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# Studying The Reactions Of Complex Formation Of Copper (II) With 2-Hydroxytiolphenol And Its Derivatives In The Presence Of Hydrophobic Amines

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***Abstract*— The purpose of this work is to systematically study the conditions for the interaction of copper with 2-hydroxythiophenol (HTP) and its derivatives {2,5-dihydroxythiophenol (DHTP), 2-hydroxy-5-chlorothiophenol (HCTP), 2-hydroxy-5-bromothiophenol (HBTP) and 2-hydroxy-5-iodothiophenol (HITP)} in the presence of Am. From Am, aniline (An) and N, N-dimethylaniline (DAn) were used.Non-aqueous solvents were used to extract MLC: chloroform, 1,2-dichloroethane, carbon tetrachloride, benzene, chlorobenzene, toluene, iso-butanol, iso-pentanol and diethyl ether. The extractability of the complexes was estimated by the distribution coefficient and the degree of extraction. With a single extraction with chloroform, 97.8-98.4% of copper is recovered as MLC. Further studies were performed with chloroform.The study of the dependence of complexation on pH showed that the optimum range of acidity at which the optical density is maximum and constant is pH 2.3-8.0. Copper MLC is formed in the presence of a large excess of complexing agents. The optimal condition for the formation and extraction of these compounds is (0.8-1.0) × $10^{-3}$ M, the concentration of L and (1.0-1.2) $10^{-3}$ M - Am. The linearity range of the calibration dependence for chloroform extracts of the complexes is maintained in the range of concentrations of copper 0.04-3.6 µg/ml.Copper MLC with L and Am is stable in aqueous and organic solvents and does not decompose for three days, and after extraction it is more than a month. Maximum optical density is achieved within 5 minutes.The maximum analytical signal with the complexation of copper with L and Am is observed at 620–650 nm. Molar absorption coefficients are (4.1–4.3) × $10^4$. In the interaction of Cu (II) with L and Am, complexes with the composition Cu (II): L: Am = 1:2:4. By the method of Nazarenko it was established that the complexing form of copper is $Cu^{2+}$. In this case, the number of protons displaced by him from one L molecule turned out to be 2. It was established that a large amount of alkaline, alkaline earth elements, REE, $F^-$, $Cl^-$, $Br^-$, $SO_4^{2-}$, $SO_3^{2}$-, $NO_2^-$, $NO_3^-$ and $C_2O_4^{2-}$ does not affect the determination of copper. Citrates and tartrates, $J^-$, $CN^-$, $S_2O_3^{2-}$, thiourea interfere. The disturbing effects of Fe (III) were eliminated with oxalic acid; Ti (IV) is sodium fluoride or tirone; Hg (II) sulfite ion; Nb (V) and Ta (V) are oxalic acid, and Mo (VI) and W (VI) are sodium fluoride and oxalic acid. When using a 1% solution of ascorbic acid, Mn (VII), V (IV), Nb (V), Cr (VI), Mo (VI) and Fe (III) do not interfere with the determination. When using a 0.01 M solution of oxalic acid V (IV), Nb (V), Ta (V), Cr (III), Mo (VI), W (VI) and Fe (III) do not interfere with the determination. The developed method is used to determine copper (II) in standard samples of alloys. The results of determination of copper in alloys indicate sufficient reliability of the proposed methods.**

***Keywords—copper; 2-hydroxythiophenol; hydrophobic amines; extraction-photometric method; determination***

## I. Introduction

Many chelating agents belonging to different classes of compounds and containing as donor atoms N, O or S are suitable for photometric determination of copper. mainly in weakly acidic and neutral environments with the formation of colored complex compounds [1]. Copper is one of those metals that have chromophore properties; therefore, among the numerous photometric methods for the determination of copper there are both methods based on the use of colored reagents with chromophore groups and methods in which colorless reagents are used. It is known that due to the improvement of the analytical parameters of the reaction of the formation of mixed-ligand complexes (RLC), they have found wide application in the photometric determination of elements [2-11].

For the extraction-spectrophotometric determination of copper (II), isonitrosopropiophenone was proposed [12]. A sensitive and selective spectrophotometric method has been developed for determining copper (II) in alloys and in water [13,14]. Spectrophotometric methods for the determination of copper in some environmental and biological objects by salicylaldehyde benzoyl hydrazone [15], alizarin yellow P and triisobutyl phosphate in food products [16,17] have been proposed.

