

*Full Paper*

## **New and Effective Analytical Reagent of 5-(4-Aminophenyl)-1,3,4-Oxadiazole-2-thiol in The Determination of Copper and Lead**

**Sagdullaeva Laylo,<sup>1</sup> Qutlimurotova Nigora,<sup>1</sup> Ismailova Dilnoza,<sup>2</sup> Davron Kuronboyev,<sup>3</sup>  
and Berdimurodov Elyor,<sup>1,\*</sup>**

<sup>1</sup>*Faculty of Chemistry, National University of Uzbekistan, Tashkent, 100034, Uzbekistan*

<sup>2</sup>*S. Yu. Yunusov Institute of the Chemistry of Plant Substances Uzbekistan Academy of Sciences,  
Tashkent, 100034, Uzbekistan*

<sup>3</sup>*Khorezm Ma'mun Academy, Khiva, 220900, Uzbekistan*

\*Corresponding Author, Tel.: +998973107060

E-Mail: [elyor170690@gmail.com](mailto:elyor170690@gmail.com)

*Received: 2 August 2022 / Received in revised form: 29 November 2022 /*

*Accepted: 6 December 2022 / Published online: 31 December 2022*

---

**Abstract-** Copper(II) and lead(II) are hazardous ions in environmental samples. Determining these ions from the samples is an important issue in analytical chemistry. Currently, various methods with analytical reagents are used in the determination of Cu(II) and Pb(II) ions, however, these methods and analytical reagents are expensive, hazardous, time-consuming, and non-recyclable. In this research, it is recommended new analytical reagent named 5-(4-aminophenyl)-1,3,4-oxadiazole-2-thiol in the determination of copper(II) and lead(II) by the amperometric titration method. It is found that this analytical reagent effectively determines the Cu(II) and Pb(II) ions from environmental samples by amperometric titration, which is time-saving and low-cost. This reagent is also recyclable. It was found: (i) the detection limit for lead(II) and copper(II) ions were 2.08 and 3 ppm, respectively; (ii) the complex of 5-(4-aminophenyl)-1,3,4-oxadiazole-2-thiol with lead(II) and copper(II) ions have a sharp angle at 0.5 V and 0.75 V, respectively, indicating that these ions are determined at one solution with this reagent; (iii) it was found that the half-wave potential of 5-(4-aminophenyl)-1,3,4-oxadiazole-2-thiol was 0.55 V, confirming that the reagent is a reducing agent. The selectivity of this reagent is very high. In the future, this reagent should be widely used in the analytical determination of Cu(II) and Pb(II) ions.

**Keywords-** 5-(4-aminophenyl)-1,3,4-oxadiazole-2-thiol; Copper; Lead; Analytical reagent; Amperometric titration; Hazardous metal; Metal determination

---

## 1. INTRODUCTION

Toxic substances coming out of car batteries contain a large number of lead ions and they are concentrated in environmental objects. Copper is also heavy toxic metal; it is concentrated in the environment and enters the human body with food. Apart from that, the copper ion is considered a necessary trace element for the human body [1–3]. Its lack leads to several negative consequences [4,5]. Copper is used in metallurgy to produce electrically and thermally conductive, drawing, corrosion-resistant alloys. The bactericidal properties of copper made it useful in the prevention of swine flu, and lesions of *Staphylococcus aureus* [6–8]. Therefore, the determination of lead and copper concentration is an urgent task in analytical chemistry. The developed methods for the determination of lead(II) can be used in metallurgical and chemical production, as well as for environmental monitoring of industrial facilities [9,10]. The method makes it possible to determine the content of lead(II) in samples of ores and alloys, to control the concentration of lead in process water during production, as well as in wastewater before and after treatment [11-13].

It is known that lead and copper ions form a black precipitate with sulphide ions, and this reaction enables the qualitative determination of copper and lead. So far, complex compounds of sulfur-containing organic oxadiazole and its derivatives with many metal ions, which are insoluble in water, have been synthesized [11,12,14,15]. However, the organic oxadiazole and its derivatives were not used for the amperometric determination of micro-quantities of copper and lead ions [16–18]. Recently, rectangular anode voltammetry, potentiometric titration, polarography, spectrophotometry, stripping voltammetry, and mass spectroscopy methods are widely used in the determination of lead and copper from various solution samples. However, these methods and analytical reagents are expensive, hazardous, time-consuming and non-recyclable. These factors are serious problems for the determination of copper and lead in analytical chemistry [5,9,19].

In this research work, it is recommended new analytical reagent named 5-(4-aminophenyl)-1,3,4-oxadiazole-2-thiol in the determination of copper(II) and lead(II) by the amperometric titration method. It is found that this analytical reagent effectively determines the Cu(II) and Pb(II) ions from environmental samples by amperometric titration, which is time-saving and low-cost. This reagent is also recyclable. The lead and copper form a complex compound with 5-(4-aminophenyl)-1,3,4-oxadiazole-2-thiol by the unshared pair of electrons of the sulfur and nitrogen atoms. These complexes are insoluble in water. Determination of the microquantity of metal ions was carried out by finding the solubility coefficient of the precipitate. The amperometric titration method, which is one of the electrochemical analysis methods, is one of the express analysis methods that are easy to perform and does not require standard samples to determine the unknown concentration. In this research, electrochemical and spectroscopic techniques were used. These methods are easily operated and low cost. In this research, it is recommended new analytical reagent named 5-(4-aminophenyl)-1,3,4-oxadiazole-2-thiol in the determination of copper(II) and lead(II) by the amperometric titration method. To determine the copper(II) and lead(II) by the amperometric titration method with the 5-(4-aminophenyl)-1,3,4-oxadiazole-2-thiol is low cost, effective and doesn't require expensive equipment.

Other methods are more expensive and required large equipment, and large laboratories, which is difficult for companies and industries.

## 2. MATERIALS AND METHODS

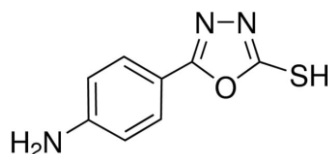
### 2.1. Materials

#### 2.1.1. Standard solution of lead(II) and copper(II) ions solutions

In this research work, the 0.1 M lead(II) and copper(II) ions solutions were used. The 3.31 g  $\text{Pb}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$  and 1.88 gr  $\text{Cu}(\text{NO}_3)_2 \cdot 5\text{H}_2\text{O}$  were moved to a 200 ml flask and filled with the distilled water to 200 ml (pH=3). All chemicals (99.99% purity) were purchased from Sigma Aldrich (USA).

#### 2.1.2. Standard solution of 5-(4-aminophenyl)-1,3,4-oxadiazole-2-thiol

A 0.1 gr 5-(4-aminophenyl)-1,3,4-oxadiazole-2-thiol (Scheme 1) was moved to a 100 ml flask and 100 ml ethyl alcohol was added into the flask, then it was mixed. As a result, the 0.1% standard solution of 5-(4-aminophenyl)-1,3,4-oxadiazole-2-thiol was formed. The molecular structures and chemical and physical characteristics were studied in [20].



**Scheme 1.** Molecular structure of 5-(4-aminophenyl)-1,3,4-oxadiazole-2-thiol

### 2.2. Methods

#### 2.2.1. Methods, equipment and installation

Heal Force CR-RO30 (China) was used to prepare bi-distilled water. The specific electrical conductivity of bi-distilled water was 0.475  $\mu\text{S}/\text{cm}$ . For titration of a solution of 5-para-aminophenyl-1,3,4-oxadiazole-2-thione, a 2.0-mL piston micro burette was used, which made it possible to dose the titrant with accuracy at 0.001 mL. A manual ammeter "Expert - 001 A" pH meter pH/mV/TEMP Meter P25 Econet (Korea) was used for titration. The electrical conductivity of the solutions was measured by a Mettler Toledo KEL-1M and KEL-2M conductometer. The current-voltage curves were studied at ABC polarographs (manufactured by Russia Volta (Polarograph) - ABC-1.1) [3,14]. The inductively coupled plasma atomic emission spectroscopy (ICP-AES, Thermo Scientific iCAP Pro, USA) method was used to compare the suggested method.

#### 2.2.2. Background electrolyte solution

The solutions of potassium nitrate (1.01 g), ammonium chloride (0.535 g), ammonium nitrate (0.8 g) and lithium chloride (0.425 g) were mixed with the 1 l be-distilled water in a flask to form the background electrolyte solution. These compounds are not hydrolysed in a water solution and they

formed positive and negative ions. The background electrolyte solution supports the transportation of determinate ions on the electrode surface. These solutions can non affect the oxidation-reduction reactions [21,22].

