow brown colour is developed immediately after the mixing of Cr(II) and R solutions. For up to 2.0 mg mL^{-1} of Cu(II), the optimum concentration of R was $2.8 \times 10^{-4} \text{ mol L}^{-1}$.

Under the optimum conditions, the colouration of the organic extract remains constant for at least an hour at room temperature. It was found that the order of reagents addition is also of importance for good colour development. The correct order: Cu(II), R and buffer.

3.4. Composition of the Extracted Complex

The composition of the extracted complex was found to be 1:2 (Cu:R) by Job's continuous variation and Mole ratio method [13] (Fig. 6 and Fig. 7).

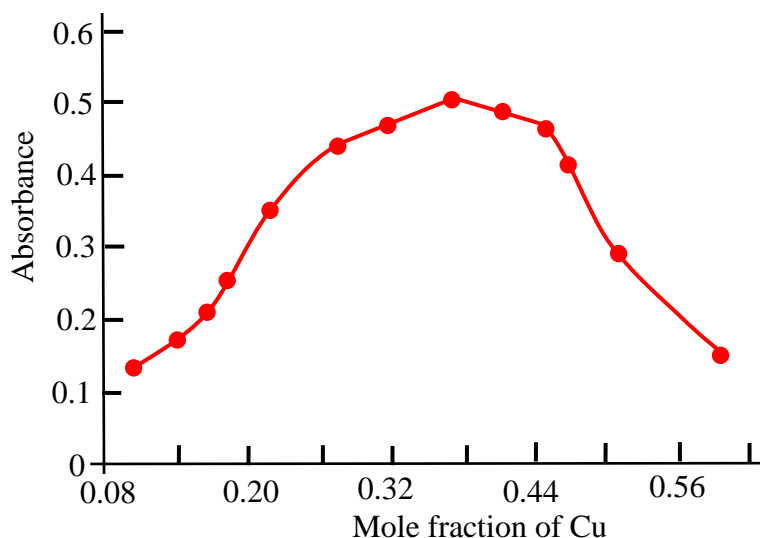


Fig. 6. Composition of extractive species Cu : R by Job's Continuous variation method.

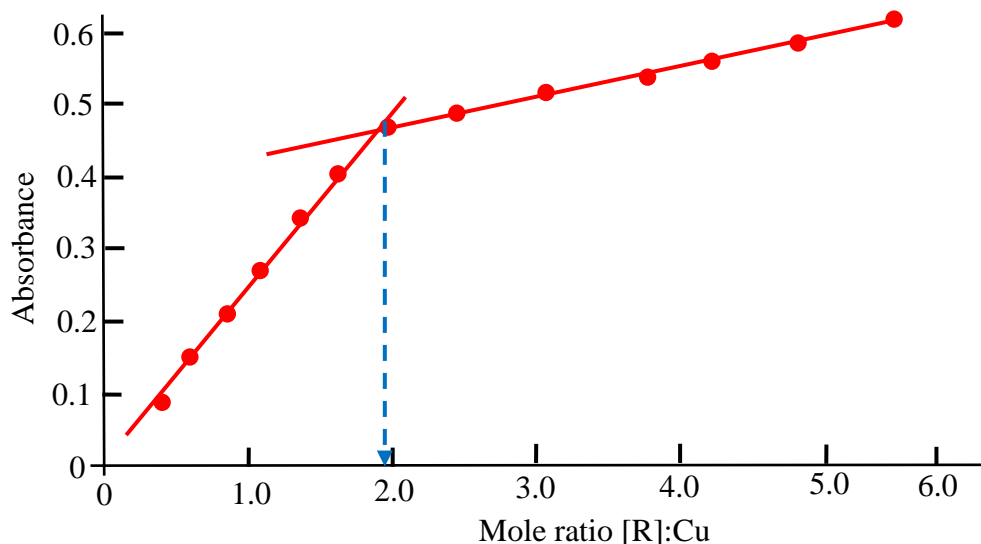


Fig. 7. Composition of extractive species Cu:R by Mole Ratio Method.

Using the Nazarenko's method [14], we found that the copper complexation form is Cu^{2+} . The disappearance of the band at 2580 cm^{-1} , characteristic for the spectrum of R, and appearance of corresponding bands in the spectrum of the complex, which are shifted toward lower frequency,

suggests that the sulphur atoms are involved in complex formation. The observed decrease in the intensity of the absorption bands at $3360\text{--}3350\text{ cm}^{-1}$ with a maximum at 3357 cm^{-1} and the appearance of a broad band in the region of $3050\text{--}3150\text{ cm}^{-1}$ shows that the NH group participates in the formation of a coordination bond [11] (Fig.8). Proceeding from the obtained data, we propose the following structure for the extracted binary complex (Scheme 2).

