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Chemistry

2,6-DIMETHYL-4-MERCAPTOQUINOLINE AS A NEW ANALYTICAL REAGENT FOR SPECTROPHOTOMETRIC DETERMINATION OF COPPER (II)

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A new efficient spectrophotometric method has been elaborated for determination of copper (II) ions using 2,6-dimethyl-4-mercaptoquinoline (R) as the analytical reagent. It has been established that the molar ratio between the reactants is Cu(II) : R = 1 : 2. The conditions for copper (II) complexation, including the effects of pH, reagent and copper (II) concentrations, and reaction duration have been studied. It has been shown that resulting complex possesses intense absorption in the visible region at a wavelength of 440 *nm*.

It has been also shown that the system obeys Bouguer–Lambert–Beer law over a concentration range of 0.032–0.8 *mg*/25 *mL* (1.28–32 *μg*/*mL*). The average value for molar absorption coefficient is 9460. The influence of extraneous ions has been studied. The method has been successfully applied for copper determination in a standard bronze sample.

The proposed reagent was shown to possess high sensitivity and selectivity compared to well-known sulfur containing reagents.

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***Keywords*:** copper (II), spectrophotometry, mercaptoquinoline, analytical reagent, complex formation.

Introduction. The determination of copper (II) in natural, technological and biological objects remains one of the actual problems of the analytical chemistry. This is due to its important biological role and the toxicity at higher concentrations [1, 2].

Highly-sensitive instrumental methods, such as atomic absorption spectrometry and inductively coupled plasma spectrometry, are widely used for quantitative analysis of copper [1, 3].

However, spectrophotometric methods retain an important place owing to their simplicity, availability and possibility to realize the analysis procedure without the use of complex scientific equipment [2].

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The choice of organic analytical reagent is a key factor for improving sensitivity and selectivity of spectrophotometric determinations. The most prospective are compounds containing nitrogen and sulfur donor atoms, which are able to form stable complexes with copper (II) ions [3, 4]. According to the concept of hard and soft acids and bases, copper (II) ions show a high affinity towards soft donor atoms of sulfur and it causes high efficiency of sulfur-containing ligands [4].

In recent decades, reagents of the thiosemicarbazone family are widely used for spectrophotometric determination of copper (II) [5–7]. It has been estimated that these compounds form intensively colored complexes obeying Bouguer–Lambert–Beer law within a wide range of copper (II) concentrations [5, 6]. The possibility of using such compounds in analyses of real objects, including food and biological systems, has been confirmed in later studies [7]. Nevertheless, such reagents cannot provide sufficient selectivity in the presence of concomitant metal ions.

An alternative approach is the use of sulfur-containing heterocyclic compounds, including thiodiazole and other S-donor ligands [8, 9]. These reagents are able to form stable chelate complexes with copper (II) ions, and it provides to reach lower detection limits, particularly when using preliminary concentration methods [9].

Current studies (2020–2025 years) are directed to the creation of new chromogenic systems with improved analytical characteristics. Particularly, it has been shown, that the introduction of thiol (mercapto-) group to the organic ligand molecule promotes the strengthening of complexation with copper (II) ions and rises the sensitivity of determination [10]. Such compounds are characterized by high molar absorption coefficient and pronounced spectral changes when interact with copper (II) ions.

In recent years, quinoline derivatives, containing mercapto-group, which forms efficient N,S-donor systems have attracted special interest. Owing to the presence of aromatic π-conjugated electronic system and donor systems, such compounds are able to form stable intensively colored complexes with copper (II) ions. A sensor based on a mercapto-quinoline fragment has been described in [8], and possesses high sensitivity copper determination using spectrophotometric and fluorimetric methods.

It is necessary to mark in addition the development of applied spectrophotometric analytical methods during the last years. So, new methods are proposed for copper (II) determination in aqueous systems and technological solutions, differing by their good reproducibility and availability for practical application [9, 11]. New combined analytical systems have also been elaborated, including copper (II) complexes with other organic reagents (for example, bathocuproine), used in indirect spectrophotometric analytical methods [12].

Despite the large number of proposed reagents, the use of simple derivatives of mercaptoquinoline for the spectrophotometric determination of copper has been not studied enough. The literature data witness high potential of such compounds as sensitive and selective reagents [8, 10], however, there are practically no systematic studies in this direction.

Thus, the synthesis and investigation of 2,6-dimethyl-4-mercaptoquinoline an analytical reagent for the spectrophotometric determination of copper (II) is an actual problem directed to the creation of new efficient analytical methods.

Materials and Methods.

Reagents and Solutions. Copper (II) solutions were prepared by solving of recrystallized $CuSO_4 \cdot 5H_2O$ in distilled water. Working solutions were prepared by diluting the initial solution.