### 2.2.3. Amperometric titration processes and method in determination of targeted ions

In a 10 ml electrochemical cell, the 1 ml 0.01 M metal standard solution and 2 ml background electrolyte solution were added. Next, the electrodes moved into this cell. The following process is that the 0.1% analytical reagent was been adding during the titration processes by the micropipette until the finish of the formation of (milky colour) solid of analytical reagent with the metal ions. In this process, the current was decreased by reducing in amounts of metal ions in the solution. At an equivalent point, the amounts of metal ions are finished. After this equivalent point, the current rose with the oxidation of the analytical reagent at the anode. The amounts of metal ions were determined as related to the equivalent point [5,15].

### 2.2.4. Polarographic analysis

20.8 ppm of 1.0 ml of lead(II) solution or 32.0 ppm of 1.0 ml of copper and 1.0 ml of 0.001 M to 0.01 M solutions of the reagent, sodium sulfite, 1% gelatin, supporting electrolyte, and the volume were adjusted to 10 ml with water, and the values of the current-voltage curves of ABC polarographs (manufactured in Russia) in a three-electrode cell were recorded. As a result, the polarographic curves were obtained and analysed [4,9,19].

### 2.2.5. Conductometric titration

1.0 ml of a 50 ppm solution of copper nitrate was added into 10.0 ml of a cell; it is poured to the mark with bi-distilled water and titrated with a 0.1% alcohol solution of 5-(4-aminophenyl)-1,3,4-oxadiazole-2-thiol. Then, the electrical conductivity was measured by conductometric titration. A similar analysis was made for lead. The conductivity of bi-distilled water is  $1 \times 10^{-6}$  Sm/cm, molar conductivity ( $\lambda_0$ ) of 5-(4-aminophenyl)-1,3,4-oxadiazole-2-thiol, lead and copper 17.2, 71 and 56.6, respectively. The specific electrical conductivity of a saturated copper solution of 5-(4-aminophenyl)-1,3,4-oxadiazole-2-thiol at 20°C was  $4 \times 10^{-6}$  Sm/cm and for the lead was also  $4 \times 10^{-6}$  Sm/cm [9,10,12].

## 3. RESULTS AND DISCUSSION

### 3.1. Amperometric titration

In this analysis, the optimal condition for the determination of Pb(II) and Cu(II) in the amperometric titration was found. Table 1 illustrates the effect of voltage on the results of amperometric titration (2.08 ppm Pb(II) and 6.42 ppm Cu(II)). To conduct the study, the influence of the potential applied to the indicator electrodes (0.25-1.25 V) on the shape of the curves was studied and the results are given in Table 1. The values in standard deviation (S), relative standard deviation (RSD%) and confidence limit ( $\Delta X$ ) were found.

In the amperometric titration, the applied voltage was stable at average voltage, and then the titration

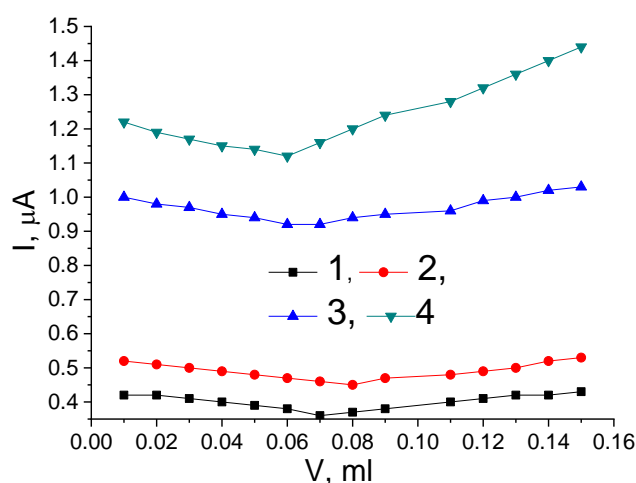
of metal ions was done. When one of the equivalent points has a sharp angle, the error will be less. From changes from 0.25 to 1.25 applied voltages, the best voltage is selected from the number of metal ions determined with a low error. It can be seen from the obtained results that the complex of 5-(4-aminophenyl)-1,3,4-oxadiazole-2-thiol with lead(II) and copper(II) ions have a sharp angle at 0.5 V and 0.75 V, respectively. The error does not increase on these voltages. It is also clear from these results that the lead(II) and copper(II) ions are determined in one solution with the 5-(4-aminophenyl)-1,3,4-oxadiazole-2-thiol. This is due to the difference in the applied voltage of lead(II) and copper(II) ions.

**Table 1.** Effect of applied voltage on results of amperometric titration of 5-(4-aminophenyl)-1,3,4-oxadiazole-2-thiol (2.08 ppm Pb(II) and 6.42 ppm Cu(II))

Applied voltage value, V	5-(4-Aminophenyl)-1,3,4-oxadiazole-2-thiol					
	Cu(II)	S	RSD%	Pb(II)	S	RSD%
0.25	6.38±0.04	0.032	0.5	2.09±0.0124	0.01	0.47
0.50	6.42±0.029	0.024	0.37	2.05±0.021	0.017	0.83
0.70	6.48±0.052	0.042	0.68	2.02±0.0198	0.016	0.79
1.00	6.39±0.069	0.056	0.87	2.13±0.026	0.021	0.98
1.25	6.52±0.845	0.068	1.0	2.0±0.023	0.0187	0.93

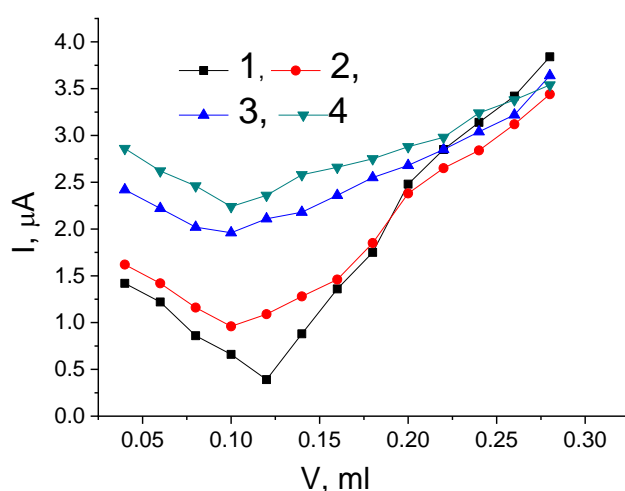
### 3.2. Impact of supporting electrolyte solution in an amperometric titration

The nature and concentration of the supporting electrolyte solution affect the results of titration of lead(II) and copper(II) with a solution of 5-(4-aminophenyl)-1,3,4-oxadiazole-2-thiol. These effects were studied. Effect of supporting electrolytes of different nature on the shape of lead(II) (Figure 1) and copper(II) (Figure 2) ions amperometric titration curves with a solution of 5-(4-aminophenyl)-1,3,4-oxadiazole-2-thiol were studied.



**Figure 1.** Effect of supporting electrolytes of different nature on the shape of lead(II) amperometric titration curves with a solution of 5-(4-aminophenyl)-1,3,4-oxadiazole-2-thiol: 1-potassium nitrate (0.01M); 2-ammonium chloride (0.01M); 3-ammonium nitrate (0.01M); 4-lithium chloride (0.01M)

It should be underlined that when the lithium chloride-based supporting electrolyte is used in the lead(II) determination, the titration curve is sharper, which explains the smaller error in the analysis. Therefore, lithium chloride was chosen as the best background electrolyte for lead(II) determination in amperometric titration. On the other hand, the potassium nitrate-based background electrolyte is used in the copper(II) determination, and the titration curve is the sharp angle, confirming that potassium nitrate is the best background electrolyte in the copper(II) determination. Precipitation of lead and copper ion with 5-(4-aminophenyl)-1,3,4-oxadiazole-2-thiol reagent resulted in a sharp angular curve for the lead at 0.01 M lithium chloride, and for copper at potassium nitrate. The ionic radius of lithium is smaller than that of other background electrolytes. This influences the lead precipitate. As a result, the lead precipitate is completely deposited. In comparison, the potassium impacts the copper precipitate. The ionic radius of lithium is smaller than that of potassium, thus, the lead was more well deposited than the copper [10,23,24].



