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Spectrophotometric determination of microconcentrations of zinc(II) and copper(II) in water and industrial alloys using a new chromogenic reagent [4-amino-5-hydroxy-6-[(5-methyl-2-pyridyl)azo]-3-sulfo-1-naphthyl]sulfonyloxysodium

Todjiyev Jamoliddin Nasiriddinovich[1, 6, *], Turabov Nurmukhammat[1], Turaeva Gulzoda Suyunovna[1,2], Xusanov Baxrom Mengdovulovich[3], Khaydar E. Yunusov[4], Tuliyev Bexruz Alimkulovich[1], Gazieva Aziza Sunnatovna[5], Pulatova Gulnoza Ubaydullayevna[5], Smanova Zulayxo Asanaliyevna[1]

[1]Department of Chemistry, National University of Uzbekistan named after Mirzo Ulugbek, 100174, Tashkent, Uzbekistan
[2]Department of Biochemistry and Physiology, Tashkent State Agrarian University, 100020, Tashkent, Uzbekistan
[3]Department of Chemistry, Denov Institute of Entrepreneurship and Pedagogy, 190507, Denov, Uzbekistan
[4]Institute of Polymer Chemistry and Physics Uzbekistan Academy of Sciences, 100128, Tashkent, Uzbekistan
[5]Faculty of Pharmacy, Tashkent Pharmaceutical Institute, 100015, Tashkent, Uzbekistan
[6]Department of Chemical Sciences, EMU University, 100100, Tashkent, Uzbekistan

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ABSTRACT

The present study aimed to develop a new spectrophotometric method for the determination of zinc(II) and copper(II) using a new chromogenic reagent, [4-amino-5-hydroxy-6-[(5-methyl-2-pyridyl)azo]-3-sulfo-1-naphthyl]sulfonyloxysodium (HR). A new organic HR reagent has been synthesized. The complexation of Zn(II) and Cu(II) with HR was studied spectrophotometrically at absorption maxima of 565 nm (Δλ=55 nm) and 595 nm (Δλ=90 nm) for Zn-HR and Cu-HR, respectively. The HR reagent interacts with Zn(II) and Cu(II) instantaneously at pH 6.5 and pH 4.0, respectively, and the absorbance of the solution is stable for 70 and 1440 minutes, respectively. Using isomolar series, Asmus straight line, equilibrium shift and spectrophotometric titration methods, the stoichiometries of the complexes were found to be 1:2 metal-to-ligand ratios for Zn and Cu. To determine the charge of the complex, the solution was passed through columns containing the cations KU-2 and KRS-10 and the anions AB-16-GS and AN-2FN. In this case, one proton is released from the reagent molecule, and a chelate cycle is formed mainly through the atoms of the oxygen-OH group, the nitrogen of the pyridine ring and the N=N group. The dilute Babko method was used to estimate the stability constant (K_{stab}) values, which were found to be on the order of $1.44 \cdot 10^{21}$ (lgβ=21.16) and $2.97 \cdot 10^{17}$ (lgβ=17.47) for the Zn and Cu complexes, respectively. The proposed spectro-photometric methodology established that the concentrations of zinc(II) and copper(II) could be estimated to be 1.0-18.0 and 0.50-6.50 ppm, respectively, corresponding to molar absorptivities of $4.2 \cdot 10^4$ and $2.0 \cdot 10^4$ l/mol·cm, respectively. Likewise, the formed complexes were stable at different pH values, allowing the simultaneous estimation of the two metals. The suggested spectrophotometric method of definition was applied in the analysis of model mixtures, industrial alloys based on aluminum and natural water, and the obtained results were metrologically evaluated (Sr=0.043).

1. Introduction

Heterocyclic azo dyes [1] have been produced and proposed as very sensitive chromogenic reagents for measuring a variety of metal ions. Heavy metals [2] have long been regarded as highly hazardous pollutants that can poison humans even at low doses. Heavy metals [3] are defined as elements with atomic weights ranging from 63.5 to 200.6 and a density of more than 5 g/cm^3. The concentrations of heavy metals [4] in aquatic systems, as well as their accumulation through the food chain, may pose a health risk and cause environmental problems. Trace amounts of toxic metals cause cellular dysfunction by inhibiting enzymes, causing oxidative stress, and impairing antioxidant processes. Reactive oxygen species are formed as a result of these pathways [5], which can

Corresponding author; e-mail: todjiyev88@mail.ru
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induce DNA damage, lipid peroxidation, biosynthesis pathway arrest, and protein sulfhydryl depletion. Direct identification of trace and hazardous heavy metals [6], such as copper (Cu(II)) and zinc (Zn(II)), has proven critical in some samples. In recent years, [7], many researchers have focused on the extraction and identification of trace metal ions or species from diverse materials. Increased atmospheric emissions of hazardous heavy metals [8], primarily due to the industrial revolution, have resulted in major pollution. Among the numerous organic and inorganic contaminants, heavy metals [9] are particularly damaging because of their solubility in water, poor biodegradation, and significant environmental contamination. Although copper [10] is harmful at high concentrations and severe oral poisoning mostly affects the blood and kidneys, it is required for the regular metabolism of many living species [11]. Copper [12] is a vital element in plants that can be used in alloy manufacturing [13-14]. Chemically [15] or physically with foreign sources [16], this can be achieved. Excess copper [17] in the human body causes neuritis and cirrhosis by damaging the nervous system and organs, particularly the liver and gallbladder. Copper reduces zinc toxicity [18] in biological systems, implying a Cu/Zn antagonistic relationship. Some lesser organisms are more poisonous than humans to salts. Because [19] of its deposition in cell membranes, it becomes toxic at higher concentrations and inhibits transport across the cell wall. Wilson's illness is a hereditary disease caused by excessive copper in the human body. It has potentially catastrophic implications, such as liver damage. Males develop violent tendencies as a result [20] of high copper levels, which can cause depression and schizophrenia. The determination [21-24] of an ultratrace amount of copper in biological samples is particularly difficult because of the complex matrix and the usually low concentration of copper, which requires sensitive instrumental techniques and frequently a preconcentration step. Excessive Cu(II) uptake [25], on the other hand, can result in major health issues such as coronary heart disease, kidney disease, neurological disease, anemia, and bone abnormalities. As a result, ultratrace amounts of Cu(II) pollutants in water, food, and the environment must be monitored.

Zinc is one of the most commonly used elements, and therefore, its concentration in the environment is very high [26]. Zinc ions are widely used in metallurgy, the electrical industry, and other fields. Zinc is a biometal that plays an important role in blood formation, cell respiration, and metabolism in the human body. However, [27-29] at concentrations exceeding the MPC, it is toxic. The MPC of zinc in drinking water is 1 mg/l; in the waters of cultural, domestic and drinking purposes, it is 5 mg/l; in fisheries, it is 0.01 mg/l; and in the soil, it is 110 mg/l.