According to the hypothesis of analogies, reactions with reagents of the R-SH type are possible for the ions of the elements forming the water-poor sulfides [18]. Procedures have been developed for determining elements in the form of RLC with 2-hydroxy-5-halogenophenol and in the presence of hydrophobic amines (Am) [7,19-23].

Of interest was the study of the interaction of copper with 2-hydroxythiophenol (HTP) and its derivatives {2,5-dihydroxythiophenol (DHTP), 2-hydroxy-5-chlorothiophenol (HCTP), 2-hydroxy-5-bromothiophenol (HBTP) and 2-hydroxy -5-iodothiophenol (HITP)} in the presence of Am. From Am used aniline (An) and N, N-dimethylaniline (DAn).

## II. Experimental

### A. Reagents and Apparatus

To prepare the initial solution (1 mg / ml) of copper, 3.9296 g of freshly crystallized CuSO4 · $5H_2O$ was dissolved in water, 2 drops of conc. $H_2SO_4$ and diluted in a volumetric flask with water up to 1 l [24]. Solutions with a concentration of 0.1 mg/ml were obtained by diluting the original solution.

The hydroxythiophenol derivatives (L) were purified by reprecipitation of ethanol from solutions by the addition of water and then by distillation. Used 0.01 M solutions of L chloroform. Purified chloroform is used as an extractant. The ionic strength of the solutions, equal to μ = 0.1, was kept constant by introducing the calculated amount of KCl. To create the necessary acidity of the solutions, use 1M NaOH solution.

The ionic strength of the solutions was kept constant (μ = 0.1) by introducing the calculated amount of KCl. To create the required acidity of the solutions, 1M solutions of HCl and $H_2SO_4$ were used.

The optical density of the organic phase was measured on a UFC-2, and a Shimadzu UV mini1240 spectrophotometer. The pH of the solutions was controlled with an I-130 ionomer with a glass electrode. IR spectra were recorded on a UR-20 spectrophotometer and a Bruker company.

### B. General Procedure

- **General Procedure for the Determination of copper (II)**

0.1-0.8 ml was injected into graduated tubes with crushed tubes with an interval of 0.1 ml of the initial solution of copper, 2.5 ml of 0.01 M solution L and 0.8-1.0 ml of Am. The required pH was adjusted by adding 1 M NaOH solution. The volume of the organic phase is adjusted to 5 ml with chloroform, and the aqueous phase to 20 ml with distilled water. After 5 minutes, the organic layer was separated and its optical density was measured at room temperature with KFK-2 at 490 nm.

The charge of homogeneous ligand complexes was established by the method of electromigration of ions. When studying the electromigration of homogeneous ligand complexes in a U-shaped tube with two cranes, the movement of blue-green ions to the positive pole was observed, on the basis of which it was concluded that the Cu (II) –L complexes are colored anions. With the introduction of Am into the system, a transition of anionic complexes to the organic phase in the form of MLC is observed.

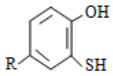
- **Determination of copper in standard alloy samples.** C

Sample weight 0.1 - 0.5 g of alloy [A 95-4 - (0.180 Al; 0.025 Fe; 0.025 Pb; 0.010 Cd; 0.010 Cu; 0.010 Sb; 0.007% Sn; OST 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; rest. Zn), A-195-3 — (11.3 Si; 0.3 Mn; 0.6 Fe ; 0.23 Zn; 0.14 Cu; 0.08 Ti; 0.17 Mg; OST. 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; OST. 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; OST. Al)] was dissolved in 10 ml of a mixture of an aqueous solution of 5 ml of HCl (1: 1) + 1-2 ml of HNO3 (1: 1) at 50 WITH. While the silicon does not dissolve, so the solution was filtered and the filtrate is transferred to a flask with a capacity of 50 ml and diluted to the mark with water. The resulting solution (1 ml) was injected into a cylinder with a capacity of 100 ml, 2 ml of a 0.01 M DGTP solution, 2 ml of An was added. The required pH was adjusted by adding a calculated amount of 0.1 M NaOH solution. The volume of the organic phase was adjusted to 5 ml with chloroform, and the total volume to 25 ml with distilled water. The resulting solution was introduced into a separatory funnel. After separation of the phases, the light absorption of the extracts was measured at KFK-2 at 490 nm in a cuvette with a thickness of 0.5 cm. The copper content was found according to the calibration curve.