**Figure 2.** Effect of supporting electrolytes of different nature on the shape of copper(II) amperometric titration curves with a solution of 5-(4-aminophenyl)-1,3,4-oxadiazole-2-thiol: 1-potassium nitrate (0.01M); 2-potassium chloride (0.01M); 3-sodium nitrate (0.01M); 4-sodium chloride (0.01M)

### 3.3. Statistical assessment of the accuracy of the developed method for the determination of lead(II) and copper(II) in amperometric titration

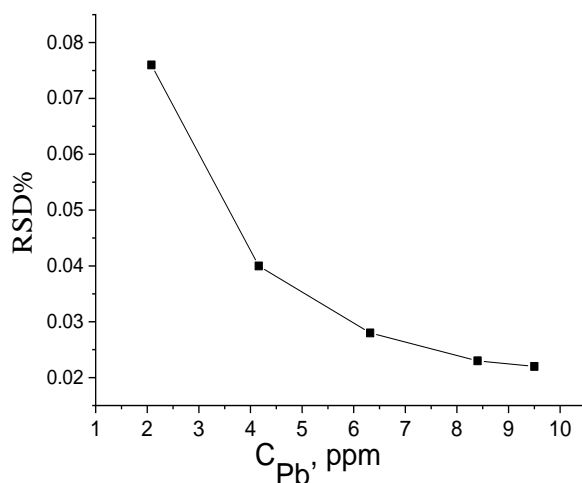
The statistical assessment of the accuracy of the developed method for the determination of lead(II) and copper(II) with a solution of 5-(4-aminophenyl)-1,3,4-oxadiazole-2-thiol was determined on platinum indicator electrodes. In this statistical analysis, the amperometric titration was repeated four times under the optimal conditions: background electrolyte 2.0 ml of 0.01 M lithium chloride for lead; a 0.01 M solution of potassium nitrate was added for copper; the total volume of the test solution was 10 ml. The amperometric titration was carried out at various concentrations of lead and copper. Tables 2 and 3 show the results of amperometric titration of various amounts of lead(II) and copper(II) ions with a solution of 5-(4-aminophenyl)-1,3,4-oxadiazole-2-thiol under optimized conditions.

**Table 2.** Results of amperometric titration of various amounts of lead(II) with a solution of 5-(4-aminophenyl)-1,3,4-oxadiazole-2-thiol under optimized conditions

№	Values of Pb(II), ppm	Determined values of Pb(II), ppm ( $\bar{X} \pm \Delta X$ ; P=0,95)	S	RSD%
1	2.08	2.09±0.198	0.16	0.76
2	4.16	4.18±0.211	0.17	0.40
3	6.32	6.33±0.223	0.18	0.28
4	8.40	8.42±0.248	0.20	0.23
5	9.50	9.51±0.261	0.21	0.22

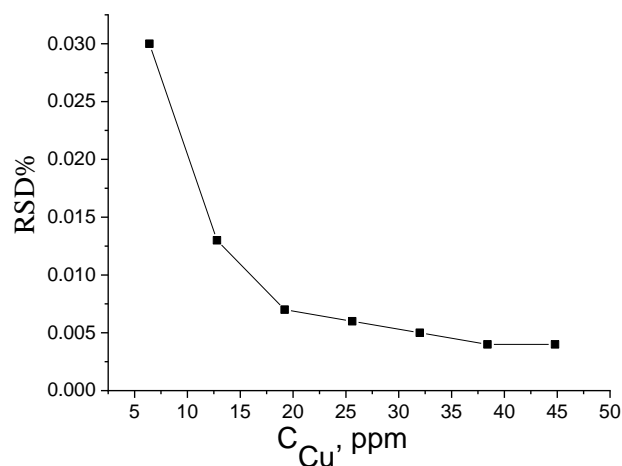
**Table 3.** Results of amperometric titration of various amounts of copper(II) with a solution of 5-(4-aminophenyl)-1,3,4-oxadiazole-2-thiol under optimized conditions

№	Values of Cu(II), ppm	Determined values of Cu(II), ppm ( $\bar{X} \pm \Delta X$ ; P=0,95)	S	RSD%
1	6.4	6.38±0.10	0.08	3
2	12.8	12.72±0.11	0.09	1.3
3	19.2	19.30±0.14	0.11	0.7
4	25.6	25.55±0.15	0.12	0.6
5	32	32.12±0.16	0.13	0.5
6	38.4	38.48±0.17	0.14	0.4
7	44.8	44.87±0.19	0.15	0.4

**Figure 3.** Correlation between the concentration of metal ions and RSD% for lead(II) and copper(II) ions

Figures 3 and 4 show the correlation between the number of metal ions and RSD% for lead(II) and copper(II) ions. It is indicated that the detection limit of the metal ions is at the point approaching 0.33. It was found that the detection limit for lead(II) and copper(II) ions were 2.08 and 3 ppm, respectively. As can be seen from Tables 2, 3 and Figures 3 and 4, the determined amounts of Pb(II) and Cu(II)

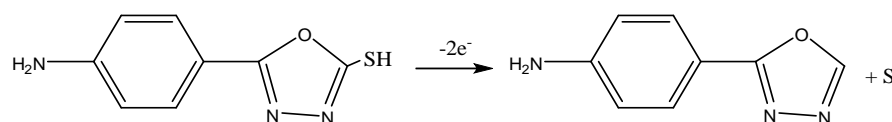
correspond to their introduced contents and do not go beyond the confidence interval, which once again confirms the high accuracy of the developed amperometric method for determining lead(II) and copper(II) with a relative standard deviation (RSD%) not exceeding 0.03 and the lower limit of the determined contents is 2.08 ppm for lead and 3 ppm for copper.



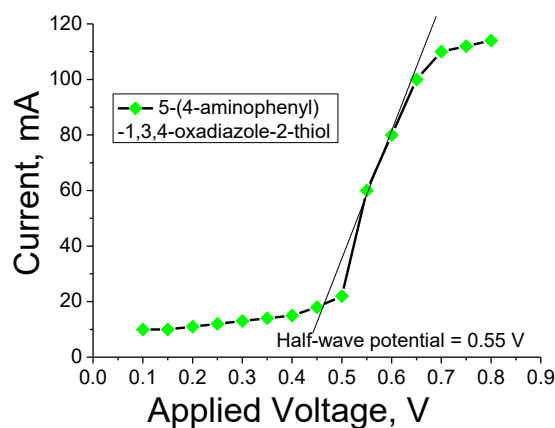
**Figure 4.** Correlation between the concentration of metal ions and RSD% for lead(II) and copper(II) ions

### 3.4. Polarographic analysis: Cation-radical exchanges of reagent

The selected analytical reagent of 5-(4-aminophenyl)-1,3,4-oxadiazole-2-thiol is an electroactive organic compound, it can be oxidized to a cation-radical state so that only one electron is transferred at a time during electron exchange without changing the molecular structure related to Scheme 2.



**Scheme 2.** Cation-radical exchanges of 5-(4-aminophenyl)-1,3,4-oxadiazole-2-thiol



**Figure 5.** Correlation between the current and applied voltage (Polarographic diagram) for 5-(4-aminophenyl)-1,3,4-oxadiazole-2-thiol



In the polarographic analysis, the half-wave potential of 5-(4-aminophenyl)-1,3,4-oxadiazole-2-thiol was measured. It is clear from the observed results that the 5-(4-aminophenyl)-1,3,4-oxadiazole-2-thiol is oxidised by the two-electron transformations. Figure 5 shows the correlation between the current and applied voltage (Polarographic diagram) for 5-(4-aminophenyl)-1,3,4-oxadiazole-2-thiol. It was found that the half-wave potential of 5-(4-aminophenyl)-1,3,4-oxadiazole-2-thiol was 0.55 V, confirming that the reagent is a reducing agent; its standard redox potential is equal to the half-wave potential [23].

### 3.5. Polarographic analysis: Chemistry of formation lead and copper complex with a reagent

In the studying of the mechanism of the electrode process of deposition of lead and copper with 5-(4-aminophenyl)-1,3,4-oxadiazole-2-thiol, the value of the number of electrons given off during its electro-oxidation was determined from the slope of the plot of dependence on E. The half-wave potential of the resulting deposits was determined in various concentrations of the reagent and the current-voltage polarographic curves were determined. The half-wave potential and the dependence on the logarithmic value of the reagent were found related to the polarographic curves [22,25]. The obtained polarographic curves are indicated in Figures 6 and 7. If the electrode reaction is reversible, the amount of the reagent that binds to the precipitant in the solution is large, and then its concentration in the volume of the solution and at the electrode surface can be assumed to be constant. The equilibrium between the  $M^{+n}$  cation and the precipitant  $L^{+m}$  (the precipitant may not have a charge) and the precipitate  $M_mL_n$  very quickly establishes a mobile equilibrium. The dependence of the half-wave potential on the concentration of the precipitating reagent can be calculated from the product of solubility and its composition according to Equation 1 [21,26].

