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# Stripping voltammetric determination of copper ions using a graphite-based electrochemical sensor modified with pyrocatechol violet

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ABSTRACT

In this research, a sensitive and selective electrochemical sensor (ES) based on graphite modified with pyrocatechol violet (PV) was developed for the anodic stripping voltammetric (ASV) determination of Cu(II) ions. The optimal conditions for modifying the electrode with PV were determined: the best results were obtained using an electrochemical sensor prepared by modifying 2.0 g of graphite powder with 4.0 mg of PV at a temperature range of 60–70°C. The optimal conditions for the ASV determination of Cu(II) ions using the ES were identified as follows: Britton Robinson buffer solution with a pH of 5.0–5.5, a supporting electrolyte of 0.1 M $HNO_3$, and an accumulation time of 100 seconds on the electrode surface. The limit of detection for the $Cu^{2+}$ ion was determined to be 0.04 ppm, and the closeness of the obtained results was confirmed by a correlation coefficient close to 1. The working surface area of the electrochemical sensor (MES) modified with pyrocatechol violet was determined to be 0.2 $cm^2$, and its working potential range was found to be from -1.8 V to +1.5 V during the experiments.

## 1. Introduction

The discharge of heavy metals into the environment, driven by industrial expansion and increasing population, poses a significant environmental issue in many nations. These metals are non-biodegradable and can accumulate in living organisms, causing long-lasting toxic effects [1]. Copper ions are widespread in environmental and industrial processes, and their presence in the environment, including water, soil, and air, poses a significant risk due to their high biological activity and toxicity [2-5]. Copper can originate from natural and industrial sources, agricultural activities, industrial production, and precious metal recycling processes [6-8]. Given the high toxicity of copper and its harmful effects on organisms, the determination of these ions is crucial for environmental and health monitoring. Copper ions in high concentrations can be harmful to biological systems, and elevated copper levels in water sources pose a threat to aquatic ecosystems [9-11].

The availability of effective and reliable analytical methods for determining copper ions is very important for environmental monitoring and health safety. Among electroanalytical methods, the stripping voltammetry (SV) technique stands out for its high sensitivity, speed, and cost-effectiveness. The SV method, especially when applied with modified electrodes, proves effective for determining copper ions [12,13]. This method differs from traditional voltammetry in electrochemical analysis as it offers the possibility of high precision and variable potential analysis. Electrodes that interact with copper ions play a key role in determining their presence and concentration [14].

Graphite-based electrodes are widely used in electroanalytical methods due