## III. Results and Discussion

L are dibasic (HTP HCTP HBTP and HITP, $H_2L$) and tribasic weak acid (DHTP, $H_3L$) and, depending on the pH of the medium, can exist in molecular and anionic forms. Some characteristics of the studied reagents are presented in table 1.

**TABLE I.** Some characteristics of the studied reagents



{R = H[HTP], OH [DHTP], Cl [HCTP], Br [HBTP], J [HITP]}

| Reagent | $pK_1$ | $pK_2$ | $pK_3$ | neutral form pH |
|---|---|---|---|---|
| HTP | 5,80 | 10,9 | - | 0-3,7<br>($\lambda$=278 нм) |
| DHTP | 6,33 | 11,2 | 12,78 | 0-4,0<br>($\lambda$=281 нм) |
| HCTP | 5,10 | 10,6 | - | 0-3,5<br>($\lambda$=283 нм) |
| HBTP | 5,05 | 10,4 | - | 0-3,3<br>($\lambda$=286 нм) |
| HITP | 5,00 | 10,2 | - | 0-3,2<br>($\lambda$=290 нм) |

### A. Optimization Procedure

- **The choice of extractant**

Non-aqueous solvents were used to extract MLC: chloroform, 1,2-dichloroethane, carbon tetrachloride, benzene, chlorobenzene, toluene, *iso*-butanol, *iso*-pentanol and diethyl ether. The extractability of the complexes was estimated by the distribution coefficient and the degree of extraction. Chloroform, dichloroethane and carbon tetrachloride turned out to be the best ex- agents. With a single extraction with chloroform, 97.8-98.4% of copper is recovered as MLC. Further studies were performed with chloroform. The copper content in the organic phase was determined photometrically by diethyldithiocarbaminate after reextraction, and in the water phase, by difference. In the extraction of copper complexes with HTP and its derivatives, chloroform molecules are not included in the extractable complexes; the solvation number characterized by the value of the slope tangent in this case is zero.

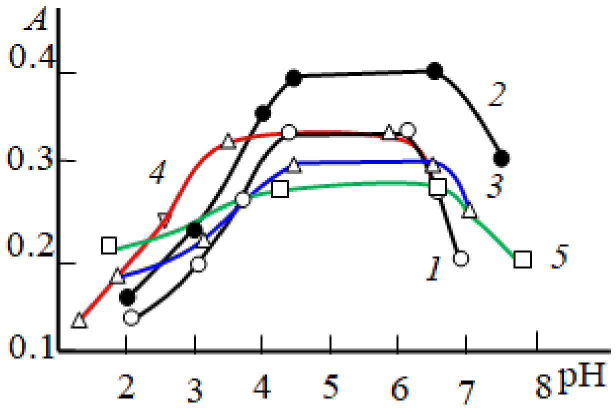


**Fig. 1:** The dependence of the optical density of MLC copper on the pH of the aqueous phase.

1. Cu-HTP-An; 2.Cu-DHTP-An; 3.Cu-HCTP-An; 4. Cu-HBTP-An; 5.Cu-HITP-An

$C_{Cu}$= 1.875×$10^{-5}$ M; $C_L$ = (0.8-1.0)×$10^{-3}$ M; $C_{An}$ = (1.0-1.2) ×$10^{-3}$ M, KFK-2, λ= 590 nm, l = 0.5 cm

- **The influence of the pH of the aqueous phase**

The study of the dependence of complexation on pH showed that the optimum acidity range at which the optical density is maximum and constant is at pH 2.3-8.0. At a pH of 8, the extraction of MLC is practically not observed, which is apparently due to an increase in the free molecules of hydrophobic amines. On the other hand, in the case of DHTP, the concentration in the aqueous solution of the non-extracted complex $[CuR_2]^{4-}$ increases, as the dissociation into the second -OH group continues to increase. The dependence of optical density on pH is shown in Figure 1. The presence of one maximum optical density within the indicated pH limits confirms the assumption that a single complex compound is formed.

- **Absorption spectra**

The maximum analytical signal with the complexation of copper with L and Am is observed at 620-650 nm (Fig. 2). L max absorb at 278-283 nm. When complexing occurs, a bathochromic shift of the maximum absorption absorption at 339-367 nm is observed. The contrast of the reactions is high: the initial reagents are almost betsvetny, and the complexes are bluish-green. Colored chloroform extracts of hydroxy-amino-amine associates absorb as much as possible at 325-335 nm. The sharp difference in the values of the maxima of the absorption of complexes and associates allows us to conclude that the compounds formed are of different ligand complexes with a mixed coordination sphere.

