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Development of a method for cyclic voltametric determination of copper (II) ions in the composition of technological objects

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ABSTRACT

The use of heteroatom organic reagents, such as 5-(o-aminophenyl)-1,3,4-oxadiazole-2-thione, is important in developing selective and sensitive methods for the detection of Cu^{2+} ions. For this purpose, the use of cyclic voltammetric analysis, one of the electrochemical analysis methods, leads to high selectivity. Optimal conditions for CV determination of Cu^{2+} ion with 5-(o-aminophenyl)-1,3,4-oxadiazole-2-thione reagent: found that the linear dependence of the analytical signal on the metal ion concentration at an electrode scanning speed of 50 mV/s in ethyl alcohol solvent is 1.12-9.4 ppm/l. It has been proven that the formation of a complex between an organic reagent and a metal ion on the electrode surface occurs within 6 seconds using chronoamperometric and integral pulse amperometric methods. The half-wave potential of the organic reagent was found to be 0.48 V, and that of the complex formed by the Cu^{2+} ion was 0.65 V, with the potential shifting to the positive side proving the formation of a complex. From the CV of the complex, it was determined that the anodic and cathodic diffusion coefficients were $Dox=2.59*10^{-6}sm^2/s$; $Dred=2,354*10^{-10}sm^2/s$. The fact that the determination of copper(II) ion is not interfered with by Cd(II), Zn(II), and Pb(II) cations in a 1:1 ratio indicates that the developed method has a high selectivity. The developed method found a lower detection limit of copper(II) ion of 1.12 μg/ml. The accuracy of the method was compared with the atomic absorption method, and the calculated Student's coefficient of 2.43 and Fisher's value of 6.37, which are smaller than the values in the table, prove that the accuracy of the method is high. The developed CV method for determining Cu^{2+} ions was applied to the analysis of process water at the Almalyk Mining and Metallurgical Combine, and the relative standard deviation not exceeding 0.0145 indicates the high accuracy of the method.

1. Introduction

Copper is among the most widely used metals in the world. Due to its high heat, electrical conductivity, and flexibility, it is used in many industrial purposes [1]. As a result, there is a need to identify and separate it from ores and technological objects. However, along with copper production, its concentration in environmental objects has been found to have a harmful effect on the environment [2]. Because copper is one of the heavy metals, it plays an important role in the management of many physiological [3] processes in the human body. A lack of copper in the human body can cause anemia and hair loss, but excessive amounts can cause serious health problems [3, 4]. If the concentration of copper (II) ions in the human body exceeds the permissible amount, it causes Wilson's disease, Parkinson's, Alzheimer's, prion diseases, jaundice, liver or kidney damage,

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gastrointestinal tract disorders and schizophrenia [4] is possible. The maximum permissible concentration of copper ions in drinking water was declared by the United States Environmental Protection Agency (USEPA) [5] to be 1.3 μg ml $^{-1}$. This requires the development of methods for determining copper ions in amounts from submicrogram to nanogram [6]. In parallel, several studies have examined copper ion sorption onto various natural and engineered materials for environmental remediation, using both experimental methods and molecular modeling [7]. Despite the insights provided by these studies, selective and quantitative detection methods remain essential for accurately monitoring copper ions in complex real-world systems.

Copper and its compounds are essential catalysts in various organic synthesis [8-10], enabling key reactions such as Ullmann couplings, C–N/C–O bond formations, CuAAC click reactions, and phenol oxidations. Their high efficiency, mild conditions, and low cost make them valuable in pharmaceutical, agrochemical, and material synthesis. This versatility necessitates accurate methods for copper detection and quantification in complex matrices. To date, spectrophotometric methods based on the formation of chelate complexes of copper (II) ion with ammonium pyrrolidinedithiocarbamate [11], 5,10,15,20-tetrakis(4-carboxyphenyl)-21H,23H-porphine [12], N-p-Nitrobenzyl-5,10,15,20-tetrakis(4-sulfonatophenyl) porphine [p-NO_2Bz(Htpps)4-] [13], [4-amino-5-hydroxy-6-[(5-methyl-2-pyridyl)azo]-3-sulfo-1-naphthyl] sulfonyloxysodium (HR) [14] reagents, as well as photometric methods using 2,6-dimercapto-4-methylphenol (DMMP) and 2,6-dimercapto-4-ethylphenol (DMEP), 2,6-dimercapto-4-tert-butylphenol (DMBP) [15] have been developed, but they do not have sufficient selectivity. In redox reactions, catalytic kinetic spectrophotometric methods for the determination of the copper (II) ion at low concentrations with cysteine in a red blood cell medium [16], the N-ethyl-N-(2-hydroxy-3-sulfopropyl)-3,5-dimethoxyaniline derivative of hydrazone 3-methyl-2-benzothiazolinone by activation with hydrogen peroxide [17], and N-phenyl-p-phenylenediamine and m-phenylenediamines [18] have been developed. A method for determining copper ion concentrations from 0.13 to 0.44 μM using a newly synthesized bis-azo dye by four-dimensional infrared spectroscopy (FT-IR) and nuclear magnetic resonance (NMR) has been proposed [19]. In addition, solid-phase extraction of crown ethers is also important for copper (II) ion separation [20], and electrochemical detection methods using oxadiazole products containing heteroatoms to increase selectivity [21] have been developed.

Copper and its oxide nanoparticles are currently also important in the creation of sensors, for example, one of the current problems is the development of electrochemical methods for detecting low levels of biological substances using its redox properties. Methods have been developed for the determination of L-DOPA in the range of 0.050-1200 μM and uric acid in the range of 0.040-2000 μM based on polypyrrole and copper oxide nanoparticles (PPy/CuO) by differential pulse voltammetry [22], paracetamol (PA) by cyclic voltammetry by modifying a carbon paste electrode (CPE) with Cu-ZnO/Np nanoparticles [23], and rutin by colorimetric determination using Cu-guanosine (Cu-Guo NRs) nanoparticles [24]. In addition, copper metal has been used for the decomposition of SO_2 [25], adsorption of NO, CO, and NO_2, vapor phase polymerization of pyrrole [26], and ultraviolet (UV) photodegradation of oxalate malachite green (MG), methyl violet (MV), and eriochrome black T (EBT) based on $La_2MnFe_2O_7$ and $La_2CuFe_2O_7$ nanocomposites [27-29]. In these studies, the detection of aromatic hydrocarbons was conducted using a nanoporous polypyrrole gas sensor with gas chromatography, where the nanoporous structure of the sensor contributed to enhancing its sensitivity. Additionally, the process of extracting and analyzing hydrocarbons was carried out using the dispersive liquid-liquid microextraction method [30]. In the study, a combination of dispersive liquid-liquid microextraction and gas chromatography was employed with a nanostructured polypyrrole-based gas sensor for the rapid detection of pyridine derivatives. As a result, the nanostructures improved the sensor's sensitivity and accelerated the process of detecting pyridine derivatives [31,32].This research developed open-tube gas sensors for the simultaneous detection of alkylamines. The sensors were modified with polypyrrole (PPy) and their sensitivity was enhanced by the addition of crown ethers [33]. The study investigated a method for synthesizing carbon quantum dots (CQDs) from apple juice and graphite. Research was conducted on the fluorescent properties and structure of these carbon quantum dots. Additionally, these CQDs were used as an electrochemical sensor for measuring letrozole.

From the above literature review, it is clear that the identification and separation of the copper (II) ion has not lost its relevance. Therefore, it was aimed to develop a cyclic voltammetric method for determining the microquantity of copper(II) ion with 5-(o-aminophenyl)-1,3,4-oxadiazole-2-thione reagen.

2. Materials and Methods

2.1. Materials

2.1.1. Preparation of copper (II) ion standard solution

In this research, to prepare a $1\cdot10^{-3}$ M solution of copper (II) ion, 0.0182 g of $Cu(CH_3COO)_2$ salt was taken, placed in a 100 ml volumetric flask, dissolved in double-distilled water, made up to the mark with bidistilled water, mixed, and standardized. All chemicals (99.99% purity) were purchased from Sigma Aldrich (USA).

2.1.2. Preparation of a standard solution of 5-(o-aminophenyl)-1,3,4-oxadiazole-2-thione

A solution was prepared by dissolving 0.0193 g (0.001 M) of 5-(o-aminophenyl)-1,3,4-oxadiazole-2-thione in a 100 ml flask and dissolving it in acetone. The purity of the 5-(o-aminophenyl)-1,3,4-oxadiazole-2-thione reagent was determined by thin-layer chromatography [34] (Figure 1).