Some spectrophotometric determinations of the investigated metals include naphthazarin (5,8-dihydroxy-1,4-naphthoquinone) [30], 1-[2-(allylamino)-1-methyl] [31], chloro-(phenyl)glyoxime [33], benzildithiosemi carbazone [34], thiomichlersketone [35], and 4,5,6-trihydroxyhexane-1,2-diylidene)bis(N-phenylhydrazine-carbothioamide) [36]. To detect Zn(II) and Cu(II), 1,5-diphenylthiocarbazone [37], azathia-crown ether dye [38], Thio-Michler,s ketone [39], 2-[(2-sulfanylphenyl) ethanimidoyl]phenol [40], 6-hydroxy-3-(2-oxoindolin-3-ylideneamino)-2-thioxo-2H-1,3-thiazin-4(3H)-one [41], diamino dihydroxy pyrimidine [42], 4,5-bis(4-methoxyphenyl)-imidazole [43], 8-hydroxy-quinoline [44] and 4,4'-bis-(2,3,4-trihidroksi-fenilazo)-difenil [45] and 2-Aminobenzoxazole-oxalic acid (2/1) [46]. Some preconcentration and separation approaches were utilized for determination [47-50] of the studied metals.

Many spectrophotometric reagents have been used for the determination of zinc(II) and copper(II) ions, but most of them have various disadvantages, such as long-term color change, overheating or interference of many ions [68-76] and others.

The current study aims to develop rapid, simple, selective, express and highly sensitive spectrophotometric methods for quantifying low levels of Zn(II) and Cu(II) ions in various samples, such as individual solutions, alloys, natural waters and real objects. The principle of the method is based on allowing the above metals to react with the reagent [4-amino-5-hydroxy-6-[(5-methyl-2-pyridyl)-azo]-3-sulfo-1-naphthyl]sulfonyloxysodium (HR) as a newly prepared azo dye reagent at a selected pH. The present work aimed to investigate the optimum conditions for reactions, such as pH, time, temperature, reagent concentration and the sequence of addition. We have also encouraged this research to produce microscopic amounts of the investigated Cu(II) and Hg(II) ions in real samples.

2.Experimental part

Methodology. Photometric, spectrophometric, Asmus straight line method equilibrium shift and spectrophometric titration, the isomolar series method, the Tolmachev method, the Babko dilution method, and the additive method were used in this investigation.

Solutions, reagents, and devices. A standard zinc solution with a titer of 1 mg/ml ($1.5295 \cdot 10^{-2}$ M) was prepared by accurately weighing 1,000 g of metallic zinc (grade of analytical grade), dissolving it in diluted hydrochloric acid in a 1000 ml volumetric flask and mixing it with distilled water [51].

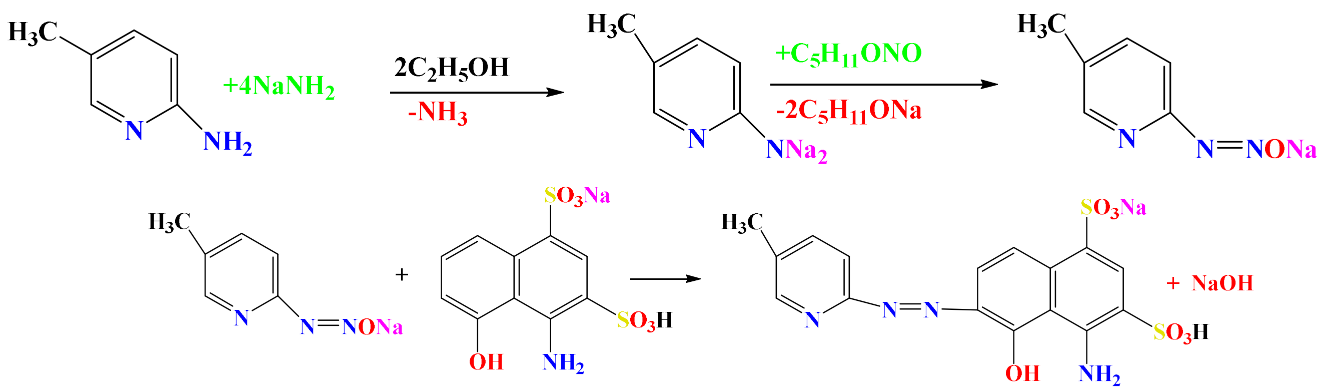
A standard solution of copper(II) with a titer of 1,0 mg/ml ($1.5737 \cdot 10^{-2}$ M) was prepared by accurately weighing 1,000 g of electrolytic copper dissolved in a minimal amount (8-10 ml) of concentrated nitric acid, and nitrogen oxides were removed during mild boiling. After cooling, the solution was transferred to a 1000.0 ml volumetric flask, adjusted to the mark with distilled water and stirred. Working solutions were prepared by diluting a standard solution. Metal solutions have exhibited titers of 50, 20 and 10 μg/ml [51, 52]. For preparation of a 0.05 % ($1.0869 \cdot 10^{-3}$ M) solution of HR, 0.1000 g of its exact weight was dissolved in a 200 ml volumetric flask, added to the mark with distilled water and stirred [53-55].

A universal buffer solution was prepared by mixing H_3BO_3, CH_3COOH and H_3PO_4 (0.04 M each) and adding 0.2 M NaOH to obtain the corresponding pH [56]. All reagents were of analytical grade and chemical grade. Distilled water was used in this study.

The optical density (OD) was measured on an SF-46 spectrophotometer and KFK-3 concentration photocolorimeters in glass cuvettes with layer thicknesses of 1.0 and 3.0 cm. The pH of the solutions was monitored with a pH meter - pH mV/-TEMP METER P25 (South Korea) and pH METTLER-TOLEDO AG 8603 (Made in China, №-B507604800).

3.Results and discussion

Synthesis of HR. HR was synthesized according to the method [58] together with the staff of the Department of Analytical Chemistry, Faculty of Chemistry, NUU N.T.Turabov and U.M.Mansurkhodjaev and the scheme of it's preparation is given below:



In a 500 mL dry flask connected with a reflux condenser (50 cm long), 4.0 g of sodium amide, thoroughly ground into powder was added and absolute ethyl alcohol. 10 g of 2-amino-5-methylpyridine in alcohol was gradually poured from a dropping funnel, after which the mixture was boiled for 30 minutes, over a water bath, then a solution (122 g) of freshly distilled isoamyl nitrite was added from the same dropping funnel, the mixture was boiled for 1.0 more hour on a water bath in a system with a reverse cooler, during which (5-methyl-2-pyridyl)-azooxysodium was released. The resulting precipitate of (5-methyl-2-pyridyl)azooxysodium was sucked off on a Buechner funnel, washed with ether and dried in a vacuum-exciter. The (5-methyl-2-pyridyl)azooxysodium was then added to 30.0 ml of absolute ethanol and added with stirring to 4.4 g of (4-amino-5-hydroxy-3-sulfo-1-naphthyl)sulfonyloxysodium in 96% of ethanol. The mixture was left for 12 hours. After that, CO_2 was passed through the resulting solution. The precipitate was filtered off and washed with absolute ethanol. Recrystallization was performed from absolute ethanol. The obtained reagent [4-amino-5-hydroxy-6-[(5-methyl-2-pyridyl)-azo]-3-sulfo-1-naphthyl]sulfonyloxy-sodium (HR) is of red-purple color powdery crystals , which is well soluble in distilled water and absolute ethanol. HR working solutions were prepared by diluting a an accurately weighed portion of the reagent with distilled water.