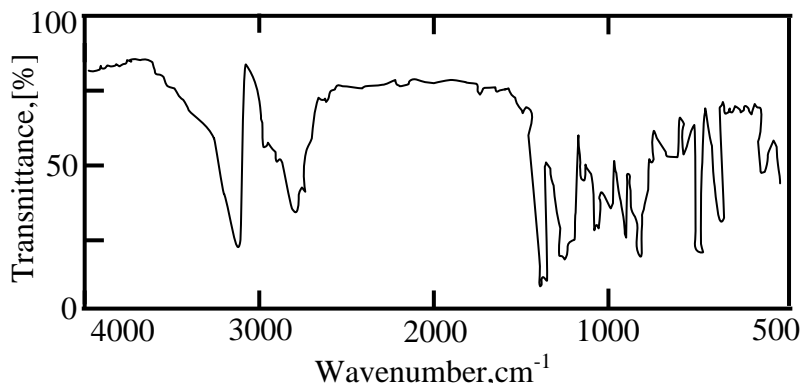
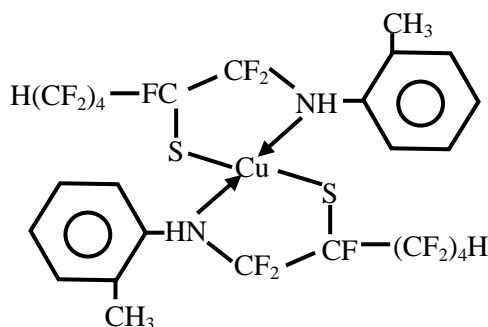


Fig. 8. IR spectrum of complex (Cu – R).



Scheme 2. Suggested structure of the binary complex

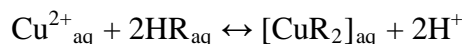
In order to establish the degree of aggregation of the complex into the organic phase calculating the degree of polymerization in the equation derived in ($\gamma = 1.12$) [12]:

$$\gamma = \frac{\lg \frac{A_i}{A_k}}{(q+1) \lg \frac{C_i \varepsilon \ell - A_i}{C_k \varepsilon \ell - A_k}}$$

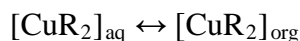
Equilibria and equilibrium constants

Several equilibrium processes are important when we describe quantitatively the formation and subsequent extraction of $[\text{CuR}_2]$.

Formation in the aqueous phase:



Distribution:



The equilibrium constants describing these processes are shown in Table 2. The association constant was determined according to a strategy by several independent methods [15], (Holme-Langmyhr method, Harvey-Manning method, Komar-Tolmachev method, and the mobile equilibrium method) (Table 2). The constant of distribution K_D was calculated from the absorption values obtained after

single and triple extraction as described above. The constant of extraction K_{ex} was calculated by the formula $K_{ex} = K_D \times \beta$. All experiments were performed at room temperature of $22 \pm 3^\circ\text{C}$ and the calculations were carried out at a probability of 96 %.

Table 2. Calculated values of $\lg K_{eq}$, $\lg K_D$ and $\lg K_{ex}$

Equilibrium constant	Value
$K_{eq} = [\text{CuR}_2] / [\text{Cu}^{2+}] \times [\text{R}^-]^2$	$\lg \beta = 8.59 \pm 0.2^a$ $\lg \beta = 8.70 \pm 0.4^b$ $\lg \beta = 8.46 \pm 0.7^c$ $\lg \beta = 8.75 \pm 0.3^d$
$K_D = [\text{CuR}_2]_{org} / [\text{CuR}_2]_{aq}$	$K_D = 1.86 \pm 0.01$
$K_{ex} = [\text{CuR}_2]_{org} / [\text{Cu}^{2+}]_{aq} \times [\text{R}^-]_{aq}^2$	$\lg K_{ex} = 10.56 \pm 0.1^e$ $\lg K_{ex} = 10.60 \pm 0.3^f$

Note: ^aCalculated by the Holme-Langmyhr method; ^bCalculated by the Harvey-Manning method; ^cCalculated by the Komar-Tolmachev method; ^dCalculated by the mobile equilibrium method; ^eCalculated by the formula $K_{ex} = K_D \times \beta$ where is determined by the Holme-Langmihir method; ^fCalculated by the formula $K_{ex} = K_D \times \beta$ where is determined by the Harvey-Manning method.