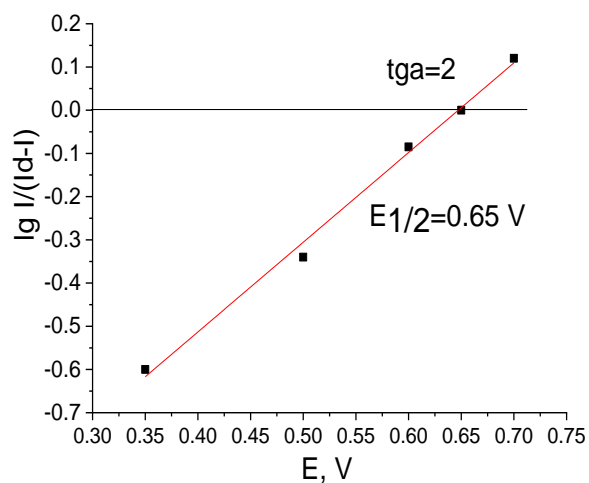
$$E = E_{1/2} - \frac{0.058}{n} \lg \frac{I}{I_d - I} \quad (1)$$

where E is a change of solution potential;  $E_{1/2}$  is half-wave potential (it is a feature indicator in metal determination, its value also shows the solubility degree);  $I_d$  is diffusion current at the studied concentration.

**Table 4.** Calculation of electrooxidation of copper(II) and lead(II) precipitates by 5-(4-aminophenyl)-1,3,4-oxadiazole-2-thiol

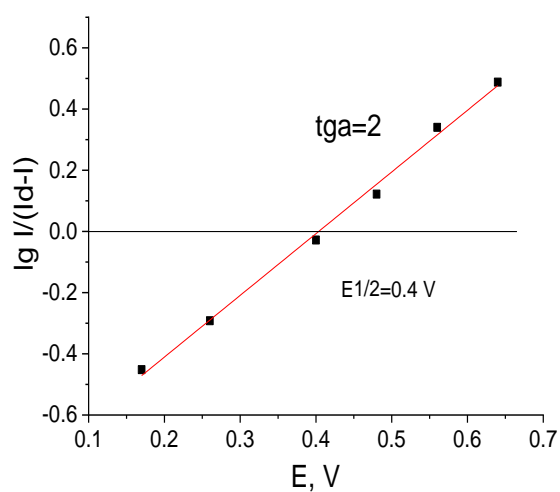
Metal and its amount	$C_M$	Background solution	E, B.	$I_d$	$\lg \frac{I}{I_d - I}$	$E_{1/2}$
20.8 ppm Pb(II) 10 ml volume	0.001	lithium chloride (0.01M)	0.35	7	-0.6	0.65
	0.002		0.5	22	-0.34	
	0.003		0.6	50	-0.085	
	0.004		0.65	56	0	
	0.005		0.7	60	0.12	
32.0 ppm Cu(II) 10 ml solution	0.001	potassium chloride (0.01M)	0.17	13	-0.452	0.4
	0.002		0.26	28	-0.292	
	0.003		0.4	32	-0.028	
	0.004		0.48	54	0.122	
	0.005		0.56	65	0.34	
	0.006		0.64	78	0.488	

The molar ratio between the ions in precipitant was found by the *tga* of Figures 6 and 7. The values of diffusion current were determined by the values of the half-wave potential in Figures 6 and 7. The solubility degree was estimated as related to the molar concentration on the  $\lg \frac{i}{i_d - i} = 0$ .



**Figure 6.** The polarographic curves of lead(II) precipitation with 5-(4-aminophenyl)-1,3,4-oxadiazole-2-thiol

The obtained results are indicated in Table 4. It is found that the *tga*=2 for copper(II) and lead(II) precipitation with 5-(4-aminophenyl)-1,3,4-oxadiazole-2-thiol, confirming that the molar ratio of Me: Reagent is 1:2 in copper(II) and lead(II) precipitation with 5-(4-aminophenyl)-1,3,4-oxadiazole-2-thiol. It is noticeable that the extrapolation of the half-wave potential from the logarithmic value of the concentration of the precipitant was zero, which confirms the thermodynamic solubility of the precipitation for lead is  $2 \times 10^{-14}$  and for copper  $4 \times 10^{-12}$ .



**Figure 7.** The polarographic curves of copper(II) precipitation with 5-(4-aminophenyl)-1,3,4-oxadiazole-2-thiol

### 3.6. Conductometric titration in the determination of the solubility of the complex

The solubility of copper and lead complex with 5-(4-aminophenyl)-1,3,4-oxadiazole-2-thiol. was determined by conductometric titration. The electrical conductivity is related to the molar concentration of the equivalent of a substance (mol /l) by Equation 2 [27,28]:

$$K = \lambda C_{eqv} \cdot 10^3 \quad (2)$$

where  $\lambda$  – equivalent electrical conductivity ( $\text{Sm} \cdot \text{cm}^2 \cdot \text{mol}^{-1}$ ).

Equivalent electrical conductivity ( $\lambda$ ) is the electrical conductivity of a volume of solution containing 1 mole equivalent to a substance (the equivalence factor is  $1/z$ , where  $z$  is the charge of the ion), provided that the electrodes are 1 cm apart. A similar value, referring not to equivalents, but to the formula units of substances, is called molar electrical conductivity ( $\Lambda$ ) [29–31].

In methods of determination in conductometric titration, 1.0 ml of a 50 ppm solution of copper nitrate was added to 10.0 ml of a cell; it is poured to the mark with bi-distilled water and titrated with a 0.1% alcohol solution of 5-(4-aminophenyl)-1,3,4-oxadiazole-2-thiol. Then, the electrical conductivity was measured by conductometric titration. A similar analysis was made for lead. The conductivity of bi-distilled water is  $1 \cdot 10^{-6}$  Sm/cm, molar conductivity ( $\lambda_0$ ) of 5-(4-aminophenyl)-1,3,4-oxadiazole-2-thiol, lead and copper 17.2, 71 and 56.6, respectively. The specific electrical conductivity of a saturated copper solution of 5-(4-aminophenyl)-1,3,4-oxadiazole-2-thiol at 20°C was  $4 \cdot 10^{-6}$  Sm/cm and for the lead was also  $4 \cdot 10^{-6}$  Sm/cm.

The main objective of the obtained results highlights the following information:

$$\lambda^0(\text{PbR}_2) = 71 + (17.2 \cdot 2) = 105,4 \text{ (Sm} \cdot \text{cm}^2 \cdot \text{mol}^{-1}\text{)}$$

$$c(\text{PbR}_2) = \frac{(4 \cdot 10^{-6} - 1,0 \cdot 10^{-6}) \cdot 10^3}{105,4} = 2,8 \cdot 10^{-5} \text{ mol/l}$$

$$K_s(\text{PbR}_2) = [\text{Pb}^{2+}][\text{R}^-]^2 = (2,8 \cdot 10^{-5})^3 = 2,2 \cdot 10^{-14}$$

$$\lambda^0(\text{CuR}_2) = 56,6 + (17,2 \cdot 2) = 91 \text{ (Sm} \cdot \text{cm}^2 \cdot \text{mol}^{-1}\text{)}$$

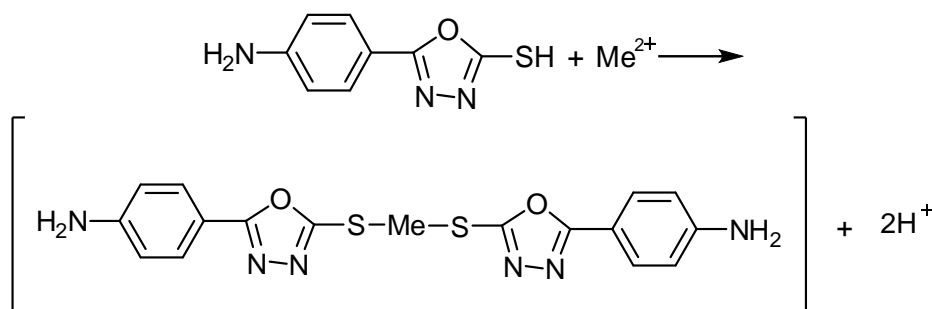
$$c(\text{CuR}_2) = \frac{(8 \cdot 10^{-6} - 1,0 \cdot 10^{-6}) \cdot 10^3}{91} = 7,7 \cdot 10^{-5} \text{ mol/l}$$

$$K_s(\text{CuR}_2) = [\text{Cu}^{2+}][\text{R}^-]^2 = (7,7 \cdot 10^{-5})^3 = 4,5 \cdot 10^{-12}$$

