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Spectrophotometric determination of copper(II) ion with 7-bromo-2-nitroso-1-oxinaphthalene-3,6-disulphocid

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An organic analytical reagent reacts violently with Cu(II) ion, forming a blue water-soluble complex. A method of spectrophotometric detection of the complex formed by Cu(II) ion with 7-bromo-2-nitroso-1-oxynaphthalene-3,6-disulfoacid (BNOKS-S, S-3,6) (HR) reagent was developed. Optimal conditions were studied: λ_{max}= 600, *p*H = 4.0, universal buffer, reagent buffer - Cu(II) - distilled water, BNOKS-S, S-3 with 0.05% relative to T_{Cu}^{2+}=10 μg/25mL. It was found that 1.4 mL volume of 6 reagents is sufficient. It was determined that the area of obedience to the Bouguer-Lambert-Behr law is 0.5-15 μg/25mL. Absorption spectra were studied: sensitivity according to Sendel was 0.00092 μg/cm2, contrast Δλ = 110 nm. The composition of the complex and the mechanism of complex formation were studied using the Nazarenko method, the isomolar series method, Asmus' straight line method, and spectrophotometric titration methods. The molar ratio of the complex is Me:R = 1:2. Actual molar extinction coefficient (ε_{real} = 58824), formation equilibrium constant (K_{equilb}= 15.23), stability constant of the complex using the Babko method (lgβ= 19.52), the confidence interval of the deviation from the mean value (ΔX = 0.117) and the lower limit of detection (Q_{min} = 0.141 μg/25mL) were determined. The results of the graduated graph were mathematically processed using the method of small squares and a linear mathematical equation was developed: $Y_i = 1{,}1 \cdot 10^{-3} + 2{,}4 \cdot 10^{-2} X_i$. The effect of foreign ions was studied. The developed method was used in an artificial mixture.

Keywords: Cu(II) ion, Bouguer-Lambert-Behr law, 7-Bromo-2-nitroso-1-oxynaphthalene-3,6-Disulfoacid

Today, as a result of the continuous development of the industry, including the operation of enterprises, factories, and plants, many chemical compounds and toxic metals that cause environmental pollution are contaminating rainwater and wastewater as ecotoxicants[1]. These ecotoxicants include copper, cadmium, nickel, and other heavy metals. It is important to identify metals from sources contaminated with these metals and to reduce their amount or even completely clean them[2,3]. For this, modern eco-analytical analysis methods such as Chromatospectrometry, Chromatomass-spectrometry, atomic absorption, plasma, X-ray fluorescence spectrometry, and others are widely used. The reliability of industrial materials often depends on the precise control of the contents of minor elements, which exist in minute amounts compared to the major components[3,4]. Many works have studied the sensitive determination of Cu(II) based on different chemical substances. Spectrophotometric determinations of benzoyl peroxide (BPO) and copper(II) were respectively, investigated by using the color reaction for N-ethyl-2-naphthylamine (NENA), BPO, and copper(II) as a metal ion in various concentrations of acetonitrile-water mixed solution as acidic media[5]. The ability of 9-ethyl-3-carbazolecarboxaldehyde-thiosemicarbazone (ECCAT) compound to form a complex and the kinetic and activation parameters of the complex were calculated based on the Arrhenius and Eyring equations for spectrophotometric determination of Cu(II) ion[6]. The parameters of using N-ethyl-3-carbazolecarboxaldehyde-3-thiosemicarbazone (ECCT)[7], 3-hydroxyacetanilide with 3-methyl-2-benzothiazolinone hydrazone (in the presence of ammonia and hydrochloric acid) compounds as a new analytical reagent for the determination of copper(II) ion was studied[8]. Trithia-9-crown-3 (TT9C3) serves as a sensitive and selective charge transfer complexing agent for Cu^{2+} ions[9]. In the present work, a method of spectrophotometric detection of the complex formed by Cu(II) ion with 7-bromo-2-nitroso-1-oxynaphthalene-3,6-disulfoacid (BNOKS-S, S-3,6) (HR) reagent is developed.

