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NEW SIMPLE METHOD FOR THE DETERMINATION OF TRACE LEVEL COPPER (II) USING 1- [2- (ALLYLAMINO) -1-METHYLETHYL] THIOUREA IN PRESENCE OF HYDROFOB AMINES BY MOLECULAR ABSORPTION SPECTRAL METHOD IN THE UV AND VISIBLE REGION

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Cu(II) with 1- [2- (allylamino) -1-methylethyl] thiourea the rapid reacts to form orange complex and also it to form to form brownish complexes in presence of the phenanthroline (Phen) and α,α' - dipyridine (α,α' -dip). The absorption spectra of the Cu(II) - AMTIC system is a curve with the maximum absorbance at 415 nm and molar absorption coefficient of $1.95 \cdot 10^4 \text{ l mol}^{-1} \text{ cm}^{-1}$. The absorption spectra of the Cu(II)- AMTIC- Phen and Cu(II) -AMTIC - α,α' -dip systems is a curve with the maximum absorbances at 437 nm and 443 nm and molar absorption coefficients of $2.94 \cdot 10^4 \text{ l mol}^{-1} \text{ cm}^{-1}$ and $2.81 \cdot 10^4 \text{ l mol}^{-1} \text{ cm}^{-1}$, respectively. The absorbance was linear for 0.25–2.07 mkg ml^{-1} of Cu(II) in the Cu(II)- AMTIC system and 0.12 –2.56 mkg ml^{-1} and 0.18–2.45 mkg ml^{-1} of Cu(II) in the Cu(II)-AMTIC- Phen and Cu(II)-AMTIC- α,α' -dipsystems, respectively. The proposed methods was successfully used in the determination of Cu(II) in several synthetic mixtures. The relative standard deviation ($n = 5$) was 0%–2.0%, for Cu(II), indicating that this methods are highly precise and reproducible. The results obtained agree well with synthetic mixture samples analyzed by inductively coupled plasma optical emission spectrometry (ICP-OES).

Keywords: copper, 1- [2- (allylamino) -1-methylethyl] thiocarbamide, phenanthroline (Phen) and α,α' - dipyridine.

INTRODUCTION

A copper is used as a conductor of heat and electricity, as a building material and as a constituent of various metal alloys such as in jewelry, cupronickel used to make marine hardware and coins and constantan used in strain gauges and thermocouples for temperature measurement. Although copper (II) ions are extremely important for several biological processes, their levels in some. While trace copper ions (II) promote rancidity and off flavors in nutrients, copper accumulation in the liver is a characteristics of Wilson's disease, producing neurological and psychiatric defects situations are indications of a problem or disease in many living systems or environments. Therefore, it is clear that in the arsenal of analysts there must be simple and rapid methods to determine copper in a wide concentration range with the highest possible sensitivity accuracy[1].

A simple sensitive and selective methods for determination of trace copper has been required. Sophisticated techniques, such as inductively coupled plasma mass spectrometry (ICP-MS) [2-4], inductively coupled plasma atomic emission spectrometry (ICP-AES) [5-6], inductively coupled plasma optical emission

spectrometry (ICP-OES) [7-8], atomic absorption spectrophotometry (AAS) [9-10], electrochemical [11-13] and spectrophotometry[14-15] have widely been applied to the determination of copper in various samples. Some factors such as initial cost of instrument, technical know-how, consumable and costly maintenance of technique restrict the wider applicability of spectrophotometric methods, particularly in laboratories with limited budget in developing countries and for field work. In the literatures wide variety of spectrophotometric methods for determination of Cu(II) have been reported, each chromogenic system has its advantages and disadvantages with respect to sensitivity, selectivity and convenience [16-22]. Many reagents used in photometric methods for the determination of Cu(II) contain sulfur in the molecule. Therefore, the synthesis of new sulfur content of organic reagents, the study of their complexation with Cu(II) is an urgent task. In this work, a reagent 1- [2- (allylamino) -1-methylethyl] thiocarbamide (AMTIC) was synthesized according to the method of and a color reaction of AMTIC with Cu(II) and in the presence of hydrofob amines - phenanthroline (Phen) and α,α' - dipyridine was carefully studied. The aim of present study is to develop a simpler spectrophotometric method for the trace determination of Cu(II) with AMTIC and in the presence of hydrofob amines - phenanthroline and α,α' - dipyridine solutions.