Molar absorption coefficients are (4,1-4,3)×$10^4$.

- **The effect of reagent concentration and shaking time**

The effect of ligand concentration and aging time. MLC copper formed in the presence of a large excess of complexing agents. The optimal condition for the formation and extraction of these compounds is (0.8-1.0)×$10^{-3}$ M concentration of L and (1.0-1.2) $10^{-3}$ M - Am.

MLC copper with L and Am are stable in aqueous and organic solvents and do not decompose for three days, and after extraction - more than a month. Maximum optical density is achieved within 5 minutes.

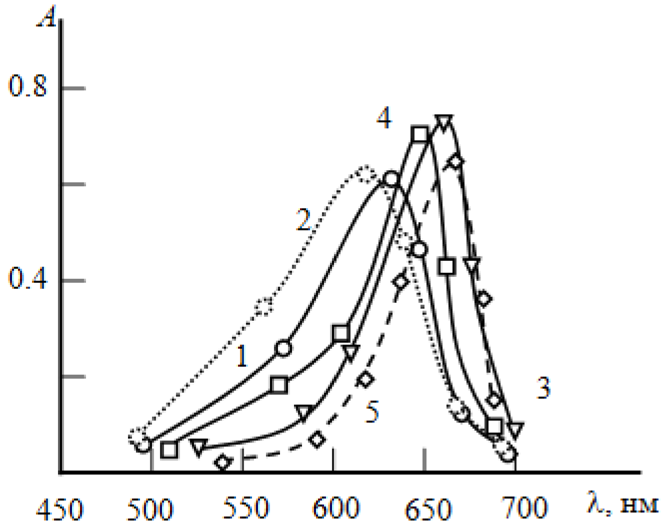


**Fig. 2:** Absorption of mixed-ligand complexes

1. Cu-HTP-An; 2.Cu-DHTP-An; 3.Cu-HCTP-An; 4. Cu-HBTP-An; 5.Cu-HITP-An

$C_{Cu}$= 1.875×$10^{-5}$ M; $C_L$ = (0.8-1.0)×$10^{-3}$ M; $C_{An}$ = (1.0-1.2) ×$10^{-3}$ M, SF-26, λ=590 nm, ℓ=1,0 cm.

### B. The composition of mixed-ligand complexes of copper (II) with 2-hydroxythiophenol and its derivatives and hydrophobic amines

The molar ratios between the components of the complex were found by several methods: Starik–Barbanel relative yield method, straight line method and equilibrium shift method [25]. The results show that the interaction of Cu (II) with L and Am forms complexes with the composition of Cu(II):L:Am = 1: 2: 4 (Fig. 2). The Nazarenko method has been established that the complexing form of copper is $Cu^{2+}$ [26]. In this case, the number of protons displaced by him from one L molecule turned out to be equal to 2.