Materials and Methods

Standard solutions of copper(II) salts with a titer of T_{Cu}^{2+} = 1000 mg/mL were prepared using accurately weighed portions of analytical-grade metallic mineral salts. Reagents from both the "Clean" and "Chemically Clean" brands were employed in the experiment. An accurately weighed portion of copper(II) salt was placed in a 1000 mL volumetric flask and dissolved in distilled water. Small concentration solutions were prepared through the serial dilution of the prepared standard solution. Reagent solutions were prepared by dissolving 0.0500 g of the reagent in distilled water in a 100 mL volumetric flask. Spectrophotometric studies of colored solutions were carried out on an EMC-31PC-UV spectrophotometer. The *p*H of the solutions was controlled using a *p*H meter (*p*H-150M OAO, Gomelsky zavod izmirtelnyx priborov) with an accuracy of ±0.05 *p*H units.

Experimental Section

One of the main conditions of the complex formation reaction is the environment of the solution. Therefore, buffer solutions with different *p*H values were used to obtain reproducible results. For this, 5 mL of universal buffer solution with a *p*H of 2.46 to 11.2, 0.05% 7-bromo-2-nitroso-1-oxynaphthalene-3,6-disulfoacid (BNOKS-S,S-3,6) are added to a 25 mL measuring flask reagent solution, 1.0 mL of Cu(II) solution containing 40 µg/mL was added and diluted by adding distilled water up to the mark of the flask. The optical density of the complex compound solution was measured in an EMC-31PC-UV spectrophotometer, at a wavelength of λ_{max}=600 nm, in cuvettes with an absorption thickness of ℓ=1.0 cm. The obtained results are presented in Fig. 1.

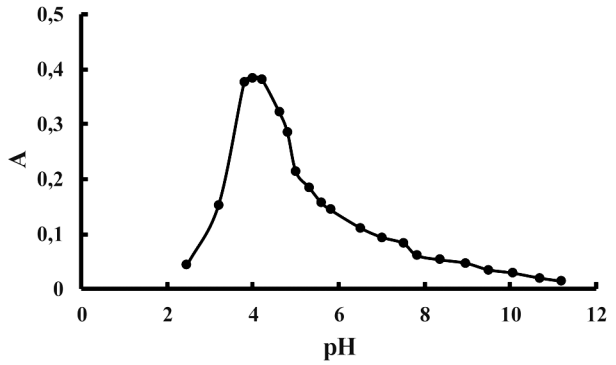

Fig. 1 — Graph showing the dependence of optical density on the solution environment. (λ_{max} = 600 nm, ℓ = 1.0 cm, n = 5)

According to the results presented in Fig. 1, the highest optical density of the complex compound was observed in the range of *p*H 3.8-4.2. The highest optical density was chosen because it was at *p*H=4.0. During the study, the effect of buffer solutions with different compositions with the same *p*H=4.0 on the light absorption of the colored complex was studied. The results are presented in Fig. 2.

According to the results presented in Fig. 2, the color complex showed the highest optical density under the influence of universal buffer solution. During the research, the time dependence of the formation of a colored complex was studied. According to the obtained results, the fact that the optical density of the formed colored complex did not change for 4 hours indicates that it is enough time for the analysis. When the order of pouring was studied, reagent-buffer-Cu(II)-distilled water produced the highest optical density in the order. In order to form a complete complex of the metal ion, the amount of reagent is taken in excess, for this purpose, the dependence on the amount of reagent was studied (Fig. 3). According to the results of the research, it was found that 1.4 mL of BNOKS-S, S-3,6 reagent with 0.05% in relation to TCu^{2+}=10 µg/25mL is sufficient[10].

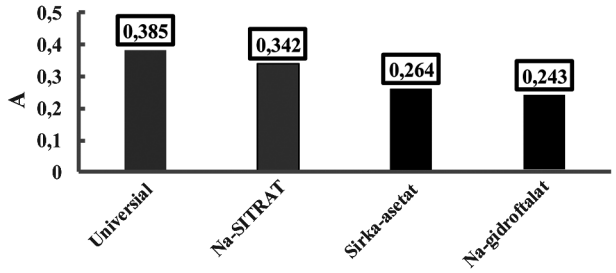

Fig. 2 — Graph showing the dependence of optical density on buffer solution content. (λ_{max} = 600 nm, ℓ = 1.0 cm, *p*H = 4.0, n = 5)