### 3.7. Chemical interaction mechanism between metal ions and analytical reagent

The conductometric, amperometric and polarographic results confirmed that the micro concentrations of lead and copper can be determined with a solution of 5-(4-aminophenyl)-1,3,4-oxadiazole-2-thiol. The chemistry of the formation of a precipitate of lead and copper by a solution with 5-(4-aminophenyl)-1,3,4-oxadiazole-2-thiol is given in Scheme 3, in which 5-(4-aminophenyl)-1,3,4-oxadiazole-2-thiol reacted with the metal ions by the electrochemical interaction between the –SH group and metal ions. As a result, the Me–S bonds are formed by electron transformations. The paired electrons of sulphur atoms are shared with vacant d-orbitals of metal [32,33]. Therefore, the ion-dipole bonds

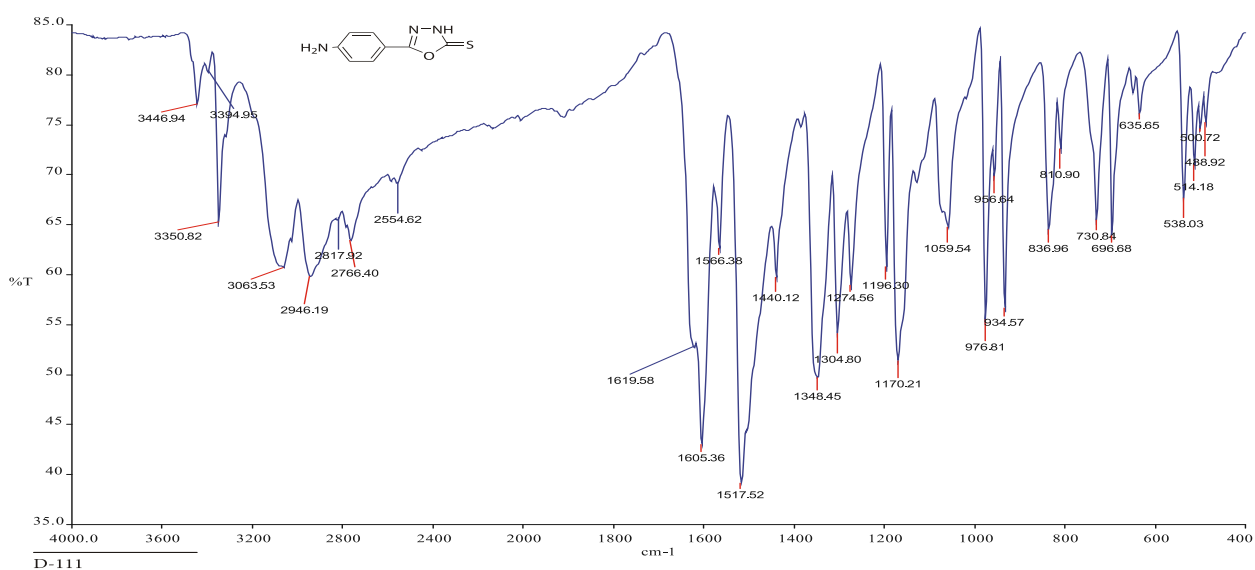
formed between the analytical reagent and metal. The selected metals (copper and lead) are strong members of d elements. Their vacant d-orbitals are mainly responsible for the coordination bond formation [34–36].



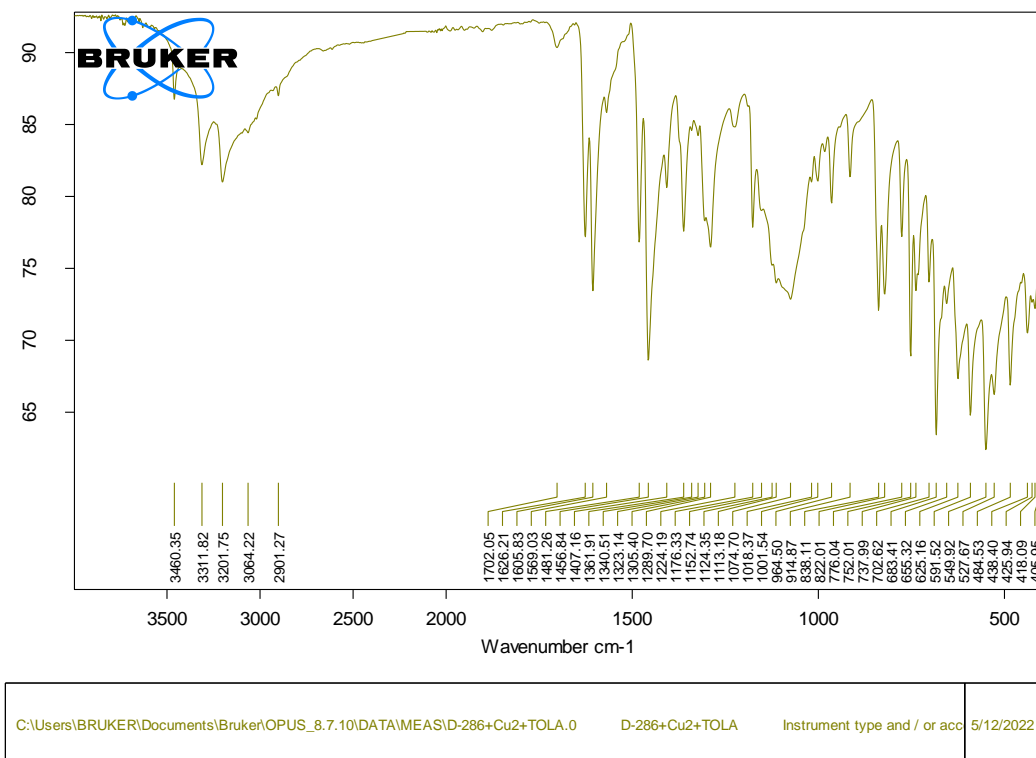
**Scheme 3.** Interactions between the metal ions and 5-(4-aminophenyl)-1,3,4-oxadiazole-2-thiol

### 3.8. Chemical structural analysis

The IR chemical structural analysis of 5-(4-aminophenyl)-1,3,4-oxadiazole-2-thiol and its complexes with copper and lead were studied; the obtained results are indicated in Figure 8 for 5-(4-aminophenyl)-1,3,4-oxadiazole-2-thiol, in Figure 9 for 5-(4-aminophenyl)-1,3,4-oxadiazole-2-thiol complexes with copper and Figure 10 for its complex with lead. The IR spectrum results show that the absorption bands of stretching vibrations of the amino group ( $NH_2-Ar$ ) appeared at  $3350\text{ cm}^{-1}$ , stretching vibrations of N–H of the oxadiazole ring was found at  $3063\text{ cm}^{-1}$ , and the stretching vibrations of thiocarbonyl group were appeared ( $C=S$ ) at  $1348\text{ cm}^{-1}$ . The IR signal for the C=O group appeared at  $1680\text{ cm}^{-1}$ . It can be seen from the IR spectrum results that when forming a complex with copper and lead with the 5-(4-aminophenyl)-1,3,4-oxadiazole-2-thiol reagent, the vibrational frequencies of the S–H and NH appeared at  $2554.62\text{ cm}^{-1}$  and  $3063\text{--}3350\text{ cm}^{-1}$ , respectively. These results confirmed the molecular structure of the 5-(4-aminophenyl)-1,3,4-oxadiazole-2-thiol complexes with copper and lead.

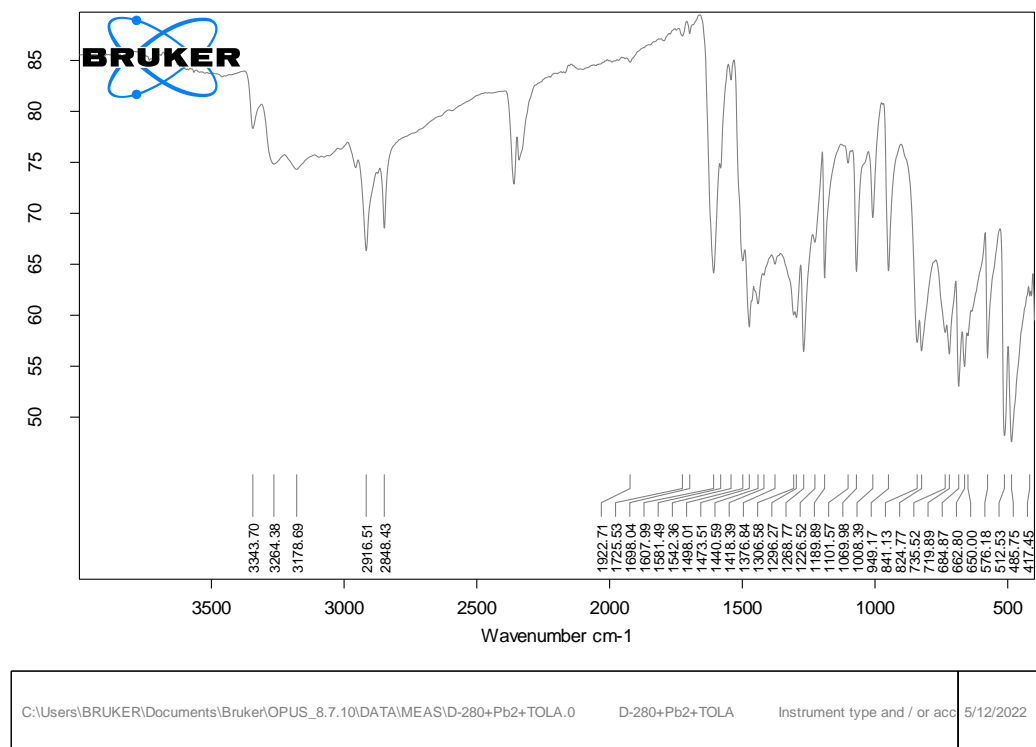


**Figure 8.** IR spectra of 5-(4-aminophenyl)-1,3,4-oxadiazole-2-thiol



Page 1/1

Figure 9. IR spectra of copper(II) complex with 5-(4-aminophenyl)-1,3,4-oxadiazole-2-thiol