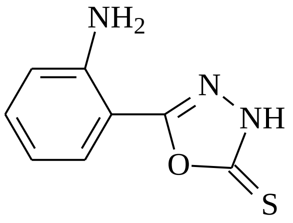


Fig. 1. Structural formula of 5-(o-aminophenyl)-1,3,4-oxadiazole-2-thione (D-117).

2.2. Methods

2.2.1. Used methods and tools

The results of the analysis were carried out on a manual potentiostat CS 350 CS Potentiostat/Galvanostat. A 3-electrode electrochemical cell was used: 2 platinum electrodes and a reference silver chloride (AgCl||Ag) electrode. Bidistilled water was obtained on a Heal Force CR-RO30 (China) instrument. The specific electrical conductivity of bidistilled water was 0.475 mcm/m. A 2.0 mL piston microburette was used to titrate the 5-(o-aminophenyl)-1,3,4-oxadiazole-2-thione solution, which allowed for titration of the titrant to an accuracy of 0.001 mL.

2.2.2. Effect of solvents

Due to the insolubility of the organic reagent in water, various solvents (ethyl alcohol, acetic acid, butyl alcohol and DMFA) were used to study the possibility of complex formation of copper(II) ion with oxadiazole by cyclic voltammetric method.

2.2.3. Cyclic voltammetric analysis method

1.0 ml of a 1.0 μg/ml Cu^{2+} standard solution and 40.0 ml of organic solvent (ethyl alcohol, acetic acid, butyl alcohol, and DMFA) were added to a 50.0 ml cell, and a 0.001 M alcoholic solution of the 5-(o-aminophenyl)-1,3,4-oxadiazole-2-thione reagent was poured on top. Electrodes were lowered into the solution, the solution was rotated at a speed of 420 revolutions, and cyclic voltammograms were obtained by applying a voltage to the electrode at a saccharification rate of 50mV/sec.

2.2.4. Chronoamperometry

There are two types of chronoamperometry: controlled potential chronoamperometry and controlled current chronoamperometry. The chronoamperometry method is crucial for studying the chemical reactions that occur in the solution on the electrode's surface, particularly the reaction mechanism of organic substances. Chronoamperometry was used to study the number of electrons participating in oxidation-reduction reactions and the speed of the reaction on the surface of the CS 350 Potentiostat/Galvanostat (Wuhan, China) electrode of the substance to be determined at different voltages and environments. For this, 1.0 ml of a 0.001 M alcoholic solution of 5-(o-aminophenyl)-1,3,4-oxadiazole-2-thione reagent was placed in an electrochemical cell, and 40.0 ml of an alcoholic solvent and 1.0 ml of a 1.0 μg/ml Cu^{2+} standard solution were added to it.

3. Results and Discussion

This section presents the results obtained by cyclic voltammetric, chronoamperometric, and amperometric methods of 5-(o-aminophenyl)-1,3,4-oxadiazole-2-thione and its copper (II) ion at a voltage of 0.2-1.2 volts, as well as graphs and mathematical calculations such as the number of electrons involved in the reaction and the diffusion coefficient.

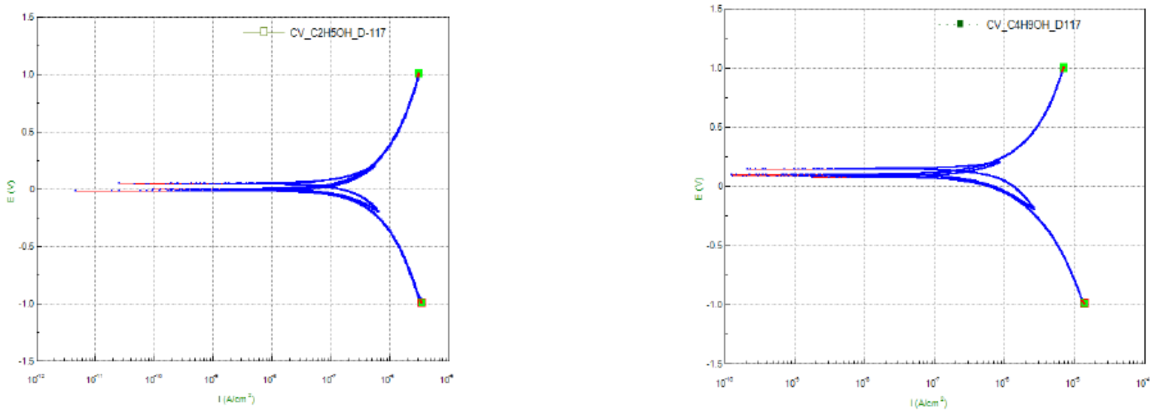
3.1. Electrochemical analysis methods

3.1.1. Cyclic voltammetry

The reaction mechanism of complex formation of Cu (II) ion using the 5-(o-aminophenyl)-1,3,4-oxadiazole-2-thione reagent and the number of electrons involved in it were determined. Manual potentiostat CS 350 Potentiostat/Galvanostat device with hermetic cell with 3 electrodes (2 platinum electrodes and silver chloride (AgCl||Ag) electrodes as a reference) by adding 1.0 ml solution of 1.0 μg/ml Cu^{2+} standard solution to the cell, a voltage of 10-120 mV/s was applied to the electrode, and voltammograms were formed when a voltage of 50 mV/s was applied; therefore, 50 mv/sec was found to be optimal.

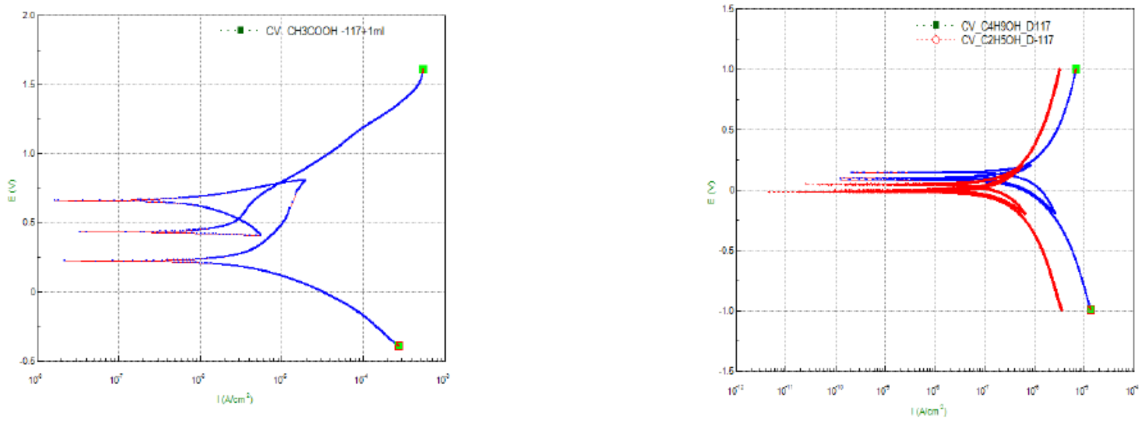
To study the effect of solvents of various natures (ethyl alcohol, acetone, acetic acid, butyl alcohol) on the combination of an organic reagent with a metal ion in solution and the reduction of the solution resistance, a potential of 50 mV/s was applied to the indicator electrode (silver chloride (AgCl||Ag) electrode as a reference), and the Tafel representation of the obtained cyclic voltammograms is presented in Figure 2.

These graphs depict the Tafel representation of the cyclic voltammetric method. This Tafel analysis provides important information for evaluating the electrochemical properties, reaction rate, and formal voltage characteristics of the electrode. Based on the results obtained, it can be concluded that the oxidation of the 5-(o-aminophenyl)-1,3,4-oxadiazole-2-thione reagent was observed on the surface of a platinum electrode under the influence of various solvents, in which the amino groups exhibit basic properties and when exposed to a weak acid, as a result of the formation of a salt, the copper ion can form a chemical bond with sulfur, and when exposed to alcohol, it is observed that a simple ether is formed with sulfur, as a result, the possibility of forming a bond with the copper ion with the amino group increases, which is explained by the peaks of the cyclic voltammograms, the formation of three peaks separated from each other in an acidic environment indicates the binding of copper and amino groups. Based on the graphs, the anode and cathode currents and the corresponding potentials were measured, and the diffusion coefficients and half-wave potentials of the organic reagent and complex compound were determined. In this case, ethyl alcohol was chosen as the optimal solvent for the binding of copper(II) ion to 5-(o-aminophenyl)-1,3,4-oxadiazole-2-thione, since the proximity of the peaks in it is explained by the binding of the nitrogen atom to the copper(II) ion, and the mobility of the copper(II) ion in the solution is achieved by the reduction in resistance due to the binding of the acetate ion to ethyl alcohol (Table 1). Based on the results obtained, the electrochemical transformations of 5-(o-aminophenyl)-1,3,4-oxadiazole-2-thione and its binding to copper (II) ion were studied in ethyl alcohol with a voltage of 50 mV/second applied to the electrode, and the half-wave potential values and diffusion coefficients were calculated (Figure 3 and Table 2).