Identification of the synthesized HR by spectrophotometry. The identification of the compound [58] was carried out by it's electronic, IR and ^{1}H NMR spectrum. The degree of purity of the reagent by light absorption spectrum was determined as follows: spectrum were taken after each recrystallization, the constancy of values ε_{HR} at λ_{max} of the reagent indicates its purity. A single recrystallization is sufficient for purification of pyridine derivatives. Spectrophotometric studies show that the pyridylazo compound (HR) used in this work as an organic reagent is characterized by one light absorption maximum located in the region of 505-540 nm. To determine the state of the reagent in solution, its absorption spectra were studied depending on the pH of the medium. The results obtained are presented in Fig. 1. Consideration of the data obtained shows that HR in the pH range 2.0-5.0 has a light absorption maximum at 505-520 nm, in the pH range 5.0-7.0 at 515-530 nm, in the pH range 7.0-10.0 at 525-530 nm and in the pH range 10.0-13.0 at 510-525 nm, respectively. As can be seen from Fig. 1, the light absorption spectra of HR depending on pH are symmetrical curves with a maximum at 505-530 nm.

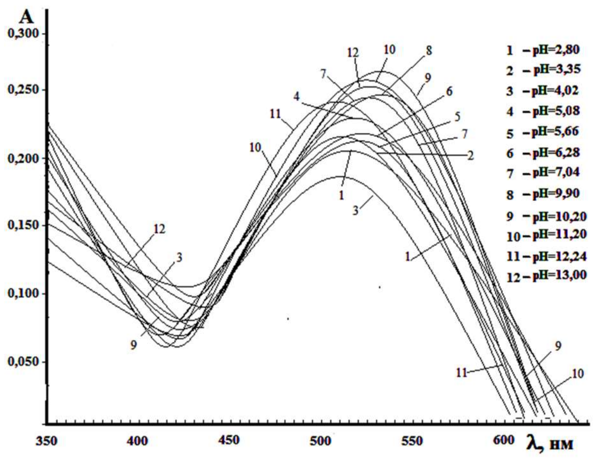


Fig.1. Electronic spectra of HR at different pH values.

Optimal conditions for the formation of a zinc complex. Zinc ions interact with the new azo reagent HR in a slightly acidic medium (pH=5.9-7.0) to form intensely colored pink compounds with an absorption maximum at 565 nm (ε_{ZnR}=42017). For the complete binding of 50 µg of zinc in the complex, 1.5 ml of a $1.086\cdot10^{-3}$ M solution of HR was sufficient. A complex that was stable for at least three hours was quantitatively formed within 0.5-1.0 min at room temperature with a 2-fold excess of reagent. The lower limit of the determined zinc content was 0.175 µg/25 ml. According to the Bouguer-Lambert-Beer law, 25 ml of zinc ions are present at concentrations ranging from 1.0-18.0 µg (Fig. 2).

The effect of outride ions and masking agents [57] on the complexation of Zn(II) with the HR reagent was studied. To determine 15 µg of zinc(II) ions, the following alkali metal ions were used: Ba^{2+}, Mg^{2+}, Al^{3+}, Cl^-, Br^-, F^-, J^-, NO_3^-, $S_2O_3^{2-}$, CH_3COO^-, PO_4^{3-}, $Cr_2O_7^{2-}$, $C_2O_4^{2-}$, and ClO_4^- (1:1000); thiourea, NO_2^-, and SO_4^{2-} (1:100); Pb^{2+}, Sn^{2+}, and SiO_3^{2-} (1:10); Cu^{2+} (1: 7.5); Bi^{3+}, Cr^{3+} (1:5); and Mn^{2+}, Co^{2+}, Hg^{2+}, Ti^{4+}, and CN (1:1). The presence of the ions Ni^{2+}, citrate (1:5), Cd^{2+}, Fe^{2+}, CSN^- (1:0,5), TI^{3+}, EDTA and OH^- (1:0.1) was prevented. A comparison of the selectivity of reagents known from the literature [58] for the determination of zinc(II) revealed tha the synthesized reagents are more selective.

Effect of reagent concentration for a copper(II) complex. To determine the minimum required amount of HR, 5.0 ml of a 5.0 ml of Cu(II) universal buffer solution with pH=4.0 containing 5.0 µg of copper(II) and increasing amounts of a 0.05% solution of HR was added to a certain amount of Cu(II) solution diluted with distilled water to 25 ml, mixed, and the OD was measured on a KFK-3 photocolorimeter with an absorption maximum at 595 nm in a ℓ=3.0 cm relative to a dummy test. The comp-lete consistency of the OD was observed in the presence of 0.8-0.9 ml of 0.05% solution of HR. This amount of reagent is considered sufficient for connecting complexes with added amounts of metal ions [57]. The complexes formed quickly and were stable for at least 24 hours.

The area of submission to the Bouguer-Lambert-Beer law for the copper(II) complex. To aliquot part of the solution containing copper(II) in the range of the calibration curve, 0.9 ml of a 0.05 % solution of HR, 5.0 ml of universal buffer solution with a pH of 4.0 and solution was deluded with water to 25 ml, and the mixture was stirred. Then, the OD of the solution of the complex compound relative to the solution of the blank experiment was measured (λ=595 nm, ℓ=3.0 cm), the exact amount of the solution was calculated via a straight line equation. The Bouguer-Lambert-Beer law was observed for 25 ml of 0.50-6.50 µg of Cu (Fig. 2).

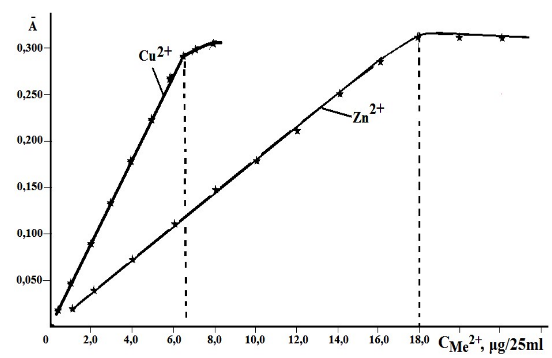


Fig. 2. Submission to the law Bera complex of Cu(II) and Zn(II) with the reagent HR.

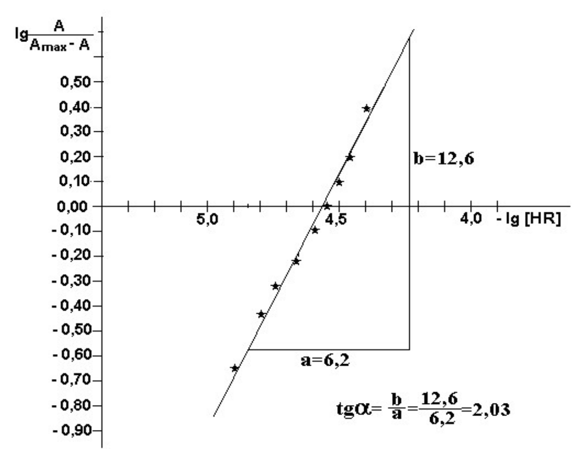


Fig. 3. Determination of molar ratios of copper(II) complex by the equilibrium shift method.

Absorption spectra of the reagent (HR) and its complexes with Zn(II) and Cu(II). The electronic light absorption spectra of the reagent solutions and their complexes were recorded. The obtained data are presented in Table 1 and Fig. 4. (SF-46, ℓ=1.0 cm).

Table 1. The basic characteristics of the spectrophotometric method for the determination of zinc(II) and copper(II) ions with the HR reagent.