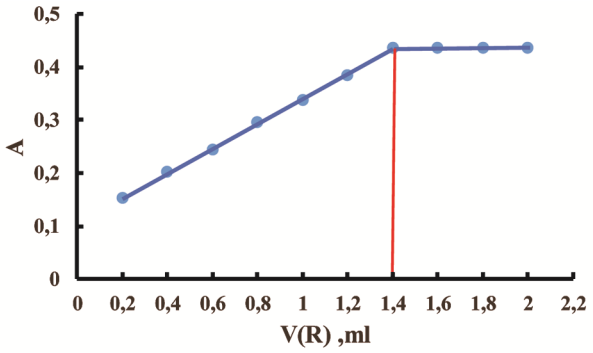

Fig. 3 — Graph depicting the dependence of the optical density of the complex compound on the amount of added reagent. (λ_{max} = 600 nm, ℓ = 1.0 cm, *p*H = 4.0, n = 5)

Results and Discussion

Bouguer-Lambert-Behr Law

Obedience to the Bouguer-Lambert-Behr law was assessed by preparing solutions as follows: 1.0 mL of a 0.05% aqueous solution of BNOKS-S, S-3.6, and 5.0 mL of universal buffer solution with *p*H=4.0 were combined in 25 mL volumetric flasks. Variable amounts of a 5 µg/mL standard solution of Cu(II) were added to each flask, and the volume was adjusted to the mark with distilled water. The optical densities of the resulting solutions were then measured and compared to a reference solution. The obtained results are presented in Fig. 4.

According to the obtained results, the range of obedience to the Bouguer-Lambert-Behr law was observed to be between 0.50-15 µg/25mL. However, at higher concentrations, a deviation from the linear relationship was noted[11].

Absorption spectra

Absorption spectra of the BNOKS-S, S-3,6 reagent and the complex formed with Cu(II) were obtained under selected optimal conditions (Table 1). The Sendel sensitivity of the method was calculated using the formula:

$$S.b.s = \frac{Q \cdot l \cdot 0{,}001}{A \cdot 25} = \frac{10 \cdot 1 \cdot 0{,}001}{0{,}435 \cdot 25} = 0.00092 \text{ mkg/sm}^2 \quad \ldots (1)$$

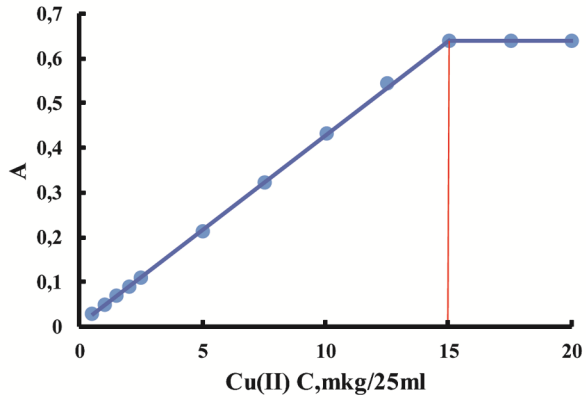

Fig. 4 — Graph depicting the dependence of the optical density on the amount of added Cu(II) (λ_{max} = 600 nm, ℓ = 1.0 cm, *p*H = 4.0, n = 5)

Here: S.b.s - Sendel sensitivity, Q-quantity of extracted metal ion, l-cuvette thickness, A-optical density.

According to the results obtained during the research, the reaction exhibits some contrast (Δλ = 110 nm) and high sensitivity (S.s = 0.00092 µg/cm^2). The composition of the complex and the mechanism of complex formation were investigated. Using the Nazarenko method, it was determined that the form of Cu(II) complexing is Cu^{2+}. The stoichiometry of the researched complex was studied using the isomolar series method (Fig. 5), Asmus' straight line method (Fig. 6), and spectrophotometric titration method (Fig. 7). All research methods confirmed that the molar ratio of the components in the complex is Me:R = 1:2[12].

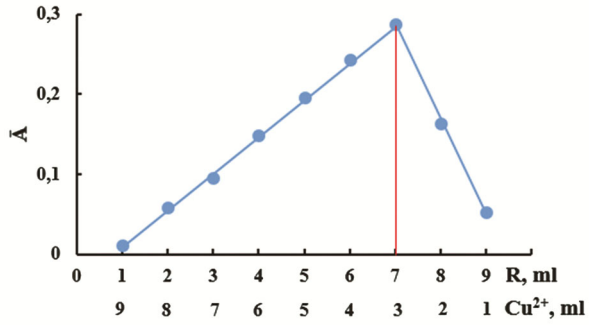

Fig. 5 — Graph depicting the isomolar series method of the composition of Cu(II) complex with BNOKS-S, S-3,6. (λmax = 600 nm, ℓ = 1.0 cm, *p*H = 4.0, n = 5)