(a) CV of a solution of 5-(o-aminophenyl)-1,3,4-oxadiazole-2-thione in ethyl alcohol

(b) CV of a solution of 5-(o-aminophenyl)-1,3,4-oxadiazole-2-thione in butyl alcohol



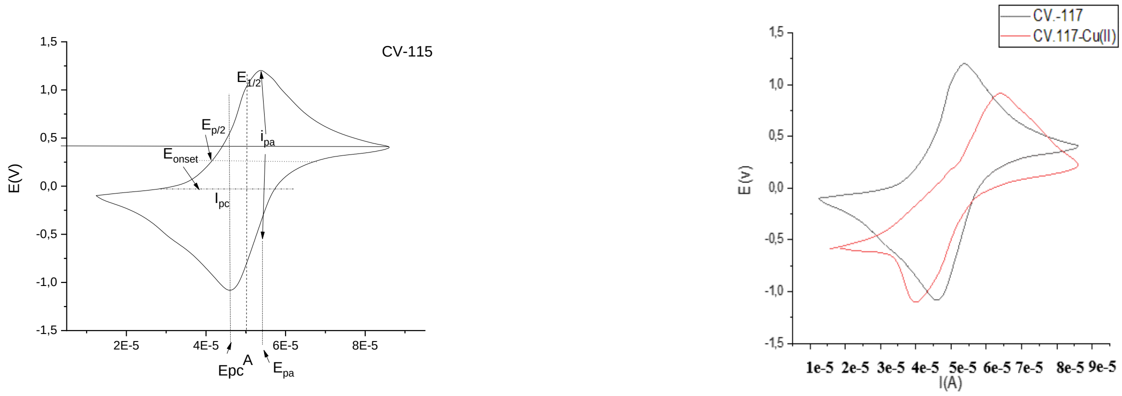
(c) CV of a solution of 5-(o-aminophenyl)-1,3,4-oxadiazole-2-thione in acetic acid

(d) CV of a solution of 5-(o-aminophenyl)-1,3,4-oxadiazole-2-thione in butyl alcohol and ethyl alcohol

Fig. 2. Cyclic voltammograms of 5-(o-aminophenyl)-1,3,4-oxadiazole-2-thione in various solvents

Table 1. Experimental data obtained by CV method of 5-(o-aminophenyl)-1,3,4-oxadiazole-2-thione

Substance	**$E_{p,\ a}$ V**	**$E_{p,\ c}$ V**	**$E_p \cdot 10^3$, V**	**$E_{1/2}$, V**	**$I_{p,\ a}$, A**	**$I_{p,\ c}$, A**
Ethyl alcohol	$3{,}58*10^{-6}$	0.3071	$0.05*10^3$	-0.017	$1.05*10^{-6}$	$9.37*10^{-7}$
Butyl alcohol	-0.079	0.0595	$0.05*10^3$	0,095	$9.98*10^{-6}$	$9.99*10^{-7}$
Acetic acid	0.54	0.1045	$0.05*10^3$	0.657	$2.37*10^{-6}$	$1.12*10^{-5}$
	0.41			0.430	$2.6*10^{-6}$	
	$1.02*10^{-5}$			0.22	0.014	



(a) CV of a solution of 5-(o-aminophenyl)-1,3,4-oxadiazole-2-thione in ethyl alcohol.

(b) CV of the complex formed by Cu (II) ion in a solution of 5-(o-aminophenyl)-1,3,4-oxadiazole-2-thione in ethyl alcohol

Fig. 3. CV of 5-(o-aminophenyl)-1,3,4-oxadiazole-2-thione

Table 2. Electrochemical parameters of the complex formed by the reagent 5-(o-aminophenyl)-1,3,4-oxadiazole-2-thione with copper (II) ion

Substance	**$E_{p,\ a}$ V**	**$E_{p,\ c}$ V**	**$E_p \cdot 10^3$, V**	**$E_{1/2}$, V**	**$I_{p,\ a}$, A**	**$I_{p,\ c}$, A**
Ethyl alcohol	0.318	0.355	0.05 $*10^3$	9,39 $*10^{-3}$	9.3 $*10^{-6}$	9.4 $*10^{-6}$

The results of the complex formation of the 5-(o-aminophenyl)-1,3,4-oxadiazole-2-thione reagent with Cu (II) ions are presented. Calculations showed that the optimal conditions for the formation of the complex obtained using ethyl alcohol were that 2 electrons participated in the reaction. This indicates the movement of electrons in the copper (II) ion. Based on these results, a scheme of the reaction was suggested.

3.1.2. Chronoamperometry

By the method of chronoamperometric analysis, a constant voltage was applied to the electrode, and the number of electrons and the speed of the reaction were determined from the time dependence graph of the current generated as a result of the reaction, using Cottrell's formula. This allows to study the reaction mechanism. A 0.001 M alcoholic solution of the reagent 5-(o-aminophenyl)-1,3,4-oxadiazole-2-thione was placed in a 50.00 ml cell (4.1), and three electrodes were lowered, mixed at a speed of 420 rpm, then stopped, and the time dependence of the current strength was studied when a voltage of 0.1-1.2 volts was applied to the electrode. In this case, the course of the reaction was determined in 0.25 seconds (Scheme 1).

In the graph in Figure 4, the two different red and purple lines show the doubling of voltage. These voltage changes, electrochemical reactions, and oxidation-reduction processes at the electrodes prove that a complex is formed between the reagent and copper.

3.1.3. Integrated Pulse Amperometric Detection

Two platinum and silver chloride electrodes are placed in an electrolyzer containing 1 ml of a 0.001 M alcoholic solution of 5-(o-aminophenyl)-1,3,4-oxadiazole-2-thione reagent, 1.0 ml of a 1.0 µg/ml Cu^{2+} standard solution, and 0.0 ml of ethyl alcohol in a 50.0 ml cell. When the voltage Emax= 0.2±2.0 is applied to the electrode, the oxidation-reduction process occurs, Cu^{2+} changes to Cu^0, as a result, a current is generated. The amount of Cu^{2+} is found by measuring it. The optimal one was selected from the results ranging from E1=0.2 V for 60 seconds to E2=-1.2 V for 300 seconds. Among the results, amperograms obtained at voltages of 0.6 V, 1.2 V, and 2.0 V and for 25 seconds were analyzed.

In Figure 5a, when a voltage of 0.6 volts was applied to the reagent 5-(o-aminophenyl)-1,3,4-oxadiazole-2-thione, the current remained unchanged after 10 seconds, indicating that it was sufficient for the electrooxidation of the reagent, and did not increase even at a voltage of 1.2 volts in 10 seconds. Figure 5b shows that the formation of a complex of copper (II) ions with 5-(o-aminophenyl)-1,3,4-oxadiazole-2-thione took place in 5 seconds at a voltage of 0.6 volts. A rapid change in current is observed in the part of the graph around the potential of 0.6 V. This indicates the occurrence of oxidation-reduction processes, that is, the formation of a complex of 5-(o-aminophenyl)-1,3,4-oxadiazole-2-thione with copper (II) ions. Therefore, it is concluded that a complex is formed at a potential of 0.6 V. Electrochemical processes such as the reduction of copper ions and the oxidation of 5-(o-aminophenyl)-1,3,4-oxadiazole-2-thione occur at 1.2 V and 2.0 V, respectively.

3.2. Calculation of analysis results

Using certain criteria, using a standard solution of Cu^{2+} and the example of the oxidation of 5-(o-aminophenyl)-1,3,4-oxadiazole-2-thione at a platinum disk electrode, the reversibility of the heterogeneous electron transfer process was assessed and the number of electrons transferred to each molecule was calculated.