EXPERIMENTAL PART

The absorbance of solutions was measured with a Perkin Elmer (United States) (Model: Lambda-40) double-beam UV/VIS spectrophotometer and with a KFK-3 photoelectrocolorimeter (Russia), with 1 cm matched quartz cells. The pH values of solutions was controlled on the ionomer I-121 with glass electrode customized by standart bufer solutions.

A Perkin Elmer (United States) (Model: Optima-2100 DV) Inductively Coupled Plasma Optical Emission Spectrometer (ICP-OES) was used for comparing the results.

Chemicals and reagents

All chemicals solvents used were of analytical reagent grade or the highest purity available. Doubly distilled de-ionized water was used throughout. Glass vessels were cleaned by soaking in acidified solutions of KMnO_4 or $\text{K}_2\text{Cr}_2\text{O}_7$, followed by washing with concentrated HNO_3 and rinsed several times with deionized water.

Copper (II) standard solutions (10^{-2} M)

A 10^{-2} M 100 ml stock solution of copper (II) was prepared by dissolving 0.06355 g of copper (purity 99.98%) in nitric acid by warming, evaporating the solution to dryness, dissolving the residue in hydrochloric acid, evaporating the solution to half its volume, cooling and diluting with water to 100 ml in calibrated flask . Working solutions were prepared by appropriate dilution of standard solution with water.

1- [2- (allylamino) -1-methylethyl] thiocarbamide

The 1- [2- (allylamino) -1-methylethyl] thiocarbamide reagent was synthesized according to the known method . The NMR spectroscopic data of 1- [2- (allylamino) -1-methylethyl] thiocarbamide: ^1H NMR spektrum:(CCL_4 , δ .m.h) 9.48₃(2H,NH₂), 7.21d(1H, NH), 3.22m(2H,CH₂), 2.01m (1H,NH), 2.64-2.89 d(2H,CH₂), 1.50-3.03 m (1H,CH), 1.10 s (3H,CH₃), 1.10 s (3H₁,CH₃), 5.15 m (1H-C-N- sis), 5.17m (1H₁-C-N-trans), 5.83 m (1H-C-N). ^{13}C NMR Spektrum: 186, 52.0, 53.7, 55.5, 116.2, 134.2, 184.7.

The solution of 1- [2- (allylamino) -1-methylethyl] thiocarbamide reagent was prepared by dissolving the requisite amount of AMTIC in a known volume of ethanol. More dilute solution of the reagent was prepared as required.

Phenanthroline (Phen) and α,α' - dipyridine (α,α' - dip)

$1 \cdot 10^{-2}$ M solutions of phenanthroline and α,α' - dipyridine was preparing by dissolving the requisite amounts of these substances in distilled water and ethanol(1:1).

Aqueous ammonia solution

A 100 ml solution of aqueous ammonia was prepared by diluting 10 ml of concentrated NH_3 (28%–30%) ACS grade with distilled water. The solution was stored in a glass bottle.

EDTA solution

A 100 ml stock solution of EDTA (0.1% w/v) was prepared by dissolving 128 mg of ethylenediaminetetraacetic acid, disodium salt dehydrate in 100 ml distilled water.

Other solutions

Solutions of a large number of inorganic ions and complexing agents were prepared from their grade, or equivalent grade, water soluble salts.

RESULTS AND DISCUSSION

Copper (II) ion with 1- [2- (allylamino) -1-methylethyl] thiocarbamide the rapid reacts to form orange complex and also it to form brownish complexes in presence of phenanthroline and α,α' - dipyridine solutions.