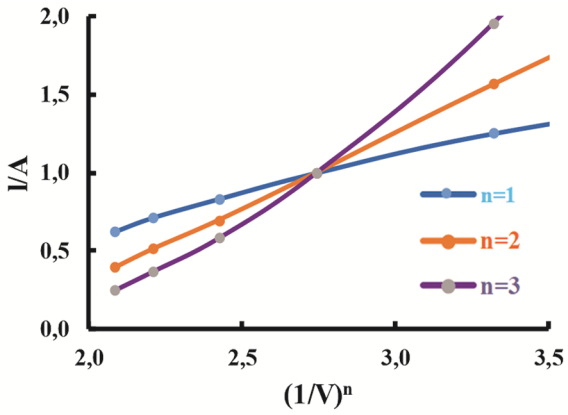

Fig. 6 — Graph illustrating the determination of the composition of the complex of Cu(II) with BNOKS-S, S-3,6 using Asmus' straight line method. (λmax = 600 nm, ℓ = 1.0 cm, *p*H = 4.0, n = 5)

Table 1 — Spectral description of BNOKS-S,S-3,6(HR) and its complex with Cu(II) (MeR) (C_{Cu2+}= 10 mkg, λ_{max}=600 nm, ℓ=1,0 cm, *p*H=4,0, n=5)

Complex color	*p*H	maximum λ, nm		Δλ	C_{Me}^{2+}, mkg/ 25 mL	C_{Me}^{2+}, mol/l	Ā	Sensitivity according to Sendel is µg/cm2
		MeR	HR					
Complex Cu(II) with R (ℓ=1.0 cm, n=5)								
Blue	4	600	490	110	10	$6.24 \cdot 10^{-6}$	0.435	0.00092

To comprehensively study the complex formation reaction of copper(II) with the BNOKS-S, S-3,6 reagent, the actual molar extinction coefficient and the formation equilibrium constant of the complex were determined based on its fundamental characteristics using Tolmachiov's graphic method (Fig. 8). Additionally, the stability constant of the complex was determined using the Babko method (Table 2).

$$\varepsilon_{real} = \frac{1}{1/\varepsilon \cdot 10^{n}} = \frac{1}{1{,}7 \cdot 10^{-5}} = 58824 \quad \ldots(2)$$

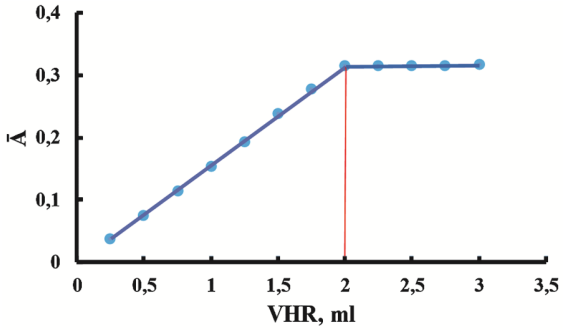

Fig. 7 — Graph illustrating the spectrophotometric titration method. (λmax = 600 nm, ℓ = 1.0 cm, *p*H = 4.0, n = 5)

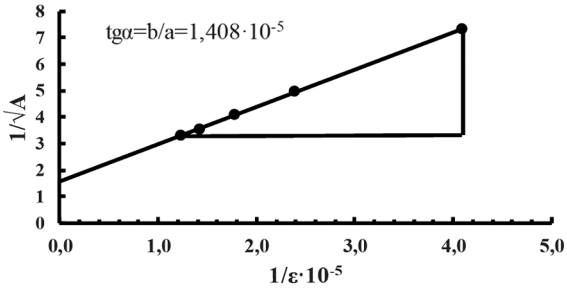

Fig. 8 — Graph depicting the determination of the molar extinction coefficient. (λmax = 600 nm, ℓ = 1.0 cm, *p*H = 4.0, n = 5)

$$K_{\text{equilibrium}} = \frac{C_H^n \cdot l^n}{n^n \cdot \varepsilon_x \cdot e^{n+1}} = \frac{(1.0 \cdot 10^{-4})^2 \cdot 1^2}{2^2 \cdot 58824 \cdot (1.408 \cdot 10^{-5})^3} = 15.23 \quad \ldots(3)$$

Here, the concentration of C_H - H^+ ions, l-thickness of the cuvette, real molar extinction coefficient of the complex, n-stoichiometric coefficient.