3.8. Molar Absorptivity, Beer's Law and other Analytical Characteristics

The Komar-Tolmachev method also allows calculating the true molar absorptivities (ϵ) of the complexes (Fig. 9). The obtained value, $\epsilon = (4.3 \pm 0.6) \times 10^4 \text{ L mol}^{-1} \text{ cm}^{-1}$, agrees well with that obtained from Beer's law (ϵ') (Table 1) and this is an indication for absence of serious side-reactions [13]. The adherence to Beer's law was studied by measuring the absorbance value of the series of solutions containing different concentrations of the metal ion. A linear calibration graph drawn between

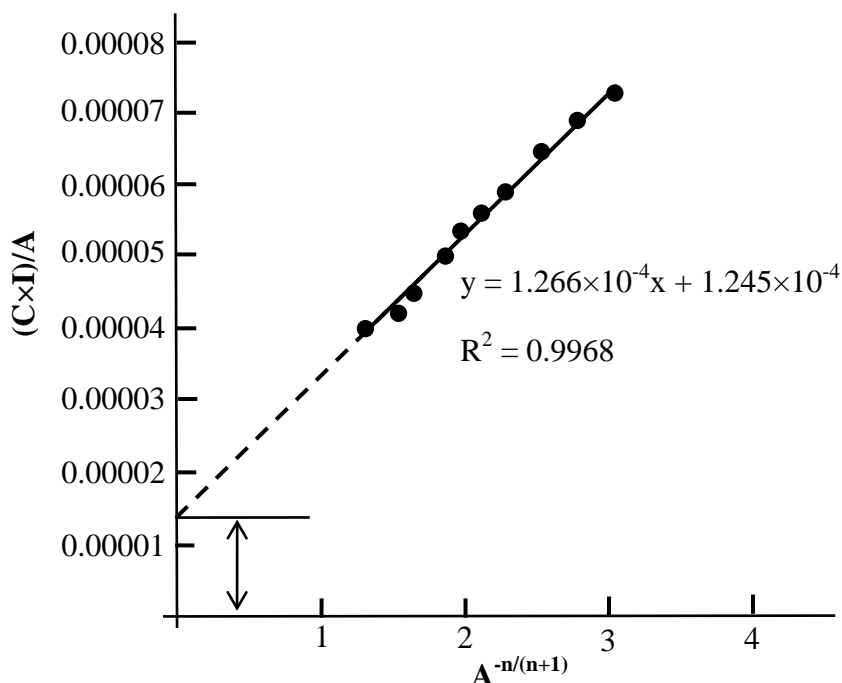


Fig. 9. Determination of the Constant of Association (β) and True Molar Absorptivity (ϵ) by the Method of Komar-Tolmachev. $n=2$, $C_R = 2.8 \times 10^{-3} \text{ mol L}^{-1}$, $\text{pH}=4.0$

absorbance and the copper ion concentration indicates that Cu(II) may be determined in the range 0.2-20 $\mu\text{g/ml}$ (Table 1). The pertaining calibration graph is shown in the Fig. 10. A straight-line with equation $y=0.0098x+0.0126$ and a correlation coefficient of 0.9994 was obtained. Sandell's sensitivity

was estimated to be 1.38 ng cm^{-2} . The limits of detection (LOD) and quantification (LOQ) were calculated as 3 times and 10 times standard deviation of the intercept divided by the slope: $\text{LOD} = 5.0 \text{ ng L}^{-1}$ and $\text{LOQ} = 18.0 \text{ ng L}^{-1}$.

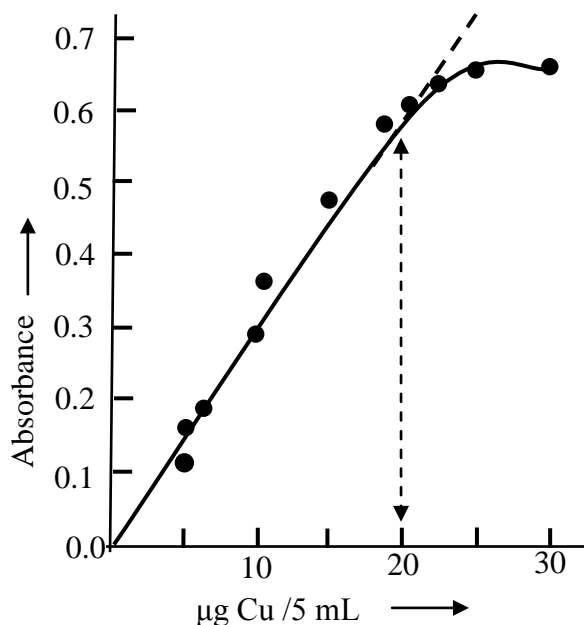


Fig.10. Beer's law range of Cu (II)- R complex in Chloroform at 440 nm.

3.9. Effect of other ions

Cu (II) ($50 \mu\text{g}$) was determined in the presence of various ions. The following ions in the amount indicated, did not interfere in the spectrophotometric determination of Cu (II) ($50 \mu\text{g}$) (Table 3). Interference due to iodide, nitrite and thiosulphate, EDTA was removed by boiling solution with concentrated HNO_3 before the adjustment of pH.