A number of computational methods are used to determine the oxidation or reduction of ongoing electrochemical processes, as well as to determine the stage of progress of the reaction. These calculations were performed using the Cottrell equation [35,36].

$$\mathrm{I = n * F * A * D^{\frac{1}{2}} * C_s * \pi^{-\frac{1}{2}} * t^{-\frac{1}{2}}} \tag{1}$$

The diffusion coefficient was calculated based on this formula:

$$\mathrm{D = \frac{I * \pi * t}{n^2 * F^2 * A * C_s^2}} \tag{2}$$

$$\mathrm{D_{ox} = \frac{1{,}05 * 10^{-6} * 3{,}14 * 298}{2^2 * 96500^2 * 1^2 * 1 * 10^{-4}} = 2{,}59 * 10^{-6}\,\frac{sm^2}{s}}$$

Dred=2,354*10-^{10}sm^2/s

n = number of electrons for the electrochemical process,

F = Faraday (1 mol of electrons and equal to 96,485.339 Coulombs per mol),

R = Universal gas constant (8.31447 J^{-}K^{-1}-mol^{-1}),

T = temperature (K)

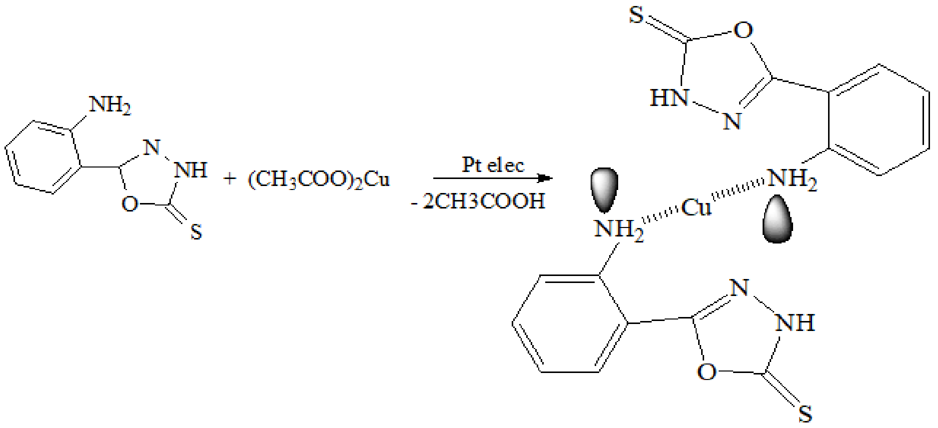
A = electrode area (cm^2),

c = concentration (mol/cm^3),

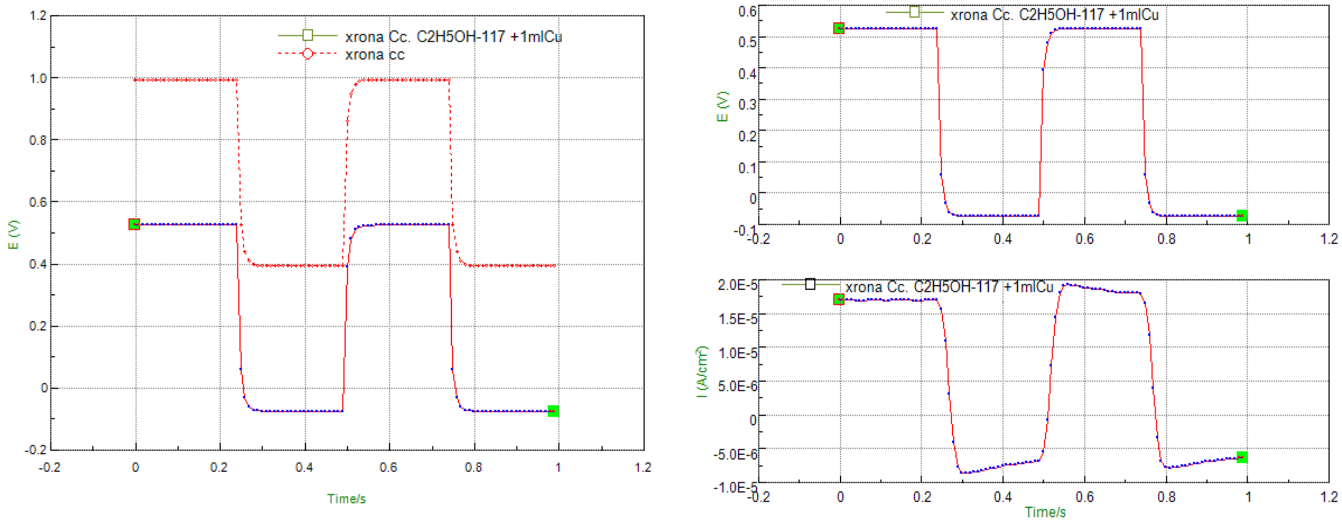
D = diffusion coefficient (cm^2/s), and

$$\mathrm{n = \sqrt{\frac{I * \pi * t}{D * F^2 * A * C_s^2}}} \tag{3}$$

2 electrons were involved in the reaction, which was carried out under optimal conditions. Formula 3 was used to find this electron number.



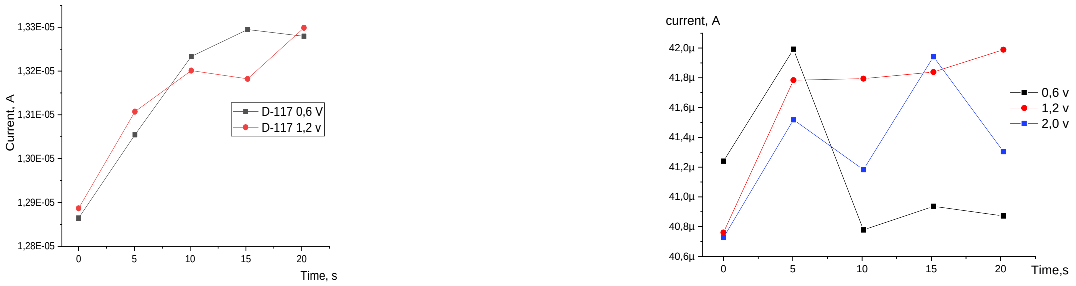
Scheme 1. The copper(II) ion combines its 2 paired electrons (total of 4) and 1 odd electron (total of 2 due to 1 hydrogen from the –NH2 group) with its empty cells.



(a) Chronoamperograms of 5-(o-aminophenyl)-1,3,4-oxadiazole-2-thione and its complexes with (2 -) copper (II) ions.

(b) Chronoamperograms of the dependence of the current strength on time and voltage of the complex of 5-(o-aminophenyl)-1,3,4-oxadiazole-2-thione with Cu (II) ions.

Fig. 4. Chronoamperograms of 5-(o-aminophenyl)-1,3,4-oxadiazole-2-thione and its complex with Cu (II) ion.



(a) Amperograms of 5-(o-aminophenyl)-1,3,4-oxadiazole-2-thione under alternating voltage.

(b) Amperograms of the complex of 5-(o-aminophenyl)-1,3,4-oxadiazole-2-thione with copper (II) ion at alternating voltages.

Fig. 5. Results of integrated pulse amperometric determination of the complex formed by 5-(o-aminophenyl)-1,3,4-oxadiazole-2-thione reagent and copper (II) ion

3.3. IQ spectrum analysis analysis

The IR chemical structure analysis of 5-(o-aminophenyl)-1,3,4-oxadiazole-2-thione and its copper complexes was studied; the results obtained are presented in Figure 6 a for 5-(o-aminophenyl)-1,3,4-oxadiazole-2-thione and in Figure 5b for the thione complex with copper. From the spectrum, the absorption band between 3200–3400 cm^{-1} is characterized by N-H vibrations, and the 1600–1700 cm^{-1} vibrations characterize C=S double bond vibrations. Peaks in the range of 1450–1600 cm^{-1} correspond to C=C vibrations in the aromatic ring. The vibrations in the 1500–1600 cm^{-1} region correspond to C=N, and the vibrations in the 2800–3000 cm^{-1} region correspond to C–H vibrations in aromatic and alkyl groups, as well as the presence of an amino group and a sulfide group, which are characteristic absorptions that allow us to confirm the structure, indicating that the substance we are analyzing is indeed 5-(o-aminophenyl)-1,3,4-oxadiazole-2-thione, and allows us to compare it with the IR spectra of the formed complexes. For this purpose, the structure of the complex formed by 5-(o-aminophenyl)-1,3,4-oxadiazole-2-thione with copper was studied using IR spectroscopy. As can be seen from the spectrum, almost all the peaks in the spectrum obtained for 5-(o-aminophenyl)-1,3,4-oxadiazole-2-thione are present, and only in the short wavelength region of the spectrum, i.e., in the region of 410–450 cm^{-1}, a peak with a higher intensity than that of the original substance appeared due to the substitution of a copper(II) ion for hydrogen to form a compound. During the analysis of the literature, it was found that the vibration in this area is indeed characteristic of metals, especially copper [37]. Through this spectroscopic analysis, it is possible to conclude that there is an interaction between 5-(o-aminophenyl)-1,3,4-oxadiazole-2-thione and copper and the formation of a complex.