Absorption spectra

The absorption spectra of the Cu(II)- AMTIC is a curve with the maximum absorbance at 415 nm and an average molar absorption coefficient of $1.95 \cdot 10^4 \text{ l mol}^{-1} \text{ cm}^{-1}$ in aqueous media. The absorption spectra of the Cu(II)-AMTIC- Phen and Cu(II)-AMTIC- α,α' -dipsystems is a curve with the maximum absorbances at 437 nm and 443 nm and average molar absorption coefficients of $2.94 \cdot 10^4 \text{ l mol}^{-1} \text{ cm}^{-1}$ and $2.81 \cdot 10^4 \text{ l mol}^{-1} \text{ cm}^{-1}$ in micellar media, respectively (fig. 1).

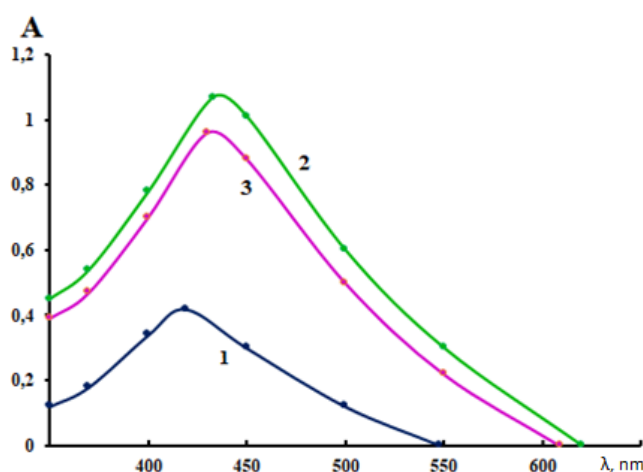


Fig.1. Absorption spectra of Cu(II)- AMTIC(1), Cu(II)-AMTIC- α,α' -dip (2) and Cu(II)-AMTIC- Phen(3).

Effect of acidity. Effect of the various pH 0-12 studied, pH 4,9,0-6,2 found to be the best acid for the Cu(II) AMTIC system and pH 4,2-5,6 found to be the best acid for the Cu(II)AMTIC- Phen and Cu(II) AMTIC- α,α' -dip systems at room temperature $(25 \pm 5)^\circ\text{C}$. The absorbance of the reagent solution and the all systems depends on the medium pH; therefore, the absorption spectra are studied relative to a blank experiment against the background of control experiment (AMTIC and AMTIC +X), which was prepared in the same conditions (fig. 2).

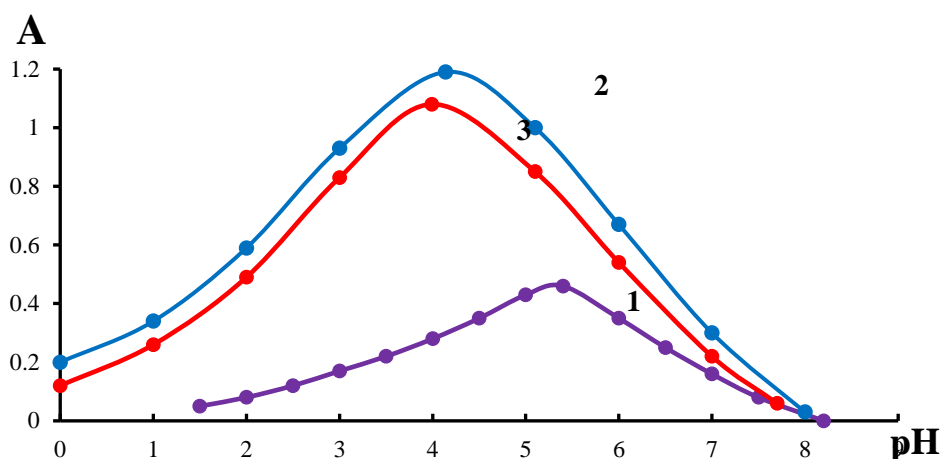


Fig.2. Effect of acidity . Cu(II)- AMTIC(1), Cu(II)-AMTIC- α,α' -dip (2) and Cu(II)-AMTIC- Phen(3).