2,6-Dimethyl-4-mercaptoquinoline (R) was synthesized using a well-known procedure at the Department of Organic Chemistry at Yerevan State University [13], and the working solution was prepared by dissolving a weighed sample in ethanol. The acidity was regulated using diluted solutions of sulfuric and hydrochloric acids.

Methods. The absorbance values of the solutions were measured using M550 Double Beam Scanning UV spectrophotometer in 1 *cm* length quartz cuvettes.

The reagent solution and acid were added to the Cu(II) aliquot solution. The volume was adjusted to the mark by distilled water. After 5 *min* the absorbanse was measured at 440 *nm* compared to the blank.

Results and Discussion. It was established by qualitative reactions that when adding R solution to the copper (II) solution, the whole solution turned red, indicating a chemical reaction with the formation of a new chemical compound.

To confirm this, the following studies were carried out: obtaining spectra for all components, determining optimal reaction conditions (concentration of R, optimal pH range, concentration limitations when absorbance is submissive Bouguer–Lambert–Beer law, the molar ratio between Cu(II) an R in the resulting complex, and the influence of accompanying elements).

The UV-Vis spectrum of the complex obtained is presented in Fig. 1.

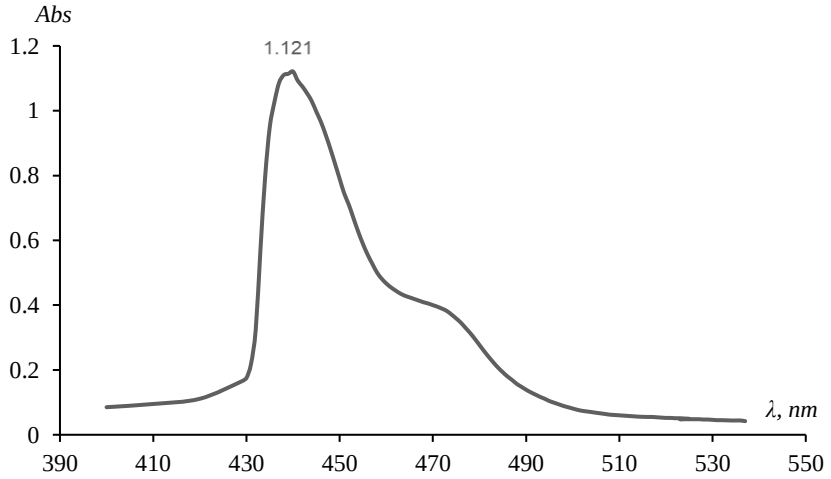

Fig. 1. UV-Vis spectrum of the obtained colored complex:
1.0 *mL* of $5 \cdot 10^{-3}$ *M* Cu^{2+}; 3.0 *mL* of $5 \cdot 10^{-3}$ *M* R; *l* = 1 *cm*; *V* = 25 *mL*.

In the stage, the optimal concentration of the reagent was determined, at which maximal and stable values of absorbance were reached. The absorbance was measured at 440 *nm*. The data obtained are presented in Fig. 2.

One can see from Fig. 2, that constant and maximal values are obtained using at least a 2.5-fold excess of the reagent compared to copper (II). Based on this, a threefold excess for all subsequent experiments was used.

To determine the optimal pH range, the series with constant concentration of Cu(II) and reagent were prepared: 0.5 *mL* of $5\cdot10^{-3}$ *M* solution of Cu(II) and 1.5 *mL* of $5\cdot10^{-3}$ *M* solution of R. By adding different amounts of sulfuric and nitric acids we change the pH values in solutions. The dependence of absorbance on the sulfuric acid concentration is presented in Fig. 3. One can see that the absorbance of the resulting complex in the presence of sulfuric acid is constant up to 1.5 *M*. In more concentrated acidic solutions de-colorization takes place.

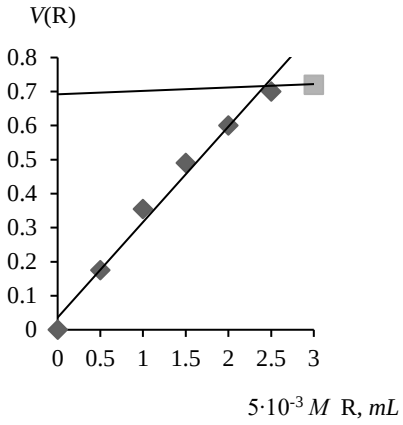

Fig. 2. Determination of the optimal concentration of R 0.5 *mL* of $5\cdot10^{-3}$*M* Cu (II), [R] = $5\cdot10^{-3}$*M*.