Table 3. Effect of foreign species

Tolerance limit [$\mu\text{g mL}^{-1}$]	Species
10 μg each of	Li(I), Ca(II), Mg(II), Al(III), Ba(II), Sr(II), Pb(II), Sn(II), Be(II), W(VI), Mo(VI), U(VI), V(VI)
5 μg each of	Zn(II), Hg(II), Ag(I), As(III), Bi(III), Sb(III)
2 μg each of	Mn(II), Cd(II)
1 μg each of	Cr(III), Ce(IV), Th(IV), Zr(IV)
0.5 μg each of	Fe(II), Fe(III), Ni(II)
0.1 μg each of	Co(II), Pt(IV), Ru(III), Ir(IV), Os(IV), Pd(II)
20 μg each of	chloride, bromide, fluoride, sulphate, persulphate, nitrate, phosphate, acetate, oxalate, citrate, tartarat

Table 4 demonstrates the data which allow a comparison of the analytical parameters of the procedures for the determination of copper with the earlier known procedures.

3.9. Analytical Applications

The proposed method under the already established optimum conditions was applied for the determination of Cu(II) in steel and in soils. The proposed procedures for determining copper in soils and in steel were verified by neokuproin [9,17] and cuproin [9,17] methods. The results of the analysis are listed in Table 5 and 6 indicate the successful applicability of the proposed method to real sample analysis.

Table 4. Comparative Characteristics of the Procedures for Determining Molybdenum

Reagent	pH (Solvent)	λ , nm	$\epsilon \cdot 10^{-4}$	Beer's law range, μg	[Ref.]
<i>Standard Method</i>					
Dietilditiocarbaminat	4-11 (CCl ₄)	436	1,40	0.8 – 16	[3,9,17]
Kuproin	4-7 (amyl alcohol)	546	0,64	1.2 – 22	[9,17]
Neokuproin	3-10 (amyl alcohol)	454	0,79	1.8 – 22	[9,17]
HITPh* + aniline	2.1–4.3 (CHCl ₃)	660	3,6	0.2 – 12	[7]
Pikramin M	0.7M HCl	530	1,67	1.0 – 14	[16]
Pikraminepsilon	0.1–0.2M HCl	550	0,26	0.4 – 14	[17]
Tioksamid + pyridine	4.5–5.0	380	1,75	0.16 – 18	[17]
HSNPhAP* + DPG*	2.0	431	2,87	0.12 – 2.56	[18]
ONT* + aniline	3.6–5.4 (CHCl ₃)	660	2,86	0.2–20	[19]
<i>Proposed Method</i>					
R	0.2 – 8.0 (CHCl ₃)	450	3.65	0.2 – 20	

Note: DEDTC – Dietilditiocarbaminat HITPh – 2-hydroxy-5-iodothiophenol; DPG – diphenylguanidine; HSNPhAP - 3- (2-hydroxy-3-sulfo-5-nitrophenylazo) 2,4-pentadione; ONT - 1-bromo-2-hydroxy-3-naphthoic acid.

Table 5. The results of the copper steel ($n = 5$; $P = 0.95$)

Method	Sample of steel	\bar{X} , %	RSD, %	$\bar{X} \pm \frac{t_p S}{\sqrt{n}}$
Proposed Method	A 95 - 4	0.010	3	0.0095±0.003
Kuproin			3	0.0093±0.003
Proposed Method	A 95 - 5	0.015	2	0.0180±0.002
Neokuproin			2	0.0182±0.002
Proposed Method	69 ^b	4.230	5	4.2400±0.120
Kuproin			4	4.2260±0.143
Proposed Method	69 ^v	4.430	3	4.4301±0.152
Neokuproin			4	4.400±0.149
Proposed Method	A 195-3	0.140	3	0.1370±0.002
Kuproin			4	0.1340±0.003
Proposed Method	A 195-4	0.110	2	0.1261±0.002
Neokuproin			1	0.1178±0.002
Proposed Method	A 195-5	0.040	3	0.0371±0.004
Neokuproin			3	0,0393±0.005

Table 6. Correctness and Reproducibility of Determination of copper in Soil. $n=5$, $P=0.95$

Method	$\bar{X} \times 10^{-4}$, %	RSD, %	$\bar{X} \pm \frac{t_p S}{\sqrt{n}}$
Kuproin	5.67	4.8	$(5.67 \pm 0.12) \times 10^{-4}$
Neokuproin	6.05	4.3	$(6.057 \pm 0.14) \times 10^{-4}$
Proposed Method	4.930	3.6	$(4.2 \pm 0.09) \times 10^{-4}$

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