Effect of time. The reaction is fast. Constant maximum absorbance was obtained after 10 min for Cu(II)-AMTIC system in aqueous media and 5 min for Cu(II)-AMTIC- Phen and Cu(II)-AMTIC- α,α' -dipsystems in micellar media, respectively.

Effect of temperature. The absorbance at different temperatures, $0-80^\circ\text{C}$, of a 25 ml solution of all systems was measured according to the standard procedure. The absorbance was found to be strictly unaltered through-out the temperature range of $10-40^\circ\text{C}$. Therefore, all measurements were performed at room temperature $(25 \pm 5)^\circ\text{C}$.

Stoichiometry. The component ratio in the complexes was found using the isomolar series method, the relative yield method by Starik and Barbanell and the equilibrium shift method. All the methods showed that the component ratio were 1:2 in the Cu(II)- AMTIC system and 1:2:1 in the Cu(II)- AMTIC-Phen and Cu(II)-AMTIC- α,α' -dipsystems. The number of protons displaced upon complexation was determined by the Astakhovs method, and the indicated component ratio in the complexes was confirmed.

Effect of the reagent and phenanthroline and α,α' - dipyridine concentration. Different molar excesses of AMTIC and phenanthroline and α,α' - dipyridine were added to a fixed Cu(II) concentration and the absorbance was measured according to the standard procedure. It was observed that a 1 mkg/ml of copper metal (optical path 1 cm in length), the reagent and phenanthroline and α,α' - dipyridine molar ratios produced a constant absorbance of Cu(II)- AMTIC-Phen and Cu(II)-AMTIC- α,α' -dipsystems. For all subsequent measurements, 2 ml of $2 \cdot 10^{-4}$ M AMTIC reagent and 4ml of $2 \cdot 10^{-4}$ M phenanthroline and α,α' - dipyridine was added.

Analytical performance of the methods

Calibration curve

The effect of metal concentration was studied over 0.01–100 mg ml⁻¹, distributed in four different sets (0.01–0.1, 0.1–1, 1–10 mg ml⁻¹) for convenience of the measurement. The absorbance was linear for 0.25 –2.07 mg ml⁻¹ of Cu(II) in the Cu(II)- AMTIC system and 0.12–2.56 mg ml⁻¹ and 0.18–2.45 mg ml⁻¹ of Cu(II) in the Cu(II)-AMTIC- Phen and Cu(II)-AMTIC- α,α' -dipsystems, respectively. From the slope of the calibration graph, the average molar absorption coefficient was found to be $1.95 \cdot 10^4$ l mol⁻¹ cm⁻¹ for Cu(II)- AMTIC system and $2.94 \cdot 10^4$ l mol⁻¹ cm⁻¹ and $2.81 \cdot 10^4$ l mol⁻¹ cm⁻¹ in the Cu(II)-AMTIC- Phen and Cu(II)-AMTIC- α,α' -dipsystems, respectively. The selected analytical parameters obtained with the optimization experiments are summarized in table 1.

Table 1
Selected analytical parameters obtained by optimization experiments

Parameters	Studied range	Selected value		
		Cu(II)-AMTIC	Cu(II)-AMTIC- Phen	Cu(II)-AMTIC- α,α' - dip
Wavelength, λ_{\max} (nm)	200-800	415	437	443
Wavelength, λ_{opt} (nm)	-	400	440	440
pH	0 - 12	5-6	4-5	4-5
Time, h	1 - 24h	5 - 10 min	5-6 min.	5-6 min.
Temperature, °C	0 - 80 °C	25 ± 5 °C	25 ± 5 °C	25 ± 5 °C
Cu(II): AMTIC:X	1:10- 10:1	1:2	1:2:1	1:2:1
Molar absorption coefficient, l mol ⁻¹ cm ⁻¹	-	$1.95 \cdot 10^4$	$2.94 \cdot 10^4$	$2.81 \cdot 10^4$
Linear range, mg ml ⁻¹	0.01-10	0.25 –2.07	0.12–2.56	0.18–2.45
lg β	-	10.23	12.56	11.78
Sandell's sensitivity, mg cm ⁻²	0.1 - 10	7	5	5
Relative Standard	0 -5	0 -2	0 -2	0 -2