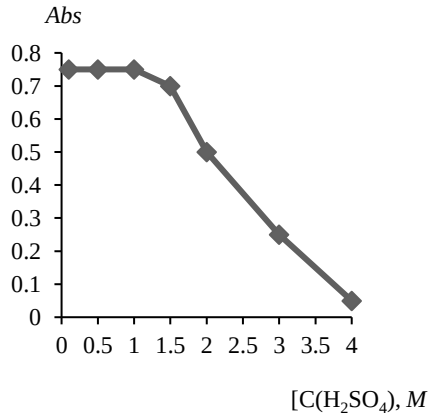

Fig. 3. Determination of the optimal concentration of sulfuric acid.

It is known from literature that the color of compounds develops and reaches its maximum value immediately after adding the reagent. There are also cases where for developing the color a certain time interval is required. In our case, a colored complex was obtained and its absorbance was measured immediately after formation and within different time intervals. It was established that color develops and reaches its maximum value immediately and remains constant during 24 *h* after preparation. It allows measurements to be taken immediately and over a long period of time.

We determine the copper (II) concentration limits that obeys the Bouguer–Lambert–Beer law.

Data of for the determination of complex composition using the isomolar series method

$1\cdot10^{-3}$ *M* Cu^{2+}, *mL*	1	2	3	4	5	6	7	8	9
$1\cdot10^{-3}$ *M* R, *mL*	9	8	7	6	5	4	3	2	1
Abs	0.29	0.62	0.61	0.53	0.41	0.33	0.23	0.15	0.1

$5\cdot10^{-3}$ *M* Cu^{2+}, *mL*	1	2	3	4	5	6	7	8	9
5.10^{-3} *M* R, *mL*	9	8	7	6	5	4	3	2	1
Abs	0.19	0.38	0.38	0.31	0.23	0.17	0.1	0.05	0.02

The concentration range was 0.032–0.8 *mg*/25 *mL* (1.28–32 $\mu g/mL$). The average value for molar absorption coefficient is 9460.

The composition of the resulting complex of copper (II) with reagent was studied using the well-known isomolar series method. It is necessary to provide the following conditions: $V(Cu) + V(R) = V = \text{const}$ and $C(Cu) + C(R) = C = \text{const}$ [14]. The experimental data for two different concentrations of copper (II) and R are presented in the Table and Fig. 5.

The composition of the complex corresponds to copper (II) : R = 1 : 2.

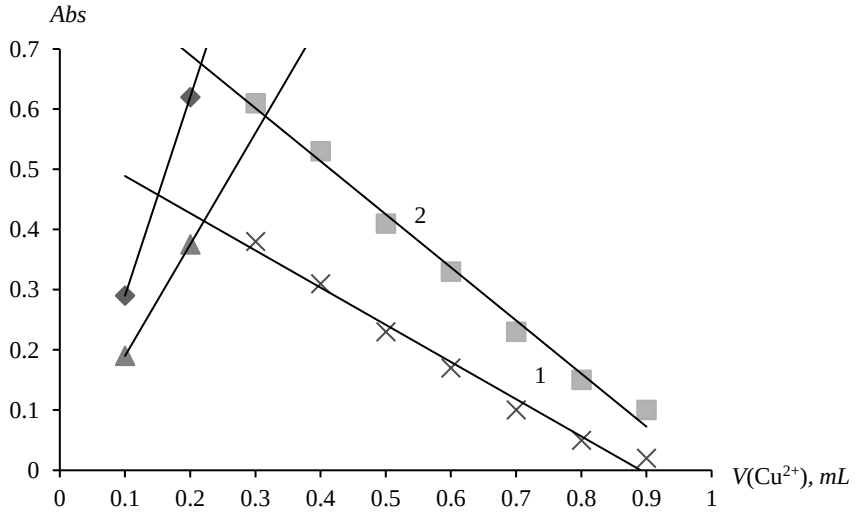

Fig. 4. Determination of the composition of resulting complex by means of iso-molar series method: 1) $[Cu^{2+}] = [R] = 1 \cdot 10^{-3}$ *M*; 2) $[Cu^{2+}] = [R] = 5 \cdot 10^{-3}$ *M*.

It is necessary to mention, that the study of complex composition by means of "saturation method" also fix copper (II) : R = 1 : 2 ratio. So, the reaction of Cu(II) with 2,6-dimethyl-4-mercaptoquinoline may be presented as follows:

$$Cu^{2+} + 2HR = CuR_2 + 2H^+.$$

The evaluation of the influence of different ions on copper (II) determination showed that alkaline and alkaline-earth ions do not interfere, whereas some transition metal ions (Fe^{3+}, Co^{2+}, Ni^{2+}) interfere it. To avoid such interference, one need to use different masking agents, such as EDTA, fluoride or citrate ions.

2,6-Dimethyl-4-mercaptoquinoline was used for determination of copper in bronze standard sample № 831, in which copper content was 65.55%.