Metal ion	Colors of the complex	pH	λ_{MeR}	λ_{HR}	Δλ, nm	ε_{MeR}	ε_{HR}	$K_{eq.MeR}$	$K_{dis.HR}$	Sendel sensitivity μg/cm^2
Zn^{2+}	Pink	6.5	565	510	55	42017	3306	$1.26\cdot10^{-4}$	$2.95\cdot10^{-8}$	0.0042
Cu^{2+}	Blue	4.0	595	505	90	20000	3306	2.73	$2.95\cdot10^{-8}$	0.0025

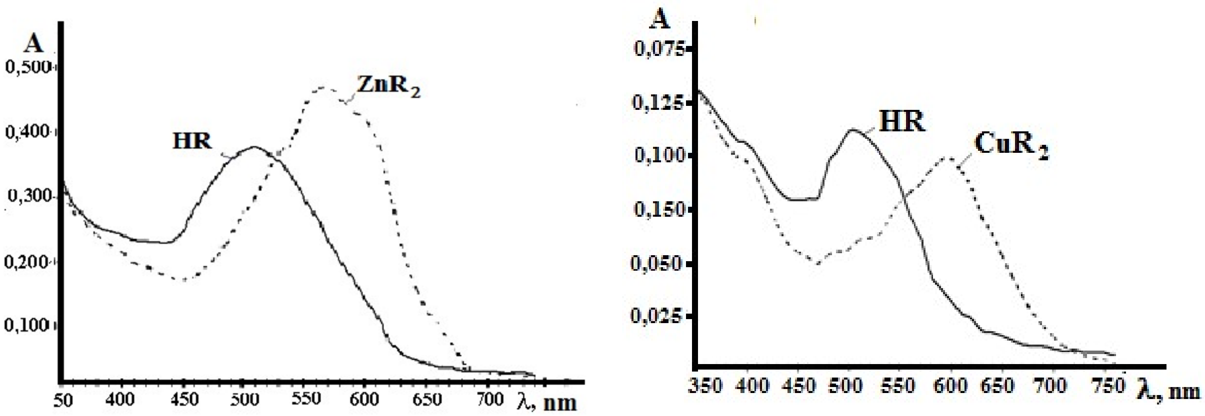


Fig. 4. Absorption spectra of the reagent HR and it's complexes with zinc(II) (ZnR_2) and copper(II) (CuR_2).

Determination of the composition of the Zn-HR complex. The stoichiometry of the zinc complex with the reagent was studied by the methods of Ostromyslensky-Zhob (method of isomolar series) [57] (Fig. 5) and the Asmus straight line [57]. To determine the composition of the zinc(II) complex with HR by the methods of Ostromyslensky-Zhob [57], equimolar concentrations of zinc(II) and reagent solutions ($C_{Zn^{2+}}=C_{HR}=1.5295\cdot10^{-4}$ M) were used.

Method of determination: Methods of the isomolar series: In 25 ml volumetric flasks, complex solutions were prepared by adding 1.0-9.0 ml of a solution of 0.05% HR and 90-10 ml of zinc(II) solution, 5 ml of universal buffer solution with a pH of 6.50, and the volumes of the flasks were adjusted to the mark by distilled water. The prepared solutions were mixed, and the optical density's were measured on a KFK-3 plate (λ=565 nm, ℓ=3.0 cm). A blank test solution was used for comparison (Fig. 5).

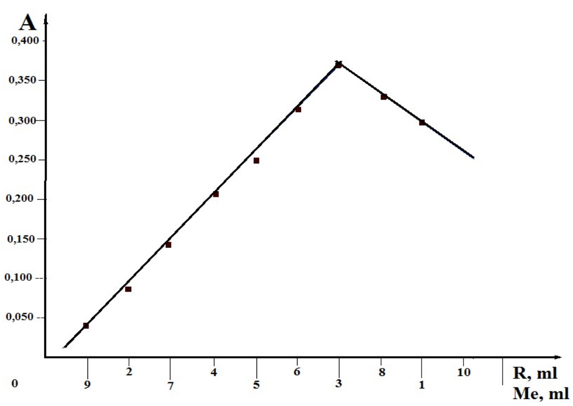


Fig. 5. Determination of molar ratios of zinc(II) complex by the method of isomolar series.

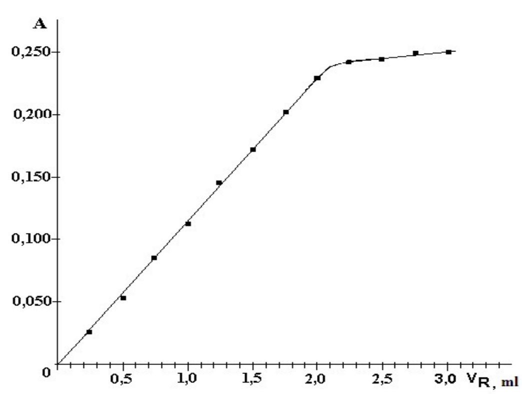


Fig. 6. Determination of molar ratios by the method of spectrophotometric titration.

Method of determination by the Asmus straight line: in 25 ml volumetric flasks, solutions of the complex were prepared with the addition of a constant amount of zinc(II) at 50.0 µg each; 5 ml of universal buffer solution with pH=6.50, variable amounts of reagent and volumes of flasks were adjusted with distilled water for marking. The solutions were mixed, and the OD was measured on a KFK-3 plate (ℓ=3.0 cm). For comparison, the solutions in Fig. 7 (1) were used. The obtained data showed that at the investigated concentrations, zinc(II) interacts with the reagent HR at a ratio of 1:2, which indicates the formation of a complex composed of ZnR_2.

Determination of the composition of the Cu-HR complex. To determine the molar ratio of the complex obtained by the interaction of copper(II) with the reagent HR, the Asmus straight line (Fig. 7 (2)) [57], equilibrium shift (Fig. 3) and spectrophotometric titration (Fig. 6) methods were used [57]. To determine the composition of the copper(II) complex with HR by the equilibrium shift method, equimolar concentrations of copper(II) and reagent solutions ($C_{Cu}^{2+}=C_{HR}=3.1473\cdot10^{-4}$ M) were used. *The procedure of determination was as follows:*

In complex flasks with a capacity of 25 ml, solutions of the complex were prepared with the addition of 5.0 ml of universal buffer solution at pH 4.0, a constant amount of copper(II) (1.0 ml of $3.1473\cdot10^{-4}$ M), a variable amount of reagent (1.0-4.0 ml), and the volumes of the solutions were adjusted to the mark with distilled water. The solutions prepared in this way were mixed, and the OD was measured at KFK-3, ℓ=3.0 cm. A solution from the blank experiment was used as a comparison solution.

The data showed that at the studied concentrations, copper(II) interacted with HR at a ratio of 1:2, which indicated the formation of a complex composed of CuR_2. In this case, one proton is released from the reagent molecule, and a chelate cycle is formed mainly through the atoms of the oxygen -OH group, the nitrogen of the pyridine ring and the N=N group.