3.4. Effect of copper (II) ion concentration on the analytical signal

In the developed CV method, the correct linearity of the concentration of copper (II) ion was determined through the dependence on the maximum current strength, and the error was found. In this case, the effect on the CV curve was determined using the optimal conditions obtained in the previous analysis, that is, with a voltage of 50 mV/s applied to the indicator electrode, 1.0 ml of 5-(o-aminophenyl)-1,3,4-oxadiazole-2-thione, variable amounts of Cu^{2+} standard solution, and ethyl alcohol were added, and the analysis was performed by lowering the three electrodes. Results are presented in Figure 7. Based on the CV result presented in Figure 7, a linear relationship was observed in the analytical signal in the Cu^{2+} concentration range of 1.12–9.40 ppm/L, with a deviation occurring at higher concentrations. This is due to the correlation laws between molecular weight and diffusion coefficients (D) in certain solvents [38]. However, it has been noted that the relationship between D and molecular weight is very complex [39]. Initially, the main reason for the increase in current with increasing concentration is that there are enough charge carriers in the solution, and the charges move more, which leads to an increase in the analytical signal. After a certain amount, excessive charge carriers increase, and, therefore, density in the paths along which charges move causes the diffusion to slow down. As a result, analytical signals become smaller. To prove the validity of the developed method, errors were found using the "entered-found" method, and the correlation coefficient was calculated based on the voltammogram values obtained from the cyclic voltammetry method of copper-5-(o-aminophenyl)-1,3,4-oxadiazole-2-thione. The obtained results are presented in Figure 8 and Table 3. Figure 8 shows that the correlation coefficient R=0.9948 was calculated for the dependence of the copper (II) ion on the analytical signal in the range of 1.12 ppm/l - 9.4 ppm/l. This indicates the correctness of the method developed for closeness 1. The lower detection limit was found based on the graph of the dependence of the error on the amount of substance found in the table of the relationship between the calculated amount of substance and the analytical signal in Table 3 and Figure 9.

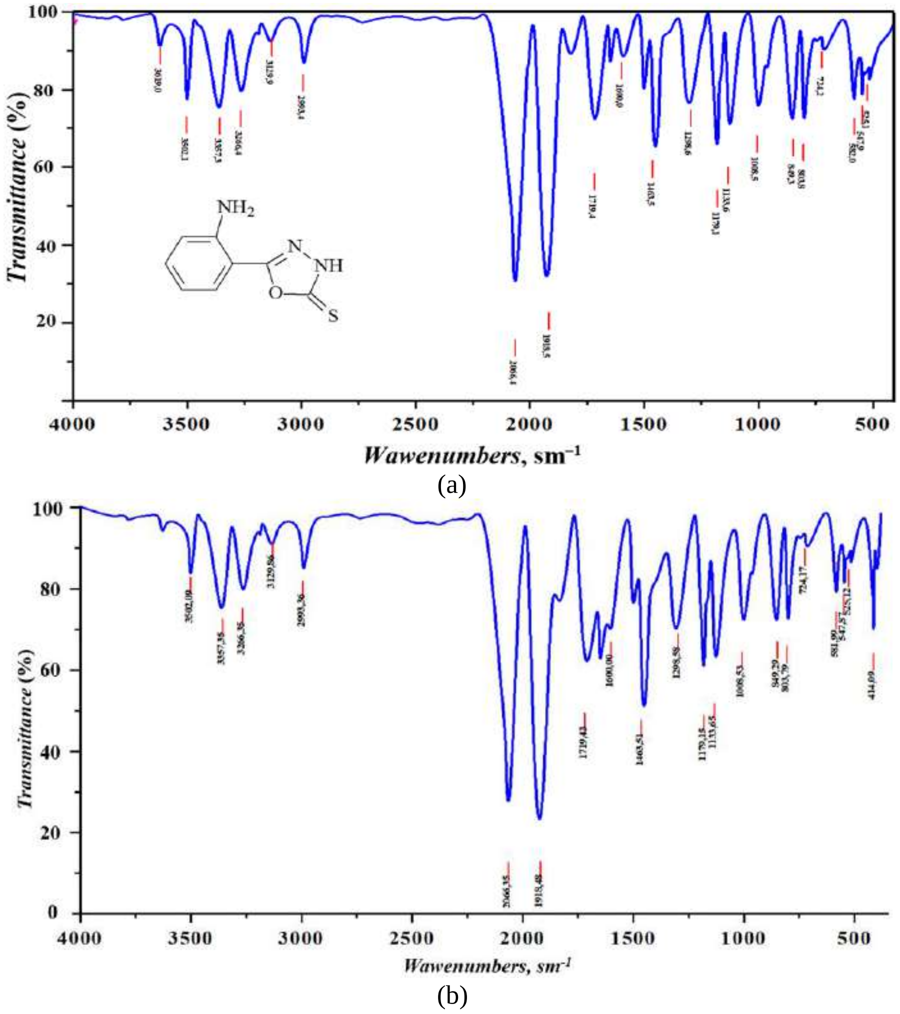


Fig. 6. (a) IR spectrum of 5-(o-aminophenyl)-1,3,4-oxadiazole-2-thione, (b) IR spectrum of the copper(II) complex with 5-(o-aminophenyl)-1,3,4-oxadiazole-2-thione

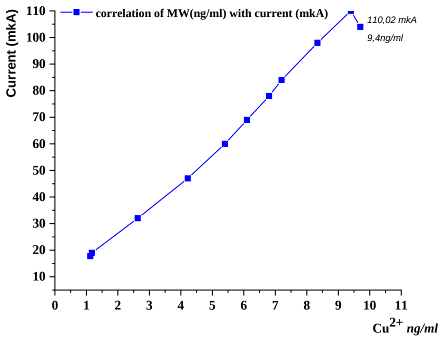


Fig. 7. Linear relationship between analytical signal and copper (II) ion concentration

Table 3. Evaluation of the accuracy of the cyclic voltammetry method in the determination of copper (II) ion with 5-(2-aminophenyl)-1,3,4-oxadiazole-2-thione

Entered Cu^{2+} ng/ml	I, mkA	Found ng/ml $\bar{X}\pm\Delta X$	S	Sr
1.12	17.75	1.10±0,04	0,025	0,014
2.60	31.77	2.59±0,03	0.02	0,011
4.22	56.50	4.2±0,03	0,017	0,099
6.40	75.18	6.39±0,01	0,012	0,007
9,40	110.02	9,39±0,02	0,007	0,004

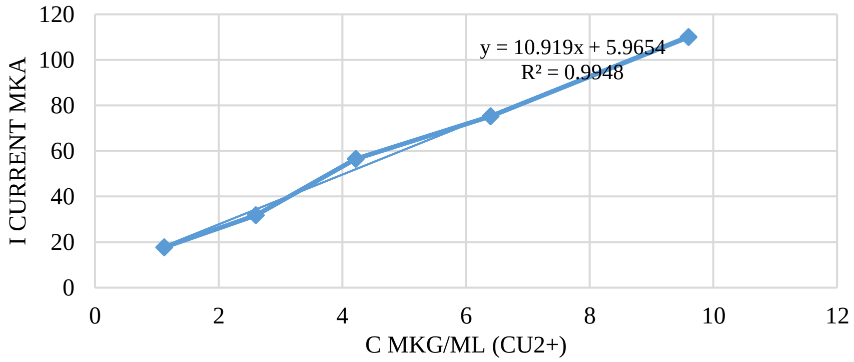


Fig. 8. Correlation coefficient between current (Ip) and Cu (II) concentration

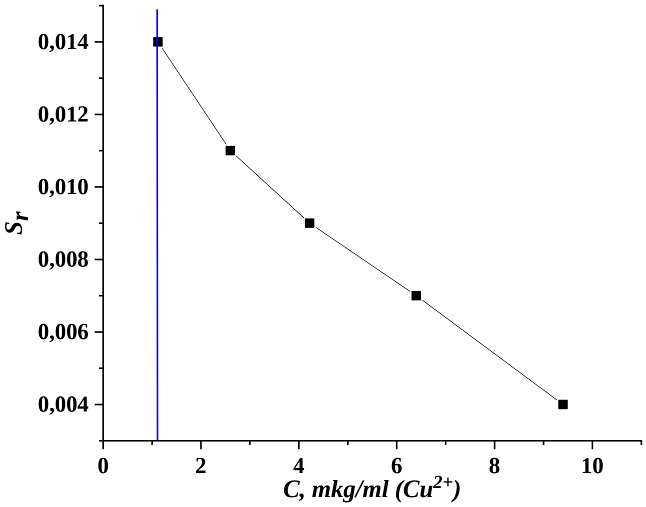


Fig. 9. Graph of copper ion content versus error (the lower detection limit of copper (II) ion was 1.12 ppm/l.)