Analysis Procedure. 5 *mL* of strong nitric acid was added to the two bronze samples 0.1 *g* each. After dissolving samples, distilled water was added and the solutions were left for several hours. After one day, the solutions were filtered through twin filter. The filtrates were undergone de-nitration, using strong sulfuric acid until SO_3 vapors were released, then the process was continued up to obtaining wet salts. Latest was dissolved in distilled water and diluted up to 100 *mL* in a volumetric flask.

Then, three parallel samples (1 *mL* and 2 *mL* each) were placed in 25 *mL* flasks. After this 10 *mL* of $5 \cdot 10^{-3}$ *M* reagent solution was added, diluted by distilled water up to mark, and the absorbance was then measured at 440 *nm*.

The copper (II) content was determined by means of calibration curve.

The corresponding calculations showed that copper content in the bronze standard sample was 66.0%. The absolute error of the determination is +0.45%, and the relative error is +0.69%.

The results obtained confirm that 2,6-dimethyl-4-mercaptoquinoline forms a stable complex with copper (II) ions, characterized by highly intensive absorption at 440 *nm*, and can be used as a new, efficient reagent for the spectrophotometric determination of copper. The use of masking methods may lower the influence of extraneous ions and increase selectivity of the determination.

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2,6-ԴԻՄԵԹԻԼ-4-ՄԵՐԿԱՊՏՈՔԻՆՈԼԻՆԸ ՈՐՊԵՍ ՆՈՐ ԱՆԱԼԻՏԻԿԱԿԱՆ ՌԵԱԳԵՆՏ ՊՂԻՆՁ(II)-Ի ՍՊԵԿՏՐԱԼՈՒՍԱՉԱՓԱԿԱՆ ՈՐՈՇՄԱՆ ՀԱՄԱՐ

2,6-Դիմեթիլ-4-մերկապտոքինոլինը (R) օգտագործվել է որպես նոր անալիտիկական ռեագենտ պղնձ (II)-ի սպեկտրալուսաչափական որոշման համար: Պարզվել է, որ առաջացող կոմպլեքսն ունի կլանում 440 *նմ* ալիքի երկարության տակ: Մոլային հարաբերակցությունների և իզոմոլային շարքերի եղանակներով հաստատվել է, որ փոխազդող բաղադրիչների մոլային հարաբերակցությունը՝ պղինձ (II) : R = 1 : 2 է:

Ուսումնասիրվել են պղինձ (II)-ի կոմպլեքսագոյացման պայմանները. ռեագենտի անհրաժեշտ կոնցենտրացիան, pH-ի ազդեցությունը, կոմպլեքսի գույնի զարգացումը ժամանակի մեջ: Ցույց է տրվել, որ համակարգը ենթարկվում է Բուգեր–Լամբերտ–Բերի օրենքին կոնցենտրացիայի 0.032–0.8 *մգ*/25 *մլ* (1.28–32 *մկգ/մլ*) տիրույթում: Կլանման մոլային գործակցի միջին արժեքը 9460 է:

Ուսումնասիրվել է խանգարիչ իոնների ազդեցությունը: Ռեագենտը հաջողությամբ կիրառվել է անագապղնձի (բրոնզի) ստանդարտ նմուշում պղնձի որոշման համար:

Ապացուցվել է, որ առաջարկվող ռեագենտն օժտված է բարձր զգայունությամբ և ընտրողականությամբ՝ համեմատած ծծումբ պարունակող հայտնի ռեագենտների հետ:

Г. Г. ДАРБИНЯН, И. А. АЛЕКСАНЯН, А. Г. ХАЧАТРЯН

2,6-ДИМЕТИЛ-4-МЕРКАПТОХИНОЛИН КАК НОВЫЙ АНАЛИТИЧЕСКИЙ РЕАГЕНТ ДЛЯ СПЕКТРОФОТОМЕТРИЧЕСКОГО ОПРЕДЕЛЕНИЯ МЕДИ (II)

Разработан новый спектрофотометрический метод определения меди (II) с использованием 2,6-диметил-4-меркаптохинолина (R) в качестве аналитического реагента. Методами мольных отношений и изомолярных серий установлено мольное соотношение реагирующих компонентов медь (II) : R = 1 : 2. Изучены условия комплексообразования меди (II) с реагентом, включая влияние pH, концентрации реагента и времени реакции.

Установлено, что образующийся комплекс характеризуется интенсивным поглощением в видимой области спектра с максимумом при 440 *нм*. Показано, что система подчиняется закону Бугера–Ламберта–Бера в диапазоне концентраций 0,032–0,8 *мг*/25 *мл* (1,28–32 *мкг/мл*). Среднее значение молярного коэффициента поглощения равно 9460. Исследовано влияние посторонних ионов. Метод успешно применен для определения меди в стандартном образце бронзы. Показано, что предложенный реагент обладает высокой чувствительностью и селективностью по сравнению с известными серосодержащими реагентами.