Page 1/1

Figure 10. IR spectra of lead(II) complex with 5-(4-aminophenyl)-1,3,4-oxadiazole-2-thiol

### 3.9. Selectivity analysis of 5-(4-aminophenyl)-1,3,4-oxadiazole-2-thiol for copper and lead

The degree of selectivity of the proposed method for the determination of lead(II) and copper(II) with a solution of 5-(4-aminophenyl)-1,3,4-oxadiazole-2-thiol was estimated in this research work. It was carried out a series of experiments on titration in the presence of increasing amounts of several interfering cations. The selectivity of lead and copper determination by 5-(4-aminophenyl)-1,3,4-oxadiazole-2-thiol was compared to Hg(II), Ag(I), Cd(II), As(III), Ni(II), Cu(II), Sn(II), Bi(III) ions for lead(II) ions (Table 5) and Cd(II), Pb(II), Al(III), Zn(II), Hg(II), Ti(IV), Ag (I), As (II) for copper(II) ions (Table 6), respectively. These results confirmed that the selectivity of lead and copper determination by 5-(4-aminophenyl)-1,3,4-oxadiazole-2-thiol is very high with around 0.2-0.3 S and 0.1 RSD%.

**Table 5.** Results of amperometric titration of 2.08 ppm of lead(II) with a solution of 5-(4-aminophenyl)-1,3,4-oxadiazole-2-thiol (P= 0.95; n=8)

No	Compared cation; [x]	Introduction [x], ppm	$\frac{[X]}{[Cu]}$	Determined Cu(II), ppm; ( $\bar{X} \pm \Delta X$ )	S	RSD%
1	Cd(II)	22.4	0.7	31.08±0,010	0.25	0.8
2	Pb(II)	20.8	0.625	31.52±0,015	0.39	1.2
3	Al(III)	27.00	0.844	31.68±0,014	0.35	1.1
4	Zn(II)	32.5	1.01	32.36±0,012	0.31	0.9
5	Hg(II)	40.5	1.27	32.42±0,013	0.34	1.0
6	Ti(IV)	48.9	1.53	32.48±0,013	0.35	1.1
7	Ag (I)	54.0	1.68	32.51±0,010	0.28	0.8
8	As (II)	43.35	1.35	32.54±0,012	0.32	0.9

**Table 6.** Results of amperometric titration of 32 ppm of copper(II) with a solution of 5-(4-aminophenyl)-1,3,4-oxadiazole-2-thiol (P = 0.95; n=8)

No	Compared cation; [x]	Introduction [x], ppm	$\frac{[x]}{[Pb]}$	Determined Pb(II), ppm; ( $\bar{X} \pm \Delta X$ )	S	RSD%
1	Hg(II)	20	0.96	20.72±0.011	0.18	0.9
2	Ag(I)	21.6	1.04	20.40±0.015	0.24	0.12
3	Cd(II)	22.4	1.08	20.52±0.0199	0.33	0.16
4	As(III)	23.5	1.08	20.62±0.023	0.38	0.18
5	Ni(II)	24.6	1.14	20.71±0.016	0.27	0.13
6	Cu(II)	25.6	1.23	20.93±0.0086	0.14	0.07
7	Sn(II)	29.75	1.43	20.94±0.007	0.12	0.057
8	Bi(III)	31.35	1.5	20.96±0.006	0.11	0.052

Tables 7 and 8 reveal the results of amperometric titration of 32 ppm of lead(II) with a solution of 5-(4-aminophenyl)-1,3,4-oxadiazole-2-thiol in complex solutions. It is clear from

the obtained results that the selectivity of lead and copper determination by 5-(4-aminophenyl)-1,3,4-oxadiazole-2-thiol in the selected complex is very high the around 0.21-0.32 S and 0.15 RSD%.

**Table 7.** Results of amperometric titration of 32 ppm of lead(II) with a solution of 5-(4-aminophenyl)-1,3,4-oxadiazole-2-thiol in complex solutions (P = 0.95; n=5)

No	The composition of the analysed mixture and the concentration of components in it, ppm	Determined Pb(II) at ppm; (P=0,95; $\bar{x} \pm \Delta x$ )	S	RSD%
1	Pb(20.8)+Ag(10.8)+Zn(21.0)	20.7±0.0096	0.16	0.77
2	Pb(20.8)+Hg(25.0)+Sn(24.0)+Cd(14.0)+Cu(24.0)	20.64±0.0132	0.22	1.06
3	Pb(41.6) +Hg (33.9) +Ni(24.0) +Cr(26.0)+Cd(45.0) + Bi(37.2)	41.2±0.0054	0.18	0.44
4	Pb(41.6) +Hg (49.0)+Bi(37.6)+Cu(25.5)+Cd(46.0) + Ag(25.0)+Sn(44.0)	41.4±0.0072	0.24	0.58
5	Pb(22.5)+Sn(40.0)+Ag(48.0)+Cd(45.0)+As(33.0)+Cu(36.0)+Ni(47.5)	41.8±0.0107	0.36	0.86

**Table 8.** Results of amperometric titration of 32 ppm of copper(II) with a solution of 5-(4-aminophenyl)-1,3,4-oxadiazole-2-thiol in complex solutions (P = 0.95; n=5)

No	The composition of the analysed mixture and the concentration of components in it, ppm	Determined Cu(II) at ppm; (P=0,95; $\bar{x} \pm \Delta x$ )	S	RSD%
1	Cu (32.0) + Ti(35.00)	32.05±0.0085	0.22	0.68
2	Cu (32.0) + Hg(48.6) + Cd(54.8)	32.21±0.0093	0.24	0.74
3	Cu (64.0) + Cd(65.00) + Sr(43.75) + Zn(85)	64.32±0.0062	0.32	0.49
4	Cu (64) +Cu(45.00)+Zn(55)+ Ni(65.00)	64.52±0.0067	0.35	0.54
5	Cu (64) + Sr(44.0)+Mg(31.4)+Cd(55.00) + Ni(65.32)	64.65±0.0073	0.38	0.59

### 3.10. Determination of lead(II) and copper(II) ions from the river water

In the next part of this research work, the values of lead(II) and copper(II) ions were measured with 5-(4-aminophenyl)-1,3,4-oxadiazole-2-thiol analytical reagent from the river water (Tashkent, Uzbekistan) by amperometric titration. The obtained results are indicated in Table 9. The compositions of river water is Na<sup>+</sup> (500 ppm) + K<sup>+</sup>(550 ppm)+ Ca<sup>2+</sup> (260 ppm)+ Mg<sup>2+</sup> (240 ppm)+ Fe<sup>3+</sup> (22 ppm)+ Cu<sup>2+</sup> (20 ppm)+ Pb<sup>2+</sup> (4 ppm)+ Zn<sup>2+</sup>(10 ppm)+ Cd<sup>2+</sup> (0.02 ppm) + Al<sup>3+</sup> (50 ppm)+ Ni<sup>2+</sup>(5 ppm)+ Mn<sup>2+</sup> (10 ppm) + Hg<sup>2+</sup>(0.01 ppm). The obtained results show that the values of S and RSD% for copper and lead were 0.52, 0.12 and 2.7, 2.9, respectively, confirming that the degree of selectivity of the proposed method for the determination of lead(II) and copper(II) with a solution of 5-(4-aminophenyl)-1,3,4-oxadiazole-2-thiol is very high in compositions of river water and targeted values of lead(II)

and copper(II) were more accurately determined with the selected analytical reagent by the amperometric titration. The obtained results were compared with the inductively coupled plasma atomic emission spectroscopy (ICP-AES) results (Tables 10 and 11), confirming that the suggested method is more sensitive. The obtained ICP-AES spectra were represented in supporting documents (Figures 1S and 2S).