3.5 Influence of foreign ions on the cyclic voltammetric determination of copper (II) ion

To assess the selectivity of the developed method, the effect of foreign ions was studied. For this, added into a 50 ml quartz glass cell, 0.001 M 0.01 ml of 5-(2-aminophenyl)-1,3,4-oxadiazol-2-thione, pH = 4.2-4.5, metal ions solution was added to a 10 ng/ml solution of Cu (II) ions in a ratio of 1:0.5 Ni(II), 1:0.12 Ti (II), 1:0.45 V(III), 1:0.27 Zn (II), 1:0.32 Fe(III), 1:0.19 Pb(II), 1:0.18 Mn(II), 1:0.40 Cd(II), and ethyl alcohol was added until the total solution was 50 ml. Three electrodes were lowered into the solution. The solution was rotated at 420 TPM (turns per minute) on a magnetic stirrer at room temperature to ensure uniform distribution of ions. Nitrogen gas was passed for 10 minutes to remove oxygen from the solution, and then the solution was quenched. The voltammetric measurements during the electrolysis process were obtained by applying a voltage of 50 mV/s to the electrode. The results are presented in Table 4 using the “entered-found” method.

As can be seen from the obtained data, it was found that Cd (II), Zn (II), and Pb (II) ions do not destroy in a 1:1 ratio during cyclic voltammetric determination of 10 ppm/l copper (II) ion. However, we know that it can exist in natural objects in ratios larger and smaller than those found in nature. Nickel(II), cadmium(II), EDTA ions, titanium(II), manganese(II), iron(II), and lead(II) ions are removed by adding tartaric acid.

The relative standard deviations of the cyclic voltammetric determination of copper (II) ion in binary, ternary, and more complex mixtures imitating real natural objects and industrial materials did not exceed 0.27, which proves that the developed method can be applied to the analysis of environmental objects, materials of various nature (natural and waste waters, concentrates, ores, minerals, and other objects). The developed method was applied to the analysis of process water of the Almalyk Mining and Metallurgical Combine. First, the water content was analyzed using atomic absorption analysis (ICP-AES, Thermo Scientific iCAP Pro, USA). After that, determination was carried out using cyclic voltammetric analysis. In this case, a 1.0 ml aliquot of the sample was taken, and 1.0 ml of 0.1% tartaric acid, 0.01

ml of 5-(o-aminophenyl)-1,3,4-oxadiazole-2-thione and ethyl alcohol were added to it; then three electrodes were lowered, and a voltage of 50 mV/s was applied to the electrodes, and the maximum current was measured. The obtained results are presented in Table 5. The calculated Fisher's exact value (F=6.37) and the Student's coefficient of the F function for a reliability probability of P=0.95 are less than 2.43 (Fcalc. < Ftable), showing high accuracy of the developed method and the absence of systematic error.

3.6 Evaluation of competitiveness with previous work

The determination of copper (II) ions from samples is an important issue in analytical chemistry. The competitiveness of the CV method for the determination of Cu (II) ion was studied and is presented in Table 6.

Table 4. Influence of foreign cations on determination of copper (II) ion with 5-(2-aminophenyl)-1,3,4-oxadiazol-2-thione by cyclic voltammetric method (CCu = 10,0ppm/l; E 1/2 =0,65V)

Foreign cation; [x]	**Entered [x] ppm/l**	**Cu^{2+}/[x]**	**Founded Cu^{2+} ppm/l ; ($\bar{x}\pm\Delta X$; P=0,95)**	**N**	**S**	**Sr**
Nickel (II)	22,0	0,50	9,97 ±0,04	5	0,03	0,003
Zinc (II)	27.,0	0,41	9,94±0,07	5	0,06	0,006
Titanium (II)	84,0	0,12	9,90 ±0,11	5	0,09	0,009
Vanadium (III)	12,0	0,45	9,93 ±0,09	5	0,07	0,007
Iron (III)	28,0	0,32	9,85 ±0,17	5	0,14	0,014
Lead (II)	46,0	0,19	9,83 ±0,18	5	0,14	0,014
Manganese (II)	52,0	0,18	9,86 ±0,19	5	0,15	0,015
Cadmium (II)	23,0	0,40	9,71 ±0,33	5	0,27	0,028

Table 5. Results of determination of copper (II) ion from the technological solution (P=0,95, n=3)

Mixing components, mkg	**Method**	**Amount of founding copper(II) X_i, mkg**	**Xi_{med}**	**S**	**S_r**	**ΔX**	**Tp**	**F**
Ca (10,6),	CV	3,18	3,2	0,025	0,0145	0.04	2,78	6,37
Fe (28),		3.21						
Pb (45),		3,23						
Ni (4,06)	Atomic absorption method	3,2	3.2	0,01	0,0057	0,02		
Cu(3,2)		3.19						
Cd (4,12),		3.21						
Mn (11,45),								
Zn (5,41),								

Table 6. Comparison with previous works in the Cu(II) determination (last 5 years)

No.	**Name of analytical agent**	**Method**	**Samples**	**Detection limit**	**Year, Ref.**
1	Tyrosinase	Colorimetric	Water and milk	Cu(II) is 0.01 μg/l	2018, [39]
2	Pyrazine triphenylamine	Fluorescent chemosensor	Water samples and others	Cu(II) is 2.47×10^{-8} mol L^{-1}	2020, [40]
3	Carbon quantum dots	Ratiometric fluorescent	River water	Cu(II) is 0.43 nM	2019, [41]
4	Waste cotton fabric- copper chelator cuprizone (WCF-CPZ)	Colorimetric sensor	Lake water and milk	Cu(II) is 0.13 mg/L	2022, [42]
5	2-aminoterephthalic acid (NH_2-H_2BDC)	Highly fluorescent	Milk samples	Cu(II) is 11.07 μM	2024, [43]
6	Mandarin peel biochar (mbc)	Multifaceted Fluorescent Probe	Tap and Drinking Water	Cu(II) is 0.01 μM	2024, [44]
7	Rice husk-based ion-imprinted polymer (RH-CIIP)	Fluorescent chromophores	Lake water	Cu(II) is 5.62 μg/L	2023, [45]
8	1,4-Benzenedithiol-2,5-diamino-hydrochloride-1,3,5-triformylbenzene (Covalent-Organic Frameworks)	Cyclic voltammetry (CV) and electrochemical impedance spectroscopy (EIS)	Wastewater	Cu(II) is 0.0660 μM	2020, [46]
9	5-(o-aminophenyl)-1,3,4-oxadiazole-2-thione	Cyclic voltammetry	River water	Cu(II) is 1.12 ppm/ L	Present work

The comparison results show that different detection methods with different analytical reagents are used to determine Cu(II) ion, but these methods and analytical reagents have disadvantages, such as high cost, time-consuming, and expensive equipment. The use of the heteroatom-containing 5-(o-aminophenyl)-1,3,4-oxadiazole-2-thione reagent in this cyclic voltammetric determination of copper (II) ion increases selectivity and sensitivity. In addition, the method of cyclic voltamperometric analysis allows for the determination of several ions in one solution with a half-wave potential difference of less than 0.05 V.

4. Conclusion

The cyclic voltammetric method for the determination of copper (II) ion in the organic phase using heteroatom organic reagents was developed. It was determined that the electrochemical parameters of the 5-(o-aminophenyl)-1,3,4-oxadiazole-2-thione reagent in the organic phase: anode and cathode diffusion coefficient D_{ox}=$2{,}59 * 10^{-6} sm^2/s$; D_{red}=$2{,}354*10^{-10}$$sm^2/s$, and half-wave potential equal to 0.65V. After the addition of copper (II) ion, based on the change in parameters, the selective effect was increased by reducing interfering ions, and the half-wave potential of the complex compound was determined to be 0.65 V, and the diffusion coefficients were determined. According to the developed method, the linear relationship is between 1.12-9.4 ppm/l, and the correlation coefficient is close to 1, which proves that the developed method has high accuracy and sensitivity. The developed method was used in the analysis of technological water at the Almalyk Mining and Metallurgical Combine, and it was determined that there was no systematic error by the atomic absorption method, and it was applied to the analysis of natural objects.