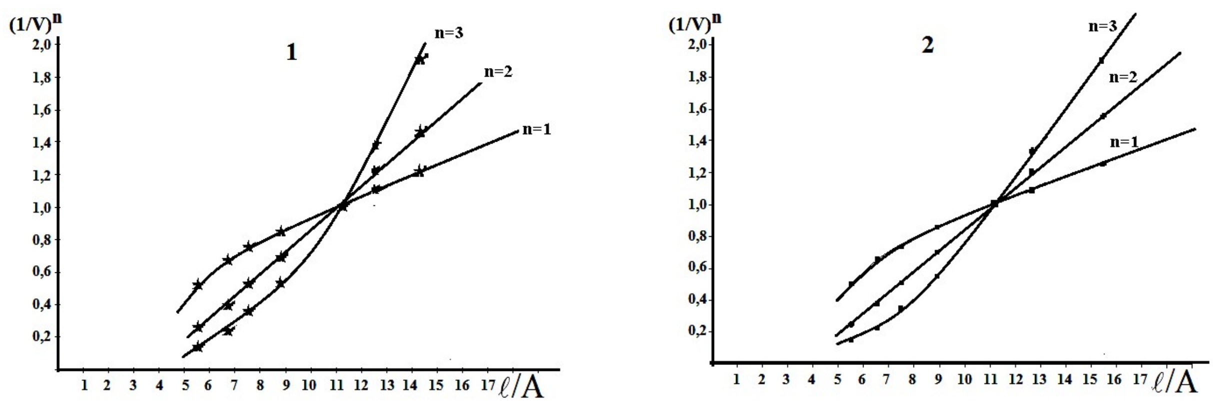


Fig. 7. Determination of the molar ratio of zinc (II) (1) and copper (II) (2) complexes with HR by method Asmus right line.

To determine the charge of the complex, the solution was passed through columns containing the cations KU-2 and KRS-10 and the anions AB-16-GS and AN-2FN.

Method for determination of the zinc(II) complex: a) First, 1.0 g of cationite KU-2 (KRS-10) was transferred to a column with a 1.0 cm diameter, treated 3 times with 10 ml of 0.1 N hydrochloric acid and then washed with 50 ml of distilled water. Then, under optimal conditions, 1.5 ml of a 0.05 % reagent solution, 1.0 ml (50 µg/ml) of Zn(II) solution, and 5 ml of universal buffer solution were poured into a volumetric flask with a volume of 25 ml, and the volume was adjusted to the mark with distilled water. Ten milliliters of the complex solution was passed through cationit KU-2 (KRS-10). The solution of the complex with a red color was not retained on cationite KU-2.

b) One gram of anionic AB-16-GS (AN-2FN) was transferred to a column with a diameter of 1.0 cm and treated 3 times with 10 ml of 0.1 N NaOH solution. The column was subsequently washed with 50 ml of distilled water, after which 10 ml of the complex solution was passed. In this case, the complex was retained on the upper layers of anionite. The solution that passed through the anionite was discoloured. The complex has a negative charge. This can be explained by the fact that the sulfone groups present in the reagent (HR) at the optimum pH (pH_{Zn}=6.50) are in a dissociated state, and owing to steric factors, they do not participate in complexation; in the case of anionite AN-2FN, similar results are obtained. On the basis of data obtained by determining the charge and composition, the expected structure of the complex can be represented as follows: $2[HR]^{2-}+Zn^{2+}=[ZnR_2]^{2-}+2H^+$.

Method for determination of the copper(II) complex: To determine the charge of the complex [57], the solution was passed through columns containing cationite KU-2, KRS-10 (the blue solution of the complex was not retained) and the anionites AV-16GS and AN-2FN (the solution of the complex passing through the anionite was discolored), which can be explained by the negative charge of the complex. Sulfo groups present in the reagent (HR) are in a dissociated state because steric factors do not participate in complexation. On the basis of the charge and composition data, the expected structure of the complex can be represented as follows: $2[HR]^{2-}+Cu^{2+}\rightarrow[CuR_2]^{2-}+2H^+$.

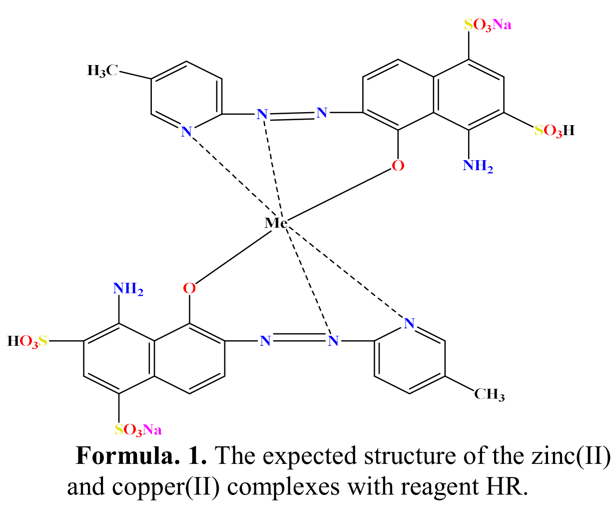
The molar coefficient of light absorption and the equilibrium constant of the complexes and the reagent were determined by the Tolmachev and Komar method [57]. The average values of the stability constants of the zinc(II) and copper(II) complexes were calculated by the Babko dilution method [57] and were 17.47 and 21.16, respectively. The obtained data are presented in Table 1.

The results of quantum-chemical calculations of the effective charges of the upper occupied atoms of the HR molecule by the MNDO method have shown that the donor-acceptor bonds of zinc(II) and copper(II) likely occur with nitrogen atoms of the pyridine ring and a diazogroup close to it and the ionic bond with the hydroxyl of the naphthol ring due to substitution with a hydrogen ion.

The structure of the obtained zinc complex with HR was confirmed by IR spectroscopy. The IR spectrum was recorded on an Avator-300 device using a KBr tablet in the frequency range of 400-4000 cm^{-1}. According to published data [59], the following characteristic frequencies have been found in the IR spectrum of the reagent: 2868, 2942 cm^{-1}, symmetric and asymmetric stretching vibrations of the methyl group ($-CH_3$), 3258 cm^{-1}, stretching vibrations of the hydroxyl group, 1542 cm^{-1}, valent vibration C=C of the aromatic ring, 1654 cm^{-1}, stretching vibration of the diazogroup (-N=N-), 1077, 1191 cm^{-1}, symmetric [60, 61] and asymmetric stretching vibrations of the sulfo group ($-SO_3^{2-}$), 673 cm^{-1} stretching vibration of the SO group, 1497 cm^{-1} deformation vibrations 3443 cm^{-1}, stretching vibrations of the amino group ($-NH_2$) and 792 cm^{-1}, deformation vibrations, C-H oscillation of the naphthalene ring.

In the IR spectrum of the complex compound, the main changes occur in the region of stretching vibrations of the hydroxyl group since, in contrast to the reagent, the observed broadened band in the IR spectrum of the complexes narrows in the region of 535 cm^{-1} (O-Zn) and 516 cm^{-1} (O-Cu), which is associated with the formation of a valence bond between the metal ion and the hydroxyl group due to the displacement of a hydrogen ion. In addition, the frequency of stretching vibrations at 1679 cm^{-1} of the diazo group at 1654 cm^{-1} changes very significantly, which indicates the formation of a coordination bond with the participation of the diazo group [62-66].

According to IR spectroscopy, quantum chemical calculations and the results of studying the molar ratios of metals:reagents (1:2) of the inverse complex compounds of zinc(II) and copper(II) with the HR reagent, the following assumption about their structures has been proposed (Formula 1.):



Formula. 1. The expected structure of the zinc(II) and copper(II) complexes with reagent HR.