$$K_{unstable.(MeR)} = \frac{[H^+] \cdot (A_1 \cdot C_2 - A_2 \cdot C_1)^{q+1}}{(C_1 \cdot \sqrt[3]{A_2} - C_2 \cdot \sqrt[3]{A_1}) \cdot (A_1 \cdot \sqrt[3]{A_2} - A_2 \cdot \sqrt[3]{A_1})^{q}} \quad \ldots(4)$$

$$K_{unstable.(MeR)} = \frac{1}{K_{unstable.(MeR)}} \quad \ldots(5)$$

where, $[H^+]$-hydrogen ion concentration, A_1, A_2 A_3-optical densities, C_1, C_2, C_3-metal ion concentrations.

Compared to the calculated numerical values of ε_{real}=58824, $K_{equilibrium}$=15.23 and lgβ=19,52, it was found that the developed method has high sensitivity, and the complex compound has average stability. The results of the graduated graph were mathematically processed using the method of small squares and a linear mathematical equation was created (Table 3 and Fig. 9). Based on the obtained results, the graduated graph (graded graph) straight line equation

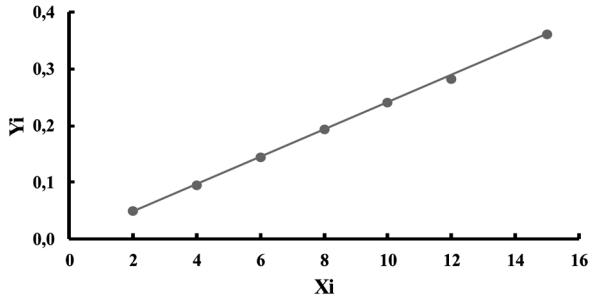

Fig. 9 — Graded graph of Cu(II) determination

Table 2 — Results of determining the stability constant of the complex using the Babko method (λ_{max} =600nm, ℓ=1.0 cm, *p*H=4.0, n=5)

No.	V_{Cu}^{2+}, mL	V_{R1}, mL	$C_1 \cdot 10^{-6}$	A_1	$C_2 \cdot 10^{-6}$	A_2	$K_{Unstable(MeR)}$	$K_{Unstable\ (MeR)}(\beta_k)$	$lgKu_{nstable\ (MeR)}(lg\beta_k)$
1	0.5	0.5	4.41	0.060	2.205	0.029	$3.26 \cdot 10^{-19}$	$3.07 \cdot 10^{18}$	18.49
2	0.75	0.75	8.81	0.176	4.405	0.087	$5.58 \cdot 10^{-20}$	$1.79 \cdot 10^{19}$	19.25
3	1.0	1.0	13.2	0.320	6.6	0.159	$2.09 \cdot 10^{-20}$	$4.79 \cdot 10^{19}$	19.68
4	1.25	1.25	17.6	0.494	8.8	0.246	$1.01 \cdot 10^{-20}$	$9.89 \cdot 10^{19}$	20.00
5	1.50	1.50	22	0.662	11	0.330	$6.57 \cdot 10^{-21}$	$1.52 \cdot 10^{20}$	20.18
			Σ				$8.38 \cdot 10^{-20}$	$6.40 \cdot 10^{19}$	19.52

Table 3 — The results of creating a graduated graph and its processing(λ_{max}=600nm, ℓ=1.0cm, *p*H=4.0, n=5, P=0.95)

№ T/r	Cu^{2+}mkg, Xi	Ā, Yi	Xi^2	Xi ·Yi	$Yi_{hisob.}$	$Yi-Yi_{hisob.}$	$(Yi- Yi_{hisob..})^2 \cdot 10^{-6}$
1	2	0.050	4	0.100	0.049	0.001	2.05
2	4	0.094	16	0.376	0.096	–0.002	5.23
3	6	0.144	36	0.864	0.144	0.000	0.07
4	8	0.193	64	1.544	0.191	0.002	3.08
5	10	0.240	100	2.400	0.239	0.001	1.37
6	12	0.282	144	3.381	0.286	–0.005	0.21
7	15	0.360	225	5.400	0.358	0.002	5.33
∑	57	1.363	589	14.065	1.363		38.62

Table 4 — Results of determination of Cu(II) ion from artificial mixture(l_{max}=600nm, ℓ=1.0cm, *p*H=4.0, n=5, P=0.95)