**Table 9.** Determination of copper and lead ions from the composition of river water

The compositions of river water at ppm	Protective agent	Determined $Me^{2+}$ at ppm, $\bar{X} \pm \Delta X$	S	RSD%
$Na^+$ (500) + $K^+$ (550) + $Ca^{2+}$ (260) + $Mg^{2+}$ (240) + $Fe^{3+}$ (22) + $Cu^{2+}$ (20) + $Pb^{2+}$ (4) + $Zn^{2+}$ (10) + $Cd^{2+}$ (0,02) + $Al^{3+}$ (50) + $Ni^{2+}$ (5) + $Mn^{2+}$ (10) + $Hg^{2+}$ (0.01)	5% Sodium fluoride + sodium thiosulfate precipitate	$Cu^{2+}$ , 19.54±0.64	0.52	2.7
		$Pb^{2+}$ , 4.08±0.15	0.12	2.9

**Table 10.** Determination of copper ion from the composition of river water by ICP-AES

№	$Cu^{2+}$	x	x-x <sub>i</sub>	(x-x <sub>i</sub> ) <sup>2</sup>	S	RSD%
	x <sub>i</sub>					
1	19.98	19.96	0.02	0.0004	0.0141	1.9
2	19.96		0	0		
3	19.94		0.02	0.0004		

**Table 11.** Determination of lead ion from the composition of river water by ICP-AES

№	$Pb^{2+}$	x	x-x <sub>i</sub>	(x-x <sub>i</sub> ) <sup>2</sup>	S	RSD%
	x <sub>i</sub>					
1	3.98	3.99	0.01	0.0001	0.0158	0.9
2	3.99		0	0		
3	4.01		0.02	0.0004		

### 3.11. Comparison with previous works

Copper(II) and lead(II) are hazardous ions in environmental samples. Determining these ions from the samples is an important issue in analytical chemistry. Table 12 shows the comparison with previous works in the Cu(II) and Pb(II) determination (last 5 years). It is clear from the comparison details that the various methods with analytical reagents are used in the determination of Cu(II) and Pb(II) ions, however, these methods and analytical reagents are expensive, hazardous, time-consuming and non-recyclable. Additionally, the used methods are



more expensive and required large equipment or large laboratories. In this present work, it is recommended new analytical reagent named 5-(4-aminophenyl)-1,3,4-oxadiazole-2-thiol in the determination of copper(II) and lead(II) by the amperometric titration method. It is found that this analytical reagent effectively determines the Cu(II) and Pb(II) ions from environmental samples by amperometric titration, which is time-saving and low-cost. This reagent is also recyclable. It was also indicated that the detection limit for lead(II) and copper(II) ions with the suggested analytical reagent was 2.08 and 3 ppm, respectively. The complex of 5-(4-aminophenyl)-1,3,4-oxadiazole-2-thiol with lead(II) and copper(II) ions have a sharp angle at 0.5 V and 0.75 V, respectively, indicating that these ions are determined at one solution with this reagent.

**Table 12.** Comparison with previous works in the Cu(II) and Pb(II) determination (last 5 years)

No	Name of analytical agent	Method	Samples	Detection limit	Year, Ref.
1	Ethylenediaminetetraacetic acid (EDTA) chelating ligand-modified polyaniline (PANI)	Differential pulse voltammetry	Water	Cu(II) is 0.08 $\mu\text{M}$ and Pb(II) is 1.65 $\mu\text{M}$	2017, [37]
2	Graphene oxide-chitosan/poly-l-lysine nanocomposite modified glassy carbon electrode	Pulse anodic stripping voltammetry	Tap water	Cu(II) is 0.02 $\mu\text{g/L}$ and Pb(II) is 0.02 $\mu\text{g/L}$	2017, [38]
3	Two-dimensional accordion-like alk-Ti <sub>3</sub> C <sub>2</sub>	Electrochemical methods	Environmental samples	Cu(II) is 0.032 $\mu\text{M}$ and Pb(II) is 0.041 $\mu\text{M}$	2017, [39]
4	Organic linker Schiff base (H <sub>2</sub> L) derived from 4-aminobenzoic acid and 2-carboxybenzaldehyde	Electrochemical methods	Environmental samples	Cu(II) is $7.5 \times 10^{-8}$ Mol/L	2021, [40]
5	Electrochemical GO/MnO <sub>2</sub> /GCE sensor	Square wave anodic stripping voltammetry	Water samples	Cu(II) is 1.67 nM and Pb(II) is 3.33 nM	2019, [41]
6	N-o-Vanillidine-2-amino-p-cresol	Flame atomic absorption spectrometry	Tap, river and seawater, rice flour and black tea samples	Cu(II) is 0.93 $\mu\text{g/L}$	2017, [42]
7	Phytic acid/polypyrrole nanowires modified glassy carbon electrode	Electrochemical methods	Water examples	Cu(II) is 3.33 $\mu\text{g/L}$	2017, [43]
8	Vial-coupled transparency electrodes	Square-wave anodic stripping voltammetry	Water samples	Pb(II) is 0.3 $\mu\text{g/L}$	2017, [44]
9	5-(4-aminophenyl)-1,3,4-oxadiazole-2-thiol	Amperometric titration	River water	Cu(II) is 3 ppm and Pb(II) is 2.08 ppm	Present work

It was also confirmed that the half-wave potential of 5-(4-aminophenyl)-1,3,4-oxadiazole-2-thiol was 0.55 V, confirming that the reagent is a reducing agent. The selectivity of this reagent is very high. In the future, this reagent should be widely used in the analytical determination of Cu(II) and Pb(II) ions.

In this research, electrochemical and spectroscopic techniques were used. These methods are easily operated and low cost. In this research, it is recommended new analytical reagent named 5-(4-aminophenyl)-1,3,4-oxadiazole-2-thiol in the determination of copper(II) and lead(II) by the amperometric titration method. To determine the copper(II) and lead(II) by the amperometric titration method with the 5-(4-aminophenyl)-1,3,4-oxadiazole-2-thiol is low cost, effective and doesn't require expensive equipment. Other methods are more expensive and required large equipment, and large laboratories, which is difficult for companies and industries.

#### 4. CONCLUSION

In this research work, the new analytical reagent of 5-(4-aminophenyl)-1,3,4-oxadiazole-2-thiol for the determination of copper(II) and lead(II) was introduced. The main properties, optimal conditions and characteristics in the determination of copper(II) and lead(II) with 5-(4-aminophenyl)-1,3,4-oxadiazole-2-thiol were studied. As a result, the following conclusions are found:

- (i) it is confirmed that 5-(4-aminophenyl)-1,3,4-oxadiazole-2-thiol high accurately determinates the lead(II) and copper(II) ions by amperometric titration;
- (ii) the suggested method is low-cost and time-saving in contrast to other methods. 5-(4-aminophenyl)-1,3,4-oxadiazole-2-thiol is a more efficient and recyclable analytical reagent in the determination of lead(II) and copper(II) ions;
- (iii) the complex of 5-(4-aminophenyl)-1,3,4-oxadiazole-2-thiol with lead(II) and copper(II) ions have a sharp angle at 0.5 V and 0.75 V, respectively, indicating that these ions are determined at one solution with this reagent. This is due to the difference in applied voltage of lead(II) and copper(II) ions;
- (iii) lithium chloride and potassium nitrate were chosen as the best background electrolyte for lead(II) and copper determination in amperometric titration, respectively;
- (iv) the detection limit for lead(II) and copper(II) ions were 2.08 and 3 ppm, respectively;
- (v) It is clear from the observed results of the polarographic analysis that the 5-(4-aminophenyl)-1,3,4-oxadiazole-2-thiol is oxidised by the two-electron transformation;
- (vi) it was found that the half-wave potential of 5-(4-aminophenyl)-1,3,4-oxadiazole-2-thiol was 0.55 V, confirming that the reagent is a reducing agent;
- (vii) the molar ratio of Me: Reagent is 1:2 in copper(II) and lead(II) precipitation with 5-(4-aminophenyl)-1,3,4-oxadiazole-2-thiol;

- (viii) molar conductivity ( $\lambda_0$ ) of 5-(4-aminophenyl)-1,3,4-oxadiazole-2-thiol, lead and copper 17.2, 71 and 56.6, respectively;
- (ix) IR results confirmed the molecular structure of the 5-(4-aminophenyl)-1,3,4-oxadiazole-2-thiol complexes with copper and lead;
- (xi) the selectivity of lead and copper determination by 5-(4-aminophenyl)-1,3,4-oxadiazole-2-thiol is very high compared to Hg(II), Ag(I), Cd(II), As(III), Ni(II), Cu(II), Sn(II), Bi(III) ions for lead(II) ions and Cd(II), Pb(II), Al(III), Zn(II), Hg(II), Ti(IV), Ag (I), As (II) ions for copper(II) ions, respectively;
- (x) the determination of copper and lead ions from the composition of river water by 5-(4-aminophenyl)-1,3,4-oxadiazole-2-thiol is more effective.