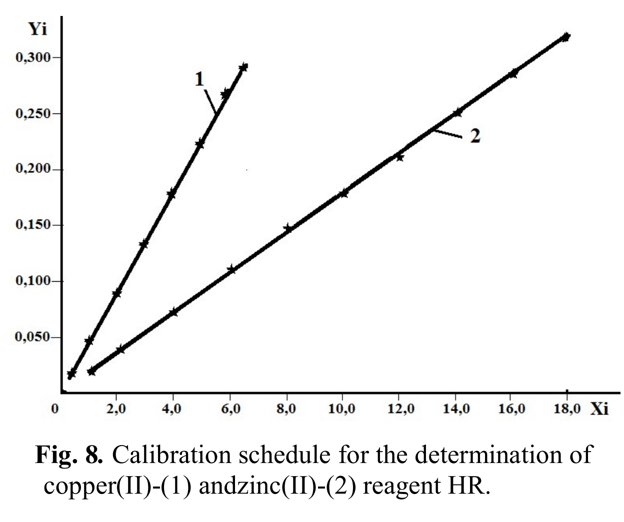


Fig. 8. Calibration schedule for the determination of copper(II)-(1) andzinc(II)-(2) reagent HR.

To assess the accuracy and reproducibility of the spectrophotometric determination of copper ions with the reagent HR, various amounts of copper ions were measured under optimal conditions for three repetitions. The experimental results showed that the relative standard deviation at 1.0-6.5 µg of copper(II) did not exceed 0.0420. The equation of the grading plot was calculated by the least squares method [57], where Yi=a+bXi, a=0.0036 and b=0.045. Based on the calculated data, a calibration graph was constructed for the dependence of $Y_{calc.}$ (Yi) on C_{Cu}, μg (Xi) (Fig. 8).

The equation of the calibration graph was calculated by the least squares method at Yi=a+bXi, a=0.0054 and b=0.0171; on the basis of the calculated data, a calibration graph was constructed for the dependence of $Y_{calc.}$ (Yi) on C_{Zn}, μg (Xi) (Fig. 8) [57].

The effect of various foreign ions on the spectrophotometric determination of Cu(II) with HR by a similar method was studied, except that they were introduced before the HR solution. The experimental data are presented as the selectivity factor $(F = \frac{C_{Me}}{C_{Cu}})$ –maximum permissible mass excess. The relative error in the determination was ±5 %. The following ratios did not interfere with the determination of the copper (II) concentration: 25 ml of silk metal ions, ClO_4^-, S^{2-}, F^-, and Br^-, (1:1000); Mg^{2+}, CH_3COO^-, and PO_4^{3-} (1:500); Al^{3+}, Ba^{2+}, NH^{4+}, Ca^{2+}, As^{3+}, Mn^{2+}, Cl^-, SO_4^{2-}, and NO_3^- (1:100); $Cr_2O_7^{2-}$, SiO_3^{2-}, (1:60); NO_2^- (1:50); Zn^{2+} (1:18); Pb^{2+}, Zr^{4+}, Ni^{2+}, Mo^{6+}, Tl^{3+}, and thiourea (1:7.5); Sn^{2+} (1:4); $C_2O_4^{2-}$(1:2); and Ti^{4+}, $S_2O_3^{2-}$, J^-, (1:1). Ions of Bi^{3+}, Co^{2+}, Fe^{2+} (1:1), Cd^{2+}, $H_2C_6H_5O_7^-$(1:0.5) interfere, etc. [57, 67]. The influence of the above ions (cations) can be eliminated by introducing the corresponding masking ions into the analyzed mixture or by extraction separation. Under the conditions of determination of copper(II) by HR, many ions at lower concentrations do not affect acidic media.

4. Analytical use

The selectivity data make it possible to apply the developed technique for the spectrophotometric determination of Zn(II) and Cu(II) ions in complex objects.

Determination of zinc(II) by HR in model mixtures. The elaborate procedure for the determination of zinc ions(II) by HR was used in the analysis of artificial mixtures with the addition of masking substances. The measurement results and their metrological data are presented in the Table. 2.

Determination of copper (II) ions by HR in model mixtures: Copper(II) ion determination (HR) was used in the analysis of artificial mixtures with the addition of masking substances (F^- 1:150, CH_3COO^- 1:100). The measurement results and their metrological data are presented in Table 3, which shows that the spectrophotometric determination of copper(II) ions in complex model mixtures imitating real objects is quite possible, and the relative standard deviation does not exceed 0.02, which indicates good accuracy and reproducibility of the developed method.

Table 2. The results of the determination of zinc(II) in an artificial mixture (V=25 ml, pH=6.50, l=3.0 cm, n=5, P=0.95, t_{pk}=2.78).

The composition of artificial mixtures (ratio)	Introduced Zn^{2+}, μg	$\bar{A}_{565}$	Found Zn^{2+}, μg	S	Sr	$\overline{Xi} \pm \Delta x$
K^+, Na^+(500)	10.00	0.180	10.21	0.228	0.023	9.85±0.28
Bi^{3+}, Ni^{2+}(0,5)		0.170	9.63			
Co^{2+}(0,03)Hg^{2+} (0,02)		0.172	9.74			
Mn^{2+}, Ba^{2+}, CH_3COO^-(100)		0.172	9.74			
NO_2^-, Cl^- (600) NO_3^-(1000)		0.175	9.92			

Table 3. The results of the determination of copper(II) ions in artificial mixtures (V=25.0 ml, pH=4.0, ℓ=3.0 cm, n=5, P=0.95).

The composition of artificial mixtures (ratio)	Introduced Cu^{2+}, μg	$\bar{A}_{595}$	Found Cu^{2+}, μg	S	Sr	$\overline{Xi} \pm \Delta x$
K^+, Na^+, Fe^{2+}(3) Br^-(500)	6.00	0.275	6.03	0,122	0.02	6.10±0.15
Mn^{2+}, Ca^{2+}(75)		0.284	6.23			
NH_4^+, Ba^{2+},Al^{3+}(75)		0.280	6.14			
Tl^{3+}, Ni^{2+}, Pb^{2+}(4)		0.270	5.92			
CH_3COO^-(100)		0.282	6.18			
F^-, PO_4^{3-}(150), NO_3^-(1000)						

Determination of zinc(II) and copper(II) ions in industrial samples. An elaborate sensitive and selective spectrophotometric method for the determination of zinc(II) and copper(II) ions with reagent HR was applied to analyze standard samples of industrial alloys. The samples AK12MK 203-1, AK12MK 203-5, M123-1 and

M99-5, which have polymetallic and elemental compositions, were used.

To prepare the samples for analysis, a 0.1000 g sample of alloy (0.050 g for M123-1 and M99-5) was dissolved in heat-resistant glass with a capacity of 50.0 ml, and a minimal volume (8.0-10.0 ml) of the tsar vodka was added. The mixture was heated with gentle boiling on an electric stove until complete dissolution and nitrogen oxides were removed. After cooling, the solution was quantitatively transferred to a 1000 ml volumetric flask (2000 ml for M123-1 and M99-5), diluted with distilled water to the mark [57] and stirred. The contents of Zn(II) and Cu(II) ions were determined from aliquots of this solution.