The composition of the mixture is μg	Entered Cu^{2+}, μg	**A**	Found $Cu^{2+,}$ μgX_i	S	S_r	$\overline{X} \pm \Delta X$
K^+, Na^+, Br^-(600);	10.0			0.209	0.021	10.10±0.259
Mn^{2+}, Ca^{2+} (70);		0.240	9.95			
NH_4^+, Ba^{2+}, Al^{3+}(80);		0.249	10.33			
Tl^{3+}, Pb^{2+} (5);		0.245	10.16			
$CH3COO^-$ (200);		0.237	9.83			
F^-, PO_4^{3-} (200);		0.247	10.25			
Fe^{2+}(2);						

Y_i=a+bX_i *i.e* Y_i =1.1·10^{-3} + 2.4·$10^{-2}X_i$ was developed. The accuracy and reproducibility of the detection method were calculated using the "inserted-found" method. The relative standard deviation (Sr) did not exceed 0.012, the confidence interval (ΔX) of the deviation from the mean did not exceed 0.117, and the lower limit of detection (Q_{min}) did not exceed 0.141 mkg/25mL[13-17].

$$Q_{min} = \frac{5 \cdot S_a \cdot M \cdot V \cdot B \cdot 1000}{\varepsilon \cdot l}$$

$$= \frac{5 \cdot 0{,}001043 \cdot 1 \cdot 25 \cdot 63{,}546 \cdot 1000}{58824 \cdot 1} = 0{,}141\ mkg/25ml$$

Here, ε_x-true molar extinction coefficient, V-volume of solution, B-element atomic mass, l-cuvette thickness, M-number of detectable atoms of Cu(II) included in the complex, S_a-standard deviation, Q_{min}– lower limit of detection.

Effect of interfering foreign ions in spectrophotometric determination of Cu(II) ion (10μg) BNOKS-S,S-3,6 reagent was studied. It was found that the following ions do not interfere with the detection of Cu(II) ion in the given ratio: ClO_4^-,S^{2-}, F^-, Br^-, (1:1000); Mg^{2+}, CH_3COO^-, PO_4^{3-} (1:500); Al^{3+}, Ba^{2+}, NH_4^+, Ca^{2+}, As^{3+}, Mn^{2+}, Cl^-,SO_4^{2-}, NO_3^- (1:100); Pb^{2+}, $Cr_2O_7^{2-}$, SiO_3^{2-}, (1:60); NO_2^-(1:50); Zn^{2+} (1:18); Pb^{2+}, Zr^{4+}, Ni^{2+}, Mo^{6+},Tl^{3+}, thiourea (1:7.5); (1:7,5); Sn^{2+} (1:4); $C_2O_4^{2-}$ (1:2); Ti^{4+}, $S_2O_3^{2-}$, J^-, (1:1). The generating ions are Bi^{3+},Co^{2+}, Fe^{2+} (1:1); Cd^{2+}, $H_2C_6H_5O_7^-$ (1:0,5). It is eliminated by masking the generating ions[18,19].

To check the accuracy and reproducibility of the method, it was applied to an artificial mixture using the "insert-found" method (Table 4). F- and CH_3COO- ions were added in a ratio of 1:200 to mask foreign ions interfering with the detection of Cu(II) ion. According to the obtained results, it is possible to determine Cu(II) from natural objects with such composition. In this case, the relative standard deviation (Sr) did not exceed 0.021[20-22].

Conclusions

The optimal conditions for complex formation of Cu(II) ion with BNOKS-S,S-3,6 reagent were studied. The field of obedience to the Bouguer-Lambert-Behr law was 0.5-15 μg/25mL, S.b.s= 0.00092 μg/cm2, Δl=110 nm. Also, based on the method of isomolar series, it was confirmed that the composition is Me:R=1:2 using the straight line method of Asmus and the spectrophotometric titration method.The true molar extinction coefficient (ε_{real}=58824) and formation equilibrium constant (K_{equil}=15.23) were determined using Tolmachiov's graphic method, and the stability constant of the complex (lgβ=19.52) was determined using Babko's method. In addition, the graduated graph (graded graph) straight line equation Y_i =1.1·10^{-3} + 2.4·$10^{-2}X_i$was developed. The value of the deviation confidence interval (ΔX) against the mean value was 0.117 and the lower limit of detection (Q_{min}) was found to be 0.141 μg/25mL. The effect of foreign ions was studied.The developed method was used in an artificial mixture, where the relative standard deviation (Sr) did not exceed 0.021.

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