References

[1] A. Khezri, L. Edjlali, M. Eshaghi, M. T. Vardini, H. Basharnavaz, A novel [3-(4-methoxyphenyl)isoxazole-5-yl]-methanol compound: synthesis and effect on corrosion inhibition of copper in 1 M sulfuric acid solution. *Chem. Rev. Lett.* 6 (2022), 113-118, https://doi.org/10.22034/crl.2022.306118.1124.

[2] T. Saeed, A. Naeem, I. U. Din, M. A. Alotaibi, A. I. Alharthi, I. W. Khan, T. Malik, Structure, nomenclature and viable synthesis of micro/nanoscale metal organic frameworks and their remarkable applications in adsorption of organic pollutants. *Microchem. J.* 159 (2020), 105579-105584.

[3] a) G. Ozzeybek, S. Erarpat, D. S. Chormey, M. Fırat, C. Buyukpınar, F. Turak, S. Bakırdere, Sensitive determination of copper in water samples using dispersive liquid-liquid microextraction-slotted quartz tube-flame atomic absorption spectrometry. *Microchem. J.* 132 (2017), 406-413; b) J. F. Zhang, Y. Zhou, J. Yoon, Y. Kim, S. J. Kim, J. S. Kim, Naphthalimide modified rhodamine derivative: ratiometric and selective fluorescent sensor for Cu2+ based on two different approaches. *Org. Lett.* 12 (2010), 3852-3862; c) S. J. Hoseyni, M. Manoochehri, M. D. Asli, A novel Copper (II) Schiff base complex: synthesis, characterization, and antibacterial activity. *Chem. Rev. Lett.* 6 (2022), 278-285, https://doi.org/10.22034/crl.2022.168076.

[4] a) S. Prasad, T. Halafihi, Development and validation of catalytic kinetic spectrophotometric method for determination of copper(II). *Microchim. Acta* 142 (2003), 237-244; b) J. Y. Noh, G. J. Park, Y. J. Na, H. Y. Jo, S. A. Lee, C. Kim, A colorimetric "naked-eye" Cu (II) chemosensor and pH indicator in 100% aqueous solution. *Dalton Trans.* 43 (2014), 5652-5656; c) H. Kim, Y. J. Na, E. J. Song, K. B. Kim, J. M. Bae, C. Kim, A single colorimetric sensor for multiple target ions: the simultaneous detection of Fe2+ and Cu2+ in aqueous media. *RSC Adv.* 4 (2014), 22463-22469; d) J. Isaad, A. El Achari, Water-soluble coumarin based sequential colorimetric and fluorescence on-off chemosensor for copper (II) and cyanide ions in water. *Opt. Mater.* 127 (2022), 112275-112284.

[5] E. Castillo, J. L. Cortina, J. L. Beltrán, M. D. Prat, M. Granados, Simultaneous determination of Cd (II), Cu (II) and Pb (II) in surface waters by solid phase extraction and flow injection analysis with spectrophotometric detection. *Analyst* 126 (2001), 1149-1153.

[6] a) N. Mahendra, P. Gangaiya, S. Sotheeswaran, R. Narayanswamy, Investigation of a Cu (II) fibre optic chemical sensor using fast sulphon black F (FSBF) immobilised onto XAD-7. *Sens. Actuators B: Chem.* 81 (2002), 196-201; b) S. G. Lee, H. S. Choe, Spectrophotometric determination of cadmium and copper with ammonium pyrrolodinedithiocarbamate in nonionic Tween 80 micellar media. *Bull. Korean Chem. Soc.* 22 (2001), 463-466.

[7] a) K. O. Eshchanov, M. Baltaeva, Study of the interaction of sorbed silver, gold and copper ions with functional groups on hydrolyzed fibroin using Charmm22 force field calculations. *Chem. Rev. Lett.* 6 (2022), 161-168, https://doi.org/10.22034/crl.2022.335548.1159; b) B. Ghanavati, A. Bozorgian, J. Ghanavati, Removal of Copper (II) Ions from the Effluent by Carbon Nanotubes Modified with Tetrahydrofuran. *Chem. Rev. Lett.* 6 (2022), 68-75, https://doi.org/10.22034/crl.2022.326950.1152.

[8] a) S. S. Amiri, Z. Hossaini, Z. Azizi, Synthesis and investigation of antioxidant and antimicrobial activity of new pyrazinopyrroloazepine derivatives using Fe3O4/CuO/ZnO@MWCNT MNCs as organometallic nanocatalyst by new MCRs. *Appl. Organomet. Chem.* 36 (2022), e6573, https://doi.org/10.1002/aoc.6573; b) S. Soleimani-Amiri, Z. Hossaini, Z. Azizi, Synthesis and Investigation of Biological Activity of New Oxazinoazepines: Application of Fe3O4/CuO/ZnO@MWCNT Magnetic Nanocomposite in Reduction of 4-Nitrophenol in Water. *Polycycl. Aromat. Comp.* 43 (2022), 2938-2959, https://doi.org/10.1080/10406638.2022.2058969.

[9] a) Z. Hossaini, S. Ahmadi, D. Zareyee, S. Soleimani Amiri, Green synthesis of new spiropyrroloisatin and spiroindenopyrroles using biosynthesized CuO/ZnO@MWCNTs nanocatalyst. *Chem. Rev. Lett.* 7

(2024), 1063-1073, https://doi.org/10.22034/CRL.2024.472507.1400; b) M. Kurdtabar, S. Soleimani-Amiri, M. Alidad, G. Bagheri Marandi, Cu-Decorated CMC-g-PAA/Fe3O4 Hydrogel Nanocomposite: High-Efficiency and Reusable Catalyst for Synthesis of 1,2,3-Triazoles via Click Reaction in Water. *J. Polym. Environ.* 33 (2025), 2334-2350, https://doi.org/10.1007/S10924-025-03536-1.

[10] a) S. Soleimani-Amiri, M. Mohammadi, N. Faal Hamedani, B. Dehbandi, An Efficient Synthesis and Study of Biological Activity of New Pyrimidoazepines Using Ag/Fe3O4/TiO2/CuO@MWCNTs Magnetic Nanocomposites: A Combined Experimental and Theoretical Investigation. *Polycycl. Aromat. Comp.* 43 (2023), 6046-6075, https://doi.org/10.1080/10406638.2022.2112709; b) Z. Azizi, S. S. Amiri, M. Ghambarian, Z. Hossaini, Cu@Fe3O4/SiO2@MWCNTs promoted green synthesis of novel bis-1,4-dihydropyridines and evaluation of biological activity. *Appl. Organomet. Chem.* 38 (2024), e7645, https://doi.org/10.1002/aoc.7645.

[11] T. Saitoh, Y. Yoshida, T. Matsudo, S. Fujiwara, A. Dobashi, K. Iwaki, C. Matsubara, Concentration of hydrophobic organic compounds by polymer-mediated extraction. *Anal. Chem.* 71 (1999), 4506-4512.

[12] M. Tabata, K. Kaneko, Spectrophotometric determination of trace amounts of copper (II) using the homolysis reaction of the copper (II)–N-p-nitrobenzyl-5, 10, 15, 20-tetrakis (4-sulphonatophenyl) porphine complex. *Analyst* 11 (1991), 1185-1188.

[13] T. J. Nasiriddinovich, T. Nurmukhammat, T. G. Suyunovna, X. B. Mengdovulovich, K. E. Yunusov, T. B. Alimkulovich, S. Z. Asanaliyevna, 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. *Chem. Rev. Lett.* 7 (2024), 388-403.

[14] K. A. Kuliyev, N. A. Verdizade, S. A. Mamedova, S. G. Aliev, Spectroscopic determination of copper (II) with dimercaptophenols and heterocyclic diamines. *Chem. Rev. Lett.* 7 (2024), 630-646.

[15] S. Prasad, T. Halafihi, Development and validation of catalytic kinetic spectrophotometric method for determination of copper (II). *Microchim. Acta* 142 (2003), 237-244.

[16] T. Kawashima, H. Itabashi, N. Teshima, M. Kurihara, S. Nakano, Flow-injection determination of copper (II) based on its catalytic effect on the oxidative coupling of 3-methyl-2-benzothiazolinone hydrazone with N-ethyl-N-(2-hydroxy-3-sulfopropyl)-3, 5-dimethoxyaniline in a micellar medium. *Anal. Sci.* 15 (1999), 835-839.

[17] S. Nakano, K. Nakaso, K. Noguchi, T. Kawashima, Catalytic flow-injection determination of copper at nanogram levels by using color formation of N-phenyl-p-phenylenediamine with m-phenylenediamine in the presence of pyridine and ammonia as activators. *Talanta* 44 (1997), 765-770.