The methods for determining zinc(II) ions were as follows: a certain amount of sample solution was placed in a 25 ml volumetric flask, 5 ml of universal buffer solution with a pH of 6.5, 1.5 ml of $1.0869 \cdot 10^{-3}$ M solution of HR, masking agents (F^-, $S_2O_3^{2-}$, CH_3COO^-) at calculated concentrations for masking ions [57] of aluminum, lead, iron, and copper were added; and the volume was adjusted to the mark with distilled water. The OD of KFK-3 was measured at an at ℓ of 3.0 cm relative to that of the blank solution. The obtained data and their mathematical processing are presented in the table. 4.

Table 4. The results of the determination of zinc(II) ions in aluminum alloys (n=5, p=0.95).

Name of sample, Zn, %	$\bar{A}_{565}$	Contined. Zn^{2+} in solution, μg	Found Zn^{2+}, μg	S	Sr	$\overline{Xi} \pm \Delta x$
A-203-1, 0.2	0.106	6.0	5.88	0.185	0.0314	5.88±0.23
	0.209	12.0	11.91	0.226	0.0190	11.91±0.28
	0.312	18.0	17.93	0.166	0.0093	17.93±0.21
A-203-5, 1.0	0.090	5.0	4.95	0.185	0.0374	4.95±0.23
	0.179	10.0	10.15	0.154	0.0154	10.15±0.19
	0.258	15.0	14.77	0.262	0.0177	14.77±0.33

For determination of copper(II) ions, a certain amount of sample solution was placed in a 25 ml volumetric flask, 5.0 ml of universal buffer solution at pH 4.0, and 0.9 ml of $1.0869 \cdot 10^{-3}$ M solution of HR were added. Masking agents (F^-1:300, CH_3COO^-1:500) were added to the calculated concentrations for masking aluminum, lead, and iron ions, and the volume of the flask was adjusted to the mark with distilled water. ODs were measured on KFK-3 at ℓ=3.0 cm relative to the blank solution. The obtained data and their mathematical processing are presented in the table. 5.

Thus, the developed spectrophotometric method for the determination of zinc(II) and copper(II) ions by the azoreagent HR is characterized by high sensitivity, selectivity and reproducibility, with a relative standard deviation (Sr) not exceeding 0.043.

Table 5. Spectrophotometric determination of copper(II) ions in standard samples. of industrial aluminum and copper alloys (pH=4.0, ℓ=3.0, n=3, P=95).

Name of sample, Cu, %	$\bar{A}_{595}$	Contined. Cu (II) in solution, μg	Found Cu^{2+}, μg	$S \cdot 10^{-2}$	$Sr \cdot 10^{-2}$	$\overline{Xi} \pm \Delta x$
A-203-1, 3.3	0.154	3.30	3.34	4.53	1.35	3.34±0.11
	0.231	4.95	5.05	4.06	0.80	5.05±0.10
	0.279	5.94	6.12	7.14	1.17	6.12±0.18
A-203-5, 1.5	0.134	3.00	2.90	7.52	2.60	2.90±0.19
	0.202	4.50	4.41	4.53	1.03	4.41±0.11
	0.278	6.00	6.09	8.70	1.43	6.09±0.22
M 123-1, 81.964	0.098	2.05	2.10	4.53	2.15	2.10±0.11
	0.183	4.10	3.98	5.20	1.31	3.98±0.13
	0.280	6.15	6.14	4.53	0.74	6.14±0.11
M 99-5, 82.14	0.098	2.05	2.10	9.00	4.28	2.10±0.22
	0.192	4.11	4.19	5.52	1.32	4.19±0.14
	0.280	6.16	6.14	4.53	0.74	6.14±0.11

The Zn(II) and Cu (II) concentrations in natural waters were determined via the addition of various additives. Photometric and spectrophotometric determination of the concentrations of the studied metal in the sample method, known as the “method of additives” in the literature and widely used in chemical analysis, has been used, which requires the observance of the basic law of light absorption [57]. Based on studies to optimize direct spectrophotometric conditions for the determi-nation of Zn (II) and Cu (II) in real objects and to obtain optimal estimates of the selectivity of its determination in individual and complex mixtures, an expressive spectrophotometric method for analyzing natural waters to determine the content of Zn(II) and Cu (II) ions was developed. Water samples taken for analysis from Omon-khon Spring (Surkhandarya region, Omonkhon village) are complex systems containing, in addition to mineral macrocomponents, cations of various heavy metals.

Composition of natural waters: elemental composition (mg/l): Al-0.007, As-0.0013, Sr-6.6, Mo-0.0016, Mn-0.0005, Cu-0.004, Zn-0.008, Ni-0.0069, Hg-0.00006, mineral composition (mEq/l): K-11.99, Na-11.99, Ca-8.0, Mg-11.39, HCO_3^--6.59, SO_4^{2-}-23.19, Cl^--1.9. A sample of 1.0 L taken from the Omonkhon spring was placed in heat-resistant glass with a capacity of 1000 ml, 10-12 ml of a 1.0 N HNO_3 solution was added, the sample was heated in a sand bath and evaporated to form wet salts. The precipitate was dissolved in 10 ml of distilled water and filtered through glass to a volume of 50 ml.

Method for determination of zinc ions in natural waters. The solution was quantitatively transferred into a flask with a volume of 25 ml, various amounts (1.0-7.0 µg) of standard zinc(II) solution (10.0 µg/ml), and 5 ml of universal buffer solution at pH 6.50 and 1 were added, 5.0 ml of a $1.086 \cdot 10^{-3}$ M solution of HR was also introduced, and the volume was adjusted to the mark with distilled water with subsequent stirring. To improve the selectivity of the method, the following masking agents were added: 4.0 ml F^- and 1 ml $S_2O_3^{2-}$ [57] (10 µg/ml) at calculated concentrations for the binding of aluminum, manganese, copper and arsenic ions. The optical density of KFK-3 was measured at ℓ=3.0 cm relative to that of a blank test solution. The experimental results obtained by the determination of Zn(II) in the composition of samples from the Omonkhon spring and their mathematical processing are presented in Table 6.

Table 6. The results of the determination of the microconcentration of Zn(II) with HR in Omonkhon spring water by the “method of additive” (V_{water}=1.0 l, pH=6.5, ℓ=3.0 cm, n=5, P=0.95).

Introduced Zn^{2+}, µg	$\bar{A}_{565}$	Contined. Zn^{2+} in solution, µg	Found Zn^{2+}, µg $\bar{X} \pm \Delta X$	Quantity of Zn^{2+} in the sample, µg	S	S_r
-	0.141	8.0	7.93±0.193	7.93	0.155	0.0195
1.00	0.158	9.0	8.92±0.180	7.92	0.143	0.0160
2.00	0.174	10.0	9.86±0.150	7.86	0.120	0.0122
3.00	0.193	11.0	10.97±0.144	7.97	0.116	0.0106
4.00	0.209	12.0	11.90±0.128	7.90	0.103	0.0086
5.00	0.225	13.0	12.84±0.195	7.84	0.195	0.0152
6.00	0.245	14.0	14.01±0.163	8.01	0.131	0.0093
7.00	0.262	15.0	15.00±0.23	8.00	0.185	0.0123

Determination of copper(II) ion concentrations in natural waters. The solution was quantitatively transferred to a flask with a volume of 25 ml, various amounts (0.5-2.0 µg) of standard solutions of copper(II) were added; 5.0 ml of universal buffer solution with a pH of 4.0 and 0.9 ml of $1.086 \cdot 10^{-3}$ M solution of HR were added, and the volume was adjusted to the mark with distilled water and mixed. To improve the selectivity of the method, 8.0 ml of F^- and 2.0 ml of OH^- (10 µg/ml) were added at the calculated concentrations for the binding of aluminum, manganese, zinc and arsenic ions. The OD of KFK-3 was measured at ℓ=3.0 cm relative to that of the blank solution. The results obtained and their mathematical processing are presented in Table 7.