Precision and accuracy

The precision of the present method was evaluated by determining different

concentrations of Cu(II) (each analyzed at least five times). The relative standard deviation ($n = 5$) was 0%–2.0%, for 0.1–8 mkg of Cu(II), indicating that this method is highly precise and reproducible. The Sandell's sensitivity for Cu(II) were found to be 6 mkg cm^{-2} in Cu(II)- AMTIC system and 5 mkg cm^{-2} , 6 mkg cm^{-2} in the Cu(II)-AMTIC- Phen and Cu(II)-AMTIC- α, α' -dip systems, respectively.

Effect of foreign Ions

The effect of foreign ions on complexation of Cu(II) with AMTIC in the absence and in the presence of third components. It was found that in the presence of third parties the selectivity of the reactions of complex education increases significantly (table 2): these reagents are more selective for spectrophotometric determination of Cu(II) in comparison with the reagents known from literature [12]. The effect of cations, anions and complexing agents on the determination of only 1 mkg ml^{-1} of Cu(II) was studied. The criterion for interference was an absorbance value varying by more than 5% from the expected value for Cu(II) alone. The results are given in table 2.

Table 2

Tolerance limits of foreign ions, tolerance ratio [Species(x)]/Cu (w/w)

Species x	Cu(II) - AMTIC	Cu(II) -AMTIC- Phen	Cu(II) AMTIC- α, α' - dip	[26]
Na(I)	210	285	260	100
K(I)	220	300	270	100
Mg(II)	270	350	330	100
Ca(II)	270	350	330	100
Cr(III)	255	340	340	70
Fe(III)	60	80	80	10
Sr(II)	80	100	95	100
Cd(II)	200	290	280	100
Hg(II)	210	315	300	100
Mo(II)	210	285	280	10
As(III)	260	340	330	100
Zn(II)	235	280	280	100
Ba(II)	200	260	260	10
Al(III)	75	130	125	100
Cs(III)	225	295	290	100
Pb(II)	60	100	100	10
Ni(II)	100	140	120	10
Pb(II)	195	230	215	10
Cl^-	750	70	70	1000
$\text{C}_2\text{O}_4^{2-}$	240	270	270	1000
CH_3COO^-	40	70	70	500
PO_4^{3-}	140	170	160	500
CN^-	110	130	130	500

Applications

The Cu(II)-AMTIC- α,α' -dipsystem was successfully applied to the determination of Cu(II) in a series of synthetic mixtures of various compositions (table 3).

Determination of Cu(II) in synthetic mixtures

Several synthetic mixtures of varying compositions containing Cu(II) and diverse ions of known concentrations were determined by the present method using EDTA as a masking agent; and the results were found to be highly reproducible. The results of synthetic mixtures analyses by the spectrophotometric method were found to be in excellent agreement with those obtained by ICP-OES. The results are given in Table 3. Accurate recoveries were achieved in all solutions.

General Procedure

To synthetic mixtures samples of varying compositions containing 1-2 mkq ml⁻¹ Cu(II) in 25 ml volumetric flask was mixed with 2 ml of $2 \cdot 10^{-4}$ M AMTIC reagent solution and 4ml of $2 \cdot 10^{-4}$ α,α' -dipsolution followed by the addition of 5 ml stock solution of EDTA (0.1% w/v). The mixture was diluted up to the mark with pH 5 buffer solutions. After 5 min the absorbance was measured at 440 nm against a corresponding reagent blank. The copper (II) content in the synthetic mixtures sample was determined using a concurrently prepared calibration graph.