[18] H. Shafiekhani, F. Mostaghni, N. Madadi Mahani, Design selective Cu2+ chemo-sensor based on Bis-Azo dye for determination of Cu2+ in water samples. *Chem. Rev. Lett.* 7 (2024), 404-412.

[19] N. K. Qutlimurotova, D. S. Mirsaidova, L. K. Kozinskaya, B. Lal, D. K. Mirkhamitova, N. A. Atakulova, A. Hosseini-Bandegharaei, Characterization and evaluation analysis of a crown ether as an effective sorbent for selective sorption of copper ions. *Desalin. Water Treat.* 314 (2023), 141-157.

[20] S. Laylo, Q. Nigora, I. Dilnoza, D. Kuronboyev, B. Elyor, New and Effective Analytical Reagent of 5-(4-Aminophenyl)-1, 3, 4-Oxadiazole-2-thiol in The Determination of Copper and Lead. *Anal. Bioanal. Electrochem.* 14 (2022), 1093-1113.

[21] M. A. Sheikh-Mohseni, S. Pirsa, Nanostructured conducting polymer/copper oxide as a modifier for fabrication of L-DOPA and uric acid electrochemical sensor. *Electroanalysis* 9 (2016), 2075-2080.

[22] K. G. Manjunatha, B. K. Swamy, G. K. Jayaprakash, S. C. Sharma, P. Lalitha, K. A. Vishnumurthy, Electrochemical determination of paracetamol at Cu doped ZnO/Nanoparticle with TX-100-surfactant MCPE: A cyclic voltammetric technique. *Inorg. Chem. Commun.* 142 (2022), 109630-109642.

[23] K. Davoodi-Rad, A. Shokrollahi, F. Shahdost-Fard, K. Azadkish, Copper-guanosine nanorods (Cu-Guo NRs) as a laccase mimicking nanozyme for colorimetric detection of rutin. *Biosensors* 13 (2023), 374-386.

[24] R. Behjatmanesh-Ardakani, T. T. Magkoev, SO2 adsorption and its direct proportional dissociation on the Cu (100), Cu (110), and Cu (111) surfaces: a periodic DFT study. *Chem. Rev. Lett.* 7 (2024), 873-883.

[25] Z. S. Ghnim, A. H. Adthab, M. S. Mahdi, A. S. Mansoor, U. K. Radi, N. S. Abd, R. O. Kareem, Enhanced adsorption performance and efficiency of graphitic GaN monolayers through functionalizing with transition metal adatoms (Co, Cu and Ni): A DFT study. *Chem. Rev. Lett.* 7 (2024), 912-925.

[26] S. Khammarnia, J. Saffari, M. S. Ekrami-Kakhki, Synthesis of La2MnFe2O7 and La2CuFe2O7 Magnetic Nanocomposites (Nano Mixed Metal Oxides) as Efficient Photocatalyst for Organic Dye Removal. *Chem. Rev. Lett.* 7 (2024), 123-133.

[27] S. Pirsa, N. Alizadeh, Nanoporous conducting polypyrrole gas sensor coupled to a gas chromatograph for determination of aromatic hydrocarbons using dispersive liquid–liquid microextraction method. *IEEE Sensors J.* 11 (2011), 3400-3405.

[28] S. Borna, R. E. Sabzi, S. Pirsa, Synthesis of carbon quantum dots from apple juice and graphite: investigation of fluorescence and structural properties and use as an electrochemical sensor for measuring Letrozole. *J. Mater. Sci.: Mater. Electron.* 8 (2021), 10866-10879.

[29] S. Pirsa, N. Alizadeh, Rapid determination of pyridine derivatives by dispersive liquid–liquid microextraction coupled with gas chromatography/gas sensor based on nanostructured conducting polypyrrole. *Talanta* 85 (2011), 249-254.

[30] N. Alizadeh et al., Design and fabrication of open-tubular array gas sensors based on conducting polypyrrole modified with crown ethers for simultaneous determination of alkylamines. *IEEE Sensors J.* 7 (2015), 4130-4136.

[31] N. Alizadeh, A. A. Ataei, S. Pirsa, Nanostructured conducting polypyrrole film prepared by chemical vapor

deposition on the interdigital electrodes at room temperature under atmospheric condition and its application as gas sensor. *J. Iran. Chem. Soc.* 12 (2015), 1585-1594.

[32] S. Borna, R. E. Sabzi, S. Pirsa, Synthesis of carbon quantum dots from apple juice and graphite: investigation of fluorescence and structural properties and use as an electrochemical sensor for measuring Letrozole. *J. Mater. Sci.: Mater. Electron.* 8 (2021), 10866-10879.

[33] D. Ismailova, A. Ziyaev, B. Elmurodov, T. Tashmurodov, K. Bobakulov, R. Zokirova, Targeted synthesis of 2-alkylthio-5-(p-aminophenyl)-1, 3 and bactericidal and fungicidal activity in vitro. 4-oxadiazoles. *J. Basic Appl. Res. Biomed.* 2 (2016), 476–479.

[34] J. C. Myland, K. B. Oldham, Cottrell's equation revisited: an intuitive, but unreliable, novel approach to the tracking of electrochemical diffusion. *Electrochem. Commun.* 6 (2004), 344-350.

[35] A. Yamada, Y. Kato, T. Yoshikuni, Y. Tanaka, N. Tanaka, Computer-assisted measurement of ion-diffusion coefficients by use of the cottrell equation. *Anal. Chim. Acta* 112 (1979), 55-63.

[36] C. M. Turaeva, D. S. Ismailova, C. Kh. Muratova, S. B. Allokulova, Insecticidal activity of alkyl derivatives of 5-(p-aminophenyl)-1, 3, 4-oxadiazole-2-thione. *Siberian J. Life Sci.* Agric. 3 (2021), 74-88. [In Russian].

[37] D. P. Valencia, F. J. González, Estimation of diffusion coefficients by using a linear correlation between the diffusion coefficient and molecular weight. *J. Electroanal. Chem.* 681 (2012), 121–126.

[38] R. Evans, G. D. Poggetto, M. Nilsson, G. A. Morris, Improving the interpretation of small molecule diffusion coefficients. *Anal. Chem.* 90 (2018), 3987–3994.

[39] G. Kaur, N. Verma, Colorimetric determination of Cu2+ ions in water and milk by apo-tyrosinase disc. *Sens. Actuators B: Chem.* 263 (2018), 524-532.

[40] F. Shi, S. Cui, H. Liu, S. Pu, A high selective fluorescent sensor for Cu2+ in solution and test paper strips. *Dyes Pigments* 173 (2020), 107914-107922.

[41] Y. Sun, M. Wei, R. Liu, H. Wang, H. Li, Q. Kang, D. Shen, A smartphone-based ratiometric fluorescent device for field analysis of soluble copper in river water using carbon quantum dots as luminophore. *Talanta* 194 (2019), 452-460.

[42] X. Jiang, Z. Zhao, Y. Liao, C. Tang, P. L. Tremblay, T. Zhang, A recyclable colorimetric sensor made of waste cotton fabric for the detection of copper ions. *Cellulose* 29 (2022), 5103-5115.

[43] K. F. Kayani, A. M. Abdullah, Eco-friendly fluorescent detection method for Cu2+ ions combined with smartphone-integrated paper strip sensors based on highly fluorescent 2-aminoterephthalic acid in milk samples. *J. Food Compos. Anal.* 135 (2024), 106577-106586.

[44] M. El-Azazy, A. AlReyashi, K. Al-Saad, N. Al-Hashimi, M. A. Al-Ghouti, M. F. Shibl, A. S. El-Shafie, Mandarin Peels-Derived Carbon Dots: A Multifaceted Fluorescent Probe for Cu (II) Detection in Tap and Drinking Water Samples. *Nanomaterials* 14 (2024), 1666-1674.

[45] X. Lv, H. Hu, L. Yao, L. Deng, X. Liu, L. Yu, H. He, Fabrication of surface ion imprinting rice husk-based polymer for selective detection and efficient adsorption of Cu2+ in lake water. *Spectrochim. Acta Part A: Mol. Biomol. Spectrosc.* 298 (2023), 122723-122742.

[46] J. Yu, J. Han, P. Li, Z. Huang, S. Chen, Simultaneous Determination of Cd2+, Cu2+, Pb2+ and Hg2+ Based on 1, 4-Benzenedithiol-2, 5-diamino-hydrochloride-1, 3, 5-triformylbenzene Covalent-Organic Frameworks. *ChemistrySelect* 5 (2020), 12345-12352.