Determination of the zinc (II) HR in rainwater. With the aim of establishing the possibility of determining zinc(II) in rainwater, the method “introduced – found” has been used. Rainwater with a known composition of minerals was obtained from the surface water laboratory of the Institute of Hydrometeorology. The composition and content of minerals are presented in the table. 8.

Determination method: In 200 ml of rainwater, 1.0 ml of a standard solution of zinc(II) (10 µg/ml) was introduced, and the system was evaporated to wet salts. Then, the solution was dissolved in 10 ml of distilled water and quantitatively transferred to a 25 ml volumetric flask. Then, 5.0 ml of universal buffer solution with pH=6.50 and 1.5 ml of a $1.0869 \cdot 10^{-3}$ M solution of HR were added, and the volume was adjusted to the mark with distilled water and stirred. The OD of KFK-3 was measured at ℓ=3.0 cm relative to that of the blank solution.

Table 7. The results of the determination of the Cu(II) content in Omonkhon spring water by the additive method (V_{water}=1.0 l, pH=4.0, ℓ=3.0 cm, n=5, P=0.95).

Introduced, Cu^{2+}, μg	$\bar{A}_{595}$	Contined. Cu^{2+} in solution, μg	Found, Cu^{2+}, μg	Quantity of Cu^{2+}, in the sample, μg	S	S_r
-	0.182	4.0	3.96±0.08	3.96	0.063	0.0159
0.50	0.205	4.5	4.48±0.06	3.98	0.050	0.0112
1.00	0.226	5.0	4.95±0.06	3.95	0.052	0.0105
1.50	0.250	5.5	5.48±0.08	3.98	0.063	0.0115
2.00	0.272	6.0	5.96±0.06	3.96	0.045	0.0076

Table 8. Rainwater analysis results (V_{water}=200 ml, pH=6.5, ℓ=3.0 cm, n=3).

Rainwater composition	Introduced Zn^{2+}, μg	A	Found Zn^{2+}, μg	$\overline{X}$	$(Xi-\overline{X})^2$	S	S_r
Ca^{2+}, Mg^{2+}		0.175	9.92		0.0016		
NH_4^+, Cl^-	10	0.172	9.74	9.96	0.0484	0.24	0.024
SO_4^{2-}, NO_3^-		0.180	10.21		0.0625		

Competitiveness of the developed spectrophotometric methods for the determination of zinc (II) and copper (II) ions. In order to establish the competitiveness of the proposed spectrophotometric methods for the determination of zinc(II) and copper(II) ions, as well as to assess the degree of reliability and accuracy of the obtained results, some metrological characteristics and analytical parameters of the developed methods were compared with similar ones obtained by other researchers using other independent methods of analysis.

As an example in tables 9 and 10 presented comparative results obtained by developed methods for the spectrophotometric determination of zinc(II) and copper(II) ions with HR, as well as data discovered by other independent methods and by different researchers when analyzing objects of different nature and complexity.

Table 9. Results of assessing the competitiveness of the developed spectrophotometric method for determining Zn(II) ions.

Analytical parameters of the method	Cloud point extraction	Spectrophotometry	Developed methodology
Buffer solution (pH value)	Acetate, citrate, borate and universal buffer solutions with pH ranges of 2.0 to 12 (pH_{opt}=9,0)	Universal buffer (pH=9.0-10.5)	Universal buffer (pH=5.9-7.0)
Lower limit of determined contents, μg/ml	0.01	0.056	0.175
Concentration range, μg/25ml	0.01-0.8	0.1-1.5	1.0-18.0
Relative standard deviation (S_r)	0.040	0.060	0.037
Sensitivity, ε	7342	35500	42017
Volume of the analyzed solution, ml	25.0	25.0	25.0
References	[68]	[69]	Developed methodology

Table 10. Competitiveness evaluation results of the developed spectrophotometric method for the determination of Cu(II) ions in other organic reagents.

Name of organic reagent	pH_{opt}	Molar ratio Me:R	True molar absorption coefficient, ε	Interfering influence of foreign components	References
Naphthol blue-black B	9.5	1:1	7600	Mn^{2+}(1:1), Ni^{2+}(1:1,5), thiourea, citrate (1:10)	[70]
2-hydroxy-5-iodothiophenol and diphenylguanidine	2,5-4,0	1:1	31700	Cd^{2+}, Co^{2+}, Pd^{2+}(1:0,8); $V^{3+}Fe^{2+}$,(1:1) $Zr^{4+}Al^{3+}$(1:10)	[71]
N^1,N^1-dialkylbenzhydrazide	6.0	1:2	1100	Fe^{2+}, thiourea, citrate	[72]
1-Phenyl-2-(2-hydroxy-3-sulfo-5-nitrophenyl-azo)-butadione-1,3	3.0	1:2	14000	Zr^{4+}, $C_2O_4{}^{2-}$, (1:33) Fe^{2+}, Bi^{3+}, Co^{2+}, Mo^{6+} (1:14), citrate (1:10), Ni^{2+}(1:3.5),	[73]
3-(2^1-Thiazolylazo)-2,6-diaminopyridine	5.90	1:2	10000	TI^{3+}, Zr^{4+}, Ni^{2+}, thiourea, citrate	[74]
Eriohromic blue-black R	3.20	1:2	13000	Ni^{2+} (1:63.5), Al^{3+} (1:24), V^{3+} (1:19.8), Ag^{+} (1:8.16), Cr^{3+} (1:8.0)	[75]
HR	4.0	1:2	20000	Bi^{3+}, Co^{2+}, Fe^{2+} (1:1); Cd^{2+}, $H_2C_6H_5O_7^-$ (1:0.5)	Developed methodology

From the data given in the tables we can conclude that the developed spectrophotometric methods for determination of zinc(II) and copper(II) ions with HR, by metrological characteristics (accuracy, reproducibility, selectivity, lower limit of determined contents, sensitivity, detection limit, expressiveness, etc.) are not inferior to the long-known and widely used analytical methods for determination of these elements and the results obtained in this case are characterized by reliability and validity, which indicates a high competitiveness of the proposed methods of spectrophotometric determination of the investigated metal ions.

5. Conclusion

The results of the analysis of artificial mixtures (Tables 2, 3), standard samples of industrial aluminum and copper alloys (Tables 4, 5), natural waters (Tables 6, 7) and rainwater (Table 8) showed that the results of the spectrophotometric method for the determination of Zn(II) and Cu(II) by HR under optimal conditions were consistent with the literature data and that the correctness, reproducibility, selectivity and low limits of the determined concentrations and relative standard deviation did not exceed 0.043 in all cases. It was shown that in all cases, the determination error did not exceed the confidence interval, which indicated the accuracy and reproducibility of the proposed spectrophotometric method for the determination of zinc(II) and copper(II) with the HR reagent.

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