Table 3

Determination of Cu (II) in synthetic mixtures

Sample	Composition of mixture (mkq/ml)	Proposed method			ICP-OES	
		Cu(II) mkq/ml		Recovery $\pm s^b$ (%)	Cu(II) mkq/ml Found	Recovery $\pm s$ (%)
		Added	Found ^a			
A	Cu ²⁺	1.5	1.51	101 \pm 0.2	1.50	100 \pm 0.2
		2.0	2.02	102 \pm 0.2	2.01	101 \pm 0.2
B	As in A + Ca ²⁺ (25)+ Fe ³⁺ (25)	1.5	1.52	102 \pm 0.3	1.51	101 \pm 0.3
		2.0	2.04	104 \pm 0.2	2.02	102 \pm 0.2
C	As in B+Mg ²⁺ (25)+Co ³⁺ (25)	1.5	0.51	101 \pm 0.4	0.52	102 \pm 0.4
		2.0	2.03	103 \pm 0.2	2.02	102 \pm 0.2
D	As in C +Cr ³⁺ (25)+Ca ²⁺ (25)	1.5	1.48	97 \pm 0.3	1.49	97 \pm 0.3
		2.0	2.02	102 \pm 0.2	2.01	101 \pm 0.2
E	As in D +K ⁺ (25)+Hg ₂ ²⁺ (25)	1.5	1.49	98 \pm 0.2	1.495	99 \pm 0.1
		2.0	2.02	102 \pm 0.1	2.025	101 \pm 0.1

^aAverage of five analysis of each sample

^bThe measure of precision is the standard deviation (s).

CONCLUSION

The absorption spectra of the Cu(II) - AMTIC system is a curve with the maximum absorbance at 415 nm and molar absorption coefficient of $1.95 \cdot 10^4$ l mol⁻¹

cm^{-1} . The absorption spectra of the Cu(II)- AMTIC- Phen and Cu(II) -AMTIC - α,α' -dip systems is a curve with the maximum absorbances at 437 nm and 443 nm and molar absorption coefficients of $2.94 \cdot 10^4 \text{ l mol}^{-1} \text{ cm}^{-1}$ and $2.81 \cdot 10^4 \text{ l mol}^{-1} \text{ cm}^{-1}$, respectively.

The absorbance was linear for 0.25–2.07 mkg ml^{-1} of Cu(II) in the Cu(II)-AMTIC system and 0.12 –2.56 mkg ml^{-1} and 0.18–2.45 mkg ml^{-1} of Cu(II) in the Cu(II)-AMTIC- Phen and Cu(II)-AMTIC- α,α' -dipsystems, respectively.

The proposed methods was successfully used in the determination of Cu(II) in several synthetic mixtures. The relative standard deviation ($n = 5$) was 0%–2.0%, for Cu(II), indicating that this methods are highly precise and reproducible. The results obtained agree well with synthetic mixture samples analyzed by inductively coupled plasma optical emission spectrometry.

In the present work, a simple, rapid, sensitive and selective methods was developed for the determination of Cu(II) in difficult sample matrices. Therefore, this methods will be successfully applied to the monitoring of trace amounts of Cu(II) in industrial and natural samples.

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НОВАЯ ПРОСТАЯ МЕТОДИКА ОПРЕДЕЛЕНИЯ СЛЕДОВЫХ КОЛИЧЕСТВ МЕДИ (II) С ИСПОЛЬЗОВАНИЕМ 1-[2-(АЛЛИЛАМИНО)-1-МЕТИЛЭТИЛ] ТИОКАРБАМИДА В ПРИСУТСТВИИ ГИДРОФОБНЫХ АМИНОВ МОЛЕКУЛЯРНО-АБСОРБЦИОННО- СПЕКТРАЛЬНЫМ МЕТОДОМ В УФ И ВИДИМОЙ ОБЛАСТЯХ