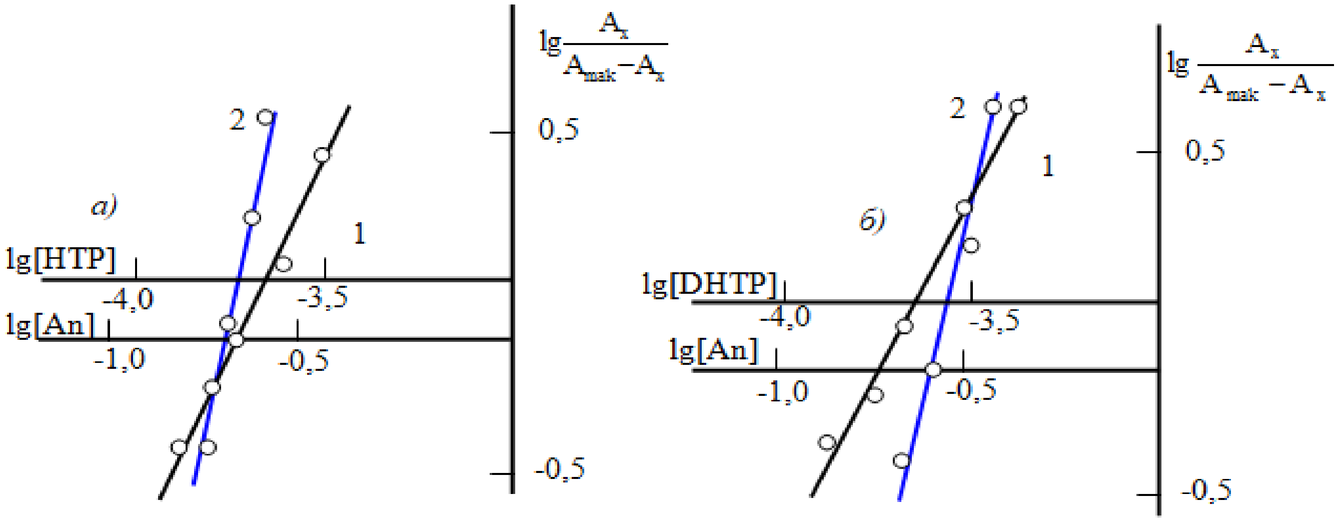


**Fig. 3:** Determination of the ratio of components in RLK using the equilibrium shift method for Cu-HTP-An (a) and Cu-DHTP-An (b). 1. Cu: L; 2. Cu: An.

$C_{Cu}$ = 1.875×$10^{-5}$ M; SF-26, ℓ = 1.0 cm.

### C. IR spectroscopic study of copper (II) complexes with DHTP and amines

In the IR spectra of the Cu(II)-DHTP-An complex in the region of 950–960 cm$^{-1}$, an intense absorption band appears, which is absent in the spectra of the reagent. This band is due to the valence vibration of the bond of the metallic ligand. The decrease in the intensity of the pronounced band at 2580 cm$^{-1}$, observed in the DHTP spectrum, and the appearance of two absorption bands in the spectra of the complex, one of which is shifted to lower frequencies, indicates that one of the - SH groups is involved in the formation of bonds. The disappearance of the absorption band in the region of 3200–3600 cm$^{-1}$ with a maximum at 3460 cm $^{-1}$ allows us to conclude that there are no free –OH groups in the synthesized complexes. The detection of absorption bands at 2270 cm $^{-1}$ indicates the presence of protonated aniline [27, 28].

### D. The chemistry of formation of mixed-ligand complexes of copper (II) with L and hydrophobic amines

The calculations made showed that MLC in the organic phase does not polymerize and is in monomeric form (γ = 0.94-1.07) [29].

In tab. 2 shows the main spectrophotometric characteristics of MLC copper. The mechanism of RLC formation can be represented as follows: L at pH 1.5-8.0 forms a compound insoluble in chloroform with an excess of copper ions. Aniline is added to such a system; an intensively colored compound soluble in chloroform is instantly given.

Aniline is a weak base due to resonant stabilization, which arose during the interaction of a lone electron pair of a nitrogen atom along π-orbitals of an aromatic ring. Due to this, aniline at pH 1.5-8.0 in solution is in the form of aniline cation ($AnH^+$) and molecular form. The composition of extractable complexes can be represented by the formula $(AnH)_2[CuL_2(An)_2]$.

**TABLE II:** Characteristics of MLC copper (II) with L and Am

| **Compound** | **The pH range of formation and extraction** | **The pH range of maximum extraction** | **λ, nm** | **$\varepsilon \cdot 10^{-4}$** | **$\lg K_{eq}$** | **$\lg K_{ex}$** | **lgβ** |
|---|---|---|---|---|---|---|---|
| $(AnH)_2[Cu(DHTP)_2(An)_2]$ | 3.4-8.0 | 3.8-6.5 | 620 | 4.3 | 3.69 | 9.69 | 10.67 |
| $(AnH)_2[Cu(HTP)_2(An)_2]$ | 3.0-7.5 | 3.5-6.0 | 630 | 4.2 | 3.49 | 9.26 | 10.28 |
| $(AnH)_2[Cu(HCTP)_2(An)_2]$ | 2.3-6.5 | 2.6-5.3 | 650 | 4.0 | 3.51 | 9.31 | 9.75 |
| $(DAnH)_2[Cu(HCTP)_2(DAn)_2]$ | 2.4-6.6 | 2.7-5.4 | 648 | 4.1 | 3.57 | 9.55 | 9.77 |
| $(AnH)_2[Cu(HBTP)_2(An)_2]$ | 1.9-6.2 | 2.4-4.8 | 655 | 3.8 | 3.43 | 9.71 | 9.45 |
| $(AnH)_2[Cu(\text{HİTP})_2(An)_2]$ | 1.5-5.5 | 2.1-4.3 | 660 | 3.6 | 3.82 | 10.26 | 9.08 |