## REFERENCES

- [1] E. Flores, J. Pizarro, F. Godoy, R. Segura, A. Gomez, N. Agurto, and P. Sepúlveda, *Sens. Actuators B* 251 (2017) 433.
- [2] W. Zhang, Y. Xu, H.E. Tahir, X. Zou, and P. Wang, *Food Chem.* 221 (2017) 541.
- [3] Z.A. Smanova, D.A. Gafurova, and A. V. Savchikov, *Russ. J. Gen. Chem.* 81 (2011) 739.
- [4] A. Haghshenas, M. Hatami-manesh, M. Sadeghi, M. Mirzaei, and B. Mohammadi Bardkashki, *J. Environ. Heal. Eng.* 5 (2018).
- [5] S.L. Jackson, J. Spence, D.J. Janssen, A.R.S. Ross, and J.T. Cullen, *J. Anal. At. Spectrom.* 33 (2018) 304.
- [6] X. Wang, Z. Zhao, H. Wang, F. Wang, and W. Dong, *J. Environ. Sci.* 124 (2023) 630.
- [7] N.K. Madusmanova, Z.A. Smanova, and I.I. Zhuraev, *J. Anal. Chem.* 75 (2020) 135.
- [8] Z. Nurmukhammadov, Z.A. Smanova, K.S. Tadjhimukhamedov, and M.S. Inatova, *Russ. J. Org. Chem.* 50 (2014) 895.
- [9] C.E. Souto-Oliveira, M. Babinski, D.F. Araújo, D.J. Weiss, and I.R. Ruiz, *Atmos. Environ.* 198 (2019) 427.
- [10] M.A. Deshmukh, R. Celiesiute, A. Ramanaviciene, M.D. Shirsat, and A. Ramanavicius, *Electrochim. Acta* 259 (2018) 930.
- [11] G. Zhao, R. Liang, F. Wang, J. Ding, and W. Qin, *Sens. Actuators B* 279 (2019) 369.
- [12] Y. Zhou, Y.-S. Li, X.-Y. Meng, Y.-Y. Zhang, L. Yang, J.-H. Zhang, X.-R. Wang, S.-Y. Lu, H.-L. Ren, and Z.-S. Liu, *Sens. Actuators B* 183 (2013) 303.
- [13] G.D. Davronbekovich, and S.Z. Asanalievna, *Indian J. Forensic Med. Toxicol.* 14 (2020).
- [14] N. Qutlimurotova, S. Mahmadioliev, Z. Smanova, Z. Tursunkulov, and Z. Yakhshiyeva, *Period. Tche Quim.* 17 (2020) 735.
- [15] U. Madatov, S. Rakhimov, B. Normatov, S. Tuychiev, L. Khalilova, and Z. Smanova, *AIP Conf. Proc* 1 (2022) 50022.
- [16] O. Tueva, N. Qutlimurotova, L. Sadullayeva, Z. Smanova, and U. Matkarimova, *AIP Conf. Proc.* 1 (2022) 50029.

- [17] C.O.B. Okoye, A.M. Chukwuneke, N.R. Ekere, and J.N. Ihedioha, *Int. J. Phys. Sci.* 8 (2013) 98.
- [18] N.K. Madusmanova, L.M. Khalilova, E.S. Zhumaeva, D.A. Gafurova, Z.A. Smanova, and K.S. Tozhimukhamedov, *J. Anal. Chem.* 77 (2022) 26.
- [19] P.-H. Li, Y.-X. Li, S.-H. Chen, S.-S. Li, M. Jiang, Z. Guo, J.-H. Liu, X.-J. Huang, and M. Yang, *Sens. Actuators B* 257 (2018) 1009.
- [20] D. Ismailova, A. Ziyaev, B. Elmurodov, T. Toshmurodov, K. Bobakulov, and R. Zakirova, *J. Basic Appl. Res. Biomed.* 2 (2016) 476.
- [21] Y.Q. Shi, X. Zhao, J. Lin, D.P. Li, H. Huang, and S.Y. Zhang, *China Environ. Sci.* 39 (2019) 1189.
- [22] B.P.D. Batvari, and D. Saravanan, *Rasayan J. Chem.* 13 (2020) 195.
- [23] Y. Ma, Y. Wang, D. Xie, Y. Gu, X. Zhu, H. Zhang, G. Wang, Y. Zhang, and H. Zhao, *Chem. Eng. J.* 347 (2018) 953.
- [24] S. Hou, N. Zheng, L. Tang, X. Ji, Y. Li, and X. Hua, *Environ. Int.* 128 (2019) 430.
- [25] O. Zvěřina, P. Coufalík, J. Šimůnek, P. Kachlík, R. Chlupová, and J. Pavelková, *Environ. Monit. Assess.* 192 (2020) 1.
- [26] S.A. Kitte, S. Li, A. Nsabimana, W. Gao, J. Lai, Z. Liu, and G. Xu, *Talanta* 191 (2019) 485.
- [27] R. Abd Rashid, N.A. Muda, M. Saaid, M.I.A. Halim, and K. Mohamed, *Int. J. Eng. Technol.* 7 (2018) 232.
- [28] P. Yang, R. Zhou, W. Zhang, R. Yi, S. Tang, L. Guo, Z. Hao, X. Li, Y. Lu, and X. Zeng, *Food Chem.* 272 (2019) 323.
- [29] N. Sadeghi, B. Jannat, M. Behzad, M.R. Oveisi, M. Hajimahmoodi, and F. Ahmadi, *Human, Heal. Halal Metrics.* 1 (2020) 24.
- [30] S. Hamida, L. Ouabdesslam, A.F. Ladjel, M. Escudero, and J. Anzano, *Anal. Lett.* 51 (2018) 2501.
- [31] S. Krzebietke, M. Daszykowski, H. Czarnik-Matusiewicz, I. Stanimirova, L. Pieszczyk, S. Sienkiewicz, and J. Wierzbowska, *Talanta* (2022) 123749.
- [32] T. V Skiba, A.R. Tsygankova, N.S. Borisova, K.N. Narozhnykh, T. V Konovalova, O.I. Sebezhko, O.S. Korotkevich, V.L. Petukhov, and L. V Osadchuk, *J. Pharm. Sci. Res.* 9 (2017) 958.
- [33] J.F. Van Staden, and M.C. Matoetoe, *Anal. Chim. Acta* 411 (2000) 201.
- [34] O. Yıldız, D. Citak, M. Tuzen, and M. Soylak, *Food Chem. Toxicol.* 49 (2011) 458.
- [35] M.F. De Oliveira, A.A. Saczk, L.L. Okumura, A.P. Fernandes, and M. De Moraes, *Anal. Bioanal. Chem.* 380 (2004) 135.
- [36] L.B. Allen, P.H. Siitonen, and H.C. Thompson Jr, *J. Am. Oil Chem. Soc.* 75 (1998) 477.
- [37] M. A. Deshmukh, R. Celiesiute, A. Ramanaviciene, M. D. Shirsat, and A. Ramanavicius, *Electrochim. Acta* 259 (2018) 930.

- [38] Z. Guo, X.K. Luo, Y.H. Li, Q.N. Zhao, M.M. Li, and Y.T. Zhao, *J. Colloid Interface Sci.* 490 (2017) 11.
- [39] X. Zhu, B. Liu, H. Hou, Z. Huang, K. M. Zeinu, L. Huang, and J. Yang, *Electrochim. Acta* 248 (2017) 46.
- [40] R.G. Deghadi, A.S. Eliwa, A.E. Ali, W. M. Hosny, G.G. Mohamed, *Comments on Inorganic Chem.* 41 (2021) 189.
- [41] H. Sun, C. Wang, Y. Xu, D. Dai, X. Deng, and H. Gao, *ChemistrySelect* 4 (2019) 11862.
- [42] C. Karadaş, and D. Kara, *Food Chem.* 220 (2019) 242.
- [43] N. Wang, H. Dai, D. Wang, H. Ma, and M. Lin, *Mater. Sci. Eng. C* 76 (2017) 139.
- [44] D. Martín-Yerga, I. Álvarez-Martos, M.C. Blanco-López, C.S. Henry, and M.T. Fernández-Abedul, *Anal. Chim. Acta* 981 (2017) 24.