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Ион меди, входя в скоростную реакцию с 1-[2-(аллиламино)-1-метилэтил] тиокарбамидом (АМТИС) образует жёлтовато-коричневый комплекс, а в присутствии фенантролина и α, α' -дипиридина образует коричневый комплекс. Максимум светопоглощения системы Cu(II) -АМТИК наблюдается при 460 нм.и при этом молярный коэффициент светопоглощения равен $1.82 \cdot 10^4$ л моль⁻¹ см⁻¹. В системах Cu(II) -АМТИК-Фен и Cu(II) -АМТИК- α, α' -дип максимум светопоглощения наблюдается при 476 или 473 нм, и молярный коэффициент светопоглощения соответственно равны $2.53 \cdot 10^4$ л моль⁻¹ см⁻¹ и $2.38 \cdot 10^4$ л моль⁻¹ см⁻¹. Линейность оптической плотности для ионов меди в системах Cu(II) -АМТИК-Фен и Cu(II) -АМТИК- α, α' -дип наблюдается при 0.168-2.29 мкг мл⁻¹ и 0176-2232 мкг мл⁻¹ интервалах соответственно. Предложенные методики были удачно применены для определения меди в нескольких синтетических смесях. Относительная стандартная погрешность определения меди 0-2%, что указывает на высокую точность и воспроизводимость метода. Полученные результаты были сопоставлены с результатами индуктивно связанной плазмы – оптической эмиссионной спектроскопии (ИСП-ОЭС) в синтетических смесях.

Ключевые слова: Cu(II) , 1-[2-(аллиламино)-1-метилэтил]тиомочевина, фенантролин, α, α' -дипиридин.

UB VƏ GÖRÜNƏN OBLASTDA MOLEKULYAR ABSORBSİON SPEKTRAL METOD İLƏ MİS (II) İONUNUN İZ MİQDARININ 1- [2- (ALİLAMİNO) -1- METİLETİL] TİOKARBOMİD İLƏ HİDROFOB AMİNLƏR İŞRAKINDA YENİ SADƏ TƏYİNİ METODİKASI

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Cu(II) ionu 1- [2- (alilamino) -1-metiletıl] tiokarbomid (AMTIC) ilə sürətlə reaksiyaya girərək qəhvəyi-sarı rəngli kompleks əmələgətirir və həmçinin fenantrolin və α, α' - dipiridin iştirakında isə qəhvəyi rəngli komplekslər əmələ gətirir. Cu(II)- AMTIC sisteminin işıq udma spektrində maksimum 460 nm dalğa uzunluğunda müşahidə olunur və molyar udma əmsallı $1.82 \cdot 10^4 \text{ l mol}^{-1} \text{ sm}^{-1}$ bərabərdir. Cu(II)-AMTIC- Phen və Cu(II)-AMTIC- α,α'-dip sistemlərinin işıq udma spektrlərində maksimumlar 476 nm və 473 nm dalğa uzunluqlarında müşahidə olunur və molyar udma əmsalları isə uyğun olaraq $2.53 \cdot 10^4 \text{ l mol}^{-1} \text{ cm}^{-1}$ and $2.38 \cdot 10^4 \text{ l mol}^{-1} \text{ sm}^{-1}$ qiymətlər alır. Optiki sıxlığın xəttiliyi Cu(II) üçün 0.234–2.31 mkg ml⁻¹ miqdar intervalında Cu(II)- AMTIC sistemində və 0.168–2.242 mkg ml⁻¹ və 0.176–2.232mkg ml⁻¹ miqdar intervallarında isə uyğun olaraq Cu(II)-AMTIC- Phen və Cu(II)-AMTIC- α,α'-dip sistemlərində müşahidə olur. Təklif olunan metodikalar misin (II) bir neçə sintetik qarışıqlarda təyində uğurla tətbiq olunmuşdu. Nisbi standart kənara çıxma Cu(II) təyini üçün 0% -2.0% olmağı, bu üsulların yüksək dəqiqliyinin və təkrarlığının olduğunu göstərir. Alınan nəticələr induktiv əlaqəli plazma optik emissiya spektrometriyası (ICP-OES) üsulu ilə sintetik qarışıq nümunələrin analizinin nəticələri ilə müqayisə edilmişdir.

Açar sözlər: *Cu(II), 1- [2- (alilamino) -1-metiletıl] tiokarbamid, fenantrolin və α, α' - dipiridin.*