### E. Equilibrium and extraction constants

It can be assumed that the following processes occur during complexation:

$$Cu^{2+} + 2H_2L \leftrightarrow [CuL_2]^{2+} + 4H^+$$

$$[CuL_2]^{2+} + 2Am + 2AmH^+ \leftrightarrow [CuL_2Am_2]\,(AmH)_2$$

Reaction equilibrium constant is

$$K_p = \frac{\{[CuL_2 Am_2](AmH)_2\}_0}{\{[CuL_2 Am_2]^{2-}\}_в \{[AmH^+]^2\}_в} = \lg \frac{A_x}{A_0 - A_x} \cdot \frac{1}{[Am]^2}$$

Since the distribution coefficient (D) is equal to,

$D = A_x / A_0 - A_x$ then $K_{eq} = D / [AmH^+]^2$

Prologue the last expression, we get

$$\lg K_{eq} = \lg D - 2\lg[AmH]$$

Extraction constants were calculated using the equations

$$\lg Kex = \lg D - 2\lg[L^{2-}] - 2\lg[HAm^+].$$

The results of the calculation of the equilibrium constant and the extraction reaction were given in Table II.

### F. Spectrophotometric determination of copper (II)

Based on the equations of the calibration graphs, the limit of photometric detection and the limit of quantitative determination of copper in the form of MLC were calculated [30]. In tab. 3 shows the analytical characteristics of some complexes of copper with L and An.

The linearity range of the calibration dependence for chloroform extracts of the complexes is maintained in the range of concentrations of copper 0.04-3.6 μg/ml (Table III). The equation of the calibration dependence for indicating the spectrophotometric signal is given in Table. III. Based on the equations of the calibration curves, the limit of photometric detection and the limit of quantitative determination of copper in the form of ionic associates were calculated.

**TABLE III.** Analytical characteristics for the Cu-L-Am triple complexes

| Value | Cu-DHTP-An | Cu-HTP-An | Cu-HCTP- An |
|---|---|---|---|
| A=*a*C+*b* | *y* =0.086+0.0066*x* | *y* = 0.062+0.0073*x* | *y* = 0.093+0.0070*x* |
| The formation of calibration curves (mg ml$^{-1}$) | 0,06-3,2 | 0,04-3,5 | 0,04-3,6 |
| Sandell's sensitivity (ng·cm$^{-2}$) | 9,2 | 8,70 | 8,50 |
| Limit of quantification: ng ·m$^{L-1}$ | 28,0 | 26,5 | 23,4 |
| Limit of detection: ng ·mL | 2,41 | 2,31 | 2,19 |

The dependencies found by us are consistent with the literature data indicating that with an increase in pK1 complexing agents, the strength of the complex compounds formed by them and the pH of complexation increase.

In tab. 4 shows the data, allowing to compare the analytical characteristics of methods for the determination of copper with some already known [6,31-33] methods. It can be seen that $H_2L$ has advantages over other reagents: the maximum absorption of light is mixed into the long-wavelength region of the spectrum [6.32,], the molar absorption coefficient is much higher than the molar absorption coefficients of other complexes [6, 32, 31], the shift of the reaction pH into a more acidic region [33], which increased selectivity.

**TABLE IV: Comparative characteristics of methods for the determination of copper (II) with already known reagents.**

| Reagent | pH (solvent) | λ, nm | Δ*λ*, нм | *ε*·10$^{-4}$ | Beer's law range (μg·ml$^{-1}$) | Ref. |
|---|---|---|---|---|---|---|
| (AnH)$_2$[Cu(DHTP)$_2$(An)$_2$] | 3.8-6.5(CHCl$_3$) | 620 | 339 | 4.3 | 0,2-20 | *Proposed method* |
| (AnH)$_2$[Cu(HTP)$_2$(An)$_2$] | 3.5-6.0(CHCl$_3$) | 630 | 352 | 4.2 | 0,2-20 | |
| (AnH)$_2$[Cu(HCTP)$_2$(An)$_2$] | 2.6-5.3(CHCl$_3$) | 650 | 367 | 4.0 | 0,2-13 | |
| (DAnH)$_2$[Cu(HCTP)$_2$(DAn)$_2$] | 2.7-5.4(CHCl$_3$) | 648 | 365 | 4.1 | 0,2-15 | |
| (AnH)$_2$[Cu(HBTP)$_2$(An)$_2$] | 2.4-4.8(CHCl$_3$) | 655 | | 3.8 | 0,2-15 | |
| (AnH)$_2$[Cu(HİTP)$_2$(An)$_2$] | 2.1-4.3(CHCl$_3$) | 660 | | 3.6 | 0,2-12 | |
| Picramine M | 0.7 M HCl | 530 | - | 1,67 | 1,0-70 | [31] |
| Picraminepsilon | 0,1-0,2M HCl | 550 | - | 0,26 | - | [32] |
| Thioxamide + pyridine | 4,5-5,0 | 380 | - | 1,75 | - | [32] |
| HSNFAP*+DPG* | 2,0 | 431 | 61 | 2,87 | 0,12-2,56 | [6] |
| HNA*+ aniline | 3,6-5,4 (CHCl$_3$) | 660 | 300 | 2,86 | 0,2-20 | [33] |

HSNFAP*-3- [2-hydroxy-3-sulfo-5-nitrofanilazo] pentadion-2,4; DPG- diphenylguanidine; HNA *-1-bromo-2-hydroxy-3-naphthoic acid*

### G. Influence of foreign ions.

To assess the applicability of the MLC for the separation and determination of copper, the interfering influence of extraneous ions has been studied. The selectivity of the spectrophotometric determination of copper in the form of the complexes studied is presented in Table. 5. It is established that large quantities of alkaline, alkaline-earth elements, REE, $F^-$, $Cl^-$, $Br^-$, $SO_4^{2-}$, $SO_3^{2-}$, $NO_2^-$, $NO_3^-$ and $C_2O_4$ do not interfere with the determination of copper.

Citrates and tartrates, $J^-$, $CN^-$, $S_2O_3^{2-}$, thiourea interfere. The interfering effects of Fe (III) were eliminated with oxalic acid; Ti (IV) is sodium fluoride or tyrone; Hg (II) -sulfite ion; Nb (V) and Ta (V) are oxalic acid, and Mo (VI) and W (VI) are sodium fluoride and oxalic acid. When using a 1% solution of ascorbic acid, Mn (VII), V (IV), Nb (V), Cr (VI), Mo (VI) and Fe (III) do not interfere with the determination. When using 0.01 M solution of oxalic acid, V (IV), Nb (V), Ta (V), Cr (III), Mo (VI), W (VI) and Fe (III) do not interfere with the determination.

**TABLE V: The influence of extraneous ions on the determination of copper with DHTP and An. *n* = 6, *P* = 0.95 (30 μg Cu (II) taken)**

| Ion | Molar Excess of the Ion | Masking reagent | Found, μg | RSD, % |
|---|---|---|---|---|
| Co(II) | 50 | | 30,0 | 0,021 |
| Ni(II) | 50 | | 29,8 | 0,023 |
| Fe(II) | 200 | | 29,8 | 0,037 |
| Cd(II) | 200 | | 29,6 | 0,045 |
| Al(III) | 180 | | 30,0 | 0,027 |
| Fe(III) | 60 | Oxalic acid | 30,2 | 0,046 |
| Zr(IV) | 50 | | 29,8 | 0,031 |
| W(VI) | 25 | Oxalic acid | 29,6 | 0,053 |
| Hg(II) | 40 | | 30,2 | 0,055 |
| Ti(IV) | 30 | Tyrone | 29,6 | 0,038 |
| V(IV) | 20 | Tyrone | 29,6 | 0,033 |
| Mo(VI) | 10 | Sodium fluoride | 30,4 | 0,048 |
| Cr(III) | 120 | | 29,8 | 0,040 |
| Nb(V) | 50 | Sodium fluoride | 30,1 | 0,057 |
| Ta(V) | 50 | Sodium fluoride | 30,1 | 0,052 |
| $UO_2^{2-}$ | 50 | | 29,2 | 0,041 |

## IV. Analytical applications

The developed technique is applied to the determination of copper (II) in standard samples of alloys.

The results of the experiments are presented in table 6. As can be seen from the table, the results of determination of copper in the alloys indicate sufficient reliability of the proposed methods.

**TABLE VI:** The results of the determination of copper in alloys (*n* = 5; *p* = 0,95)

| Анализируемый образец | Cu content on the passport, % | Found Cu, % | S | $S_r$ | The correctness of the technique, ΔC/C*100, % | $\bar{X} \pm \frac{t_P S}{\sqrt{n}}$ |
|---|---|---|---|---|---|---|
| Alloy A 95 - 4 | 0,010 | 0,0097 | 0,0064 | 0,030 | 3,00 | 0,0097±0,004 |
| Alloy A 95 - 5 | 0,015 | 0,0148 | 0,0045 | 0,021 | 1,33 | 0,0148±0,003 |
| Alloy A 195-3 | 0,140 | 0,1371 | 0,0050 | 0,023 | 2,07 | 0,1371±0,003 |
| Alloy A 195-4 | 0,110 | 0,1099 | 0,0044 | 0,025 | 0,91 | 0,1099±0,002 |
| Alloy A 195-5 | 0,040 | 0,0408 | 0,0038 | 0,022 | 2,00 | 0,0413±0,003 |

## 5. CONCLUSION

1. The purpose of this work is to systematically study the conditions for the interaction of copper with 2-hydroxythiophenol (HTP) and its derivatives {2,5-dihydroxythiophenol (DHTP), 2-hydroxy-5-chlorothiophenol (HCTP), 2-hydroxy-5-bromothiophenol (HBTP) and 2-hydroxy-5-iodothiophenol (HITP)} in the presence of Am. From Am, aniline (An) and N, N-dimethylaniline (DAn) were used.

2. Non-aqueous solvents were used to extract MLC: chloroform, 1,2-dichloroethane, carbon tetrachloride, benzene, chlorobenzene, toluene, iso - butanol, iso-pentanol and diethyl ether. The extractability of the complexes was estimated by the distribution coefficient and the degree of extraction. Chloroform, dichloroethane and carbon tetrachloride turned out to be the best ex- agents. With a single extraction with chloroform, 97.8-98.4% of copper is recovered as MLC. Further studies were performed with chloroform.

3. The study of the dependence of complexation on pH showed that the optimum range of acidity at which the optical density is maximum and constant is pH 2.3-8.0.

4. Copper MLC is formed in the presence of a large excess of complexing agents. The optimal condition for the formation and extraction of these compounds is (0.8-1.0) × $10^{-3}$ M, the concentration of L and (1.0-1.2) $10^{-3}$ M - Am. The linearity range of the calibration dependence for chloroform extracts of the complexes is maintained in the range of concentrations of copper 0.04-3.6 μg/ml.

5. Copper MLC with L and Am is stable in aqueous and organic solvents and does not decompose for three days, and after extraction it is more than a month. Maximum optical density is achieved within 5 minutes.

6. The maximum analytical signal with the complexation of copper with L and Am is observed at 620–650 nm. L max absorb at 278-283 nm. When complexing occurs, a bathochromic shift of the maximum absorption of absorption at 339-367 nm is

observed. The reaction contrast is high: the initial reagents are almost non-colored, and the complexes are bluish-green.Molar absorption coefficients are (4.1–4.3) × $10^4$.

7. In the interaction of Cu (II) with L and Am, complexes with the composition Cu (II):L:Am = 1:2:4. By the method of Nazarenko it was established that the complexing form of copper is $Cu^{2+}$. In this case, the number of protons displaced by him from one L molecule turned out to be 2.

8. It was established that a large amount of alkaline, alkaline earth elements, REE, $F^-$, $Cl^-$, $Br^-$, $SO_4^{2-}$, $SO_3^{2}$-, $NO_2^-$, $NO_3^-$ and $C_2O_4^{2-}$ does not affect the determination of copper. Citrates and tartrates, $J^-$, $CN^-$, $S_2O_3^{2-}$, thiourea interfere. The disturbing effects of Fe (III) were eliminated with oxalic acid; Ti (IV) is sodium fluoride or tirone; Hg (II) sulfite ion; Nb (V) and Ta (V) are oxalic acid, and Mo (VI) and W (VI) are sodium fluoride and oxalic acid. When using a 1% solution of ascorbic acid, Mn (VII), V (IV), Nb (V), Cr (VI), Mo (VI) and Fe (III) do not interfere with the determination. When using a 0.01 M solution of oxalic acid V (IV), Nb (V), Ta (V), Cr (III), Mo (VI), W (VI) and Fe (III) do not interfere with the determination.

9. The developed method is used to determine copper (II) in standard samples of alloys. The results of determination of copper in alloys indicate sufficient reliability of the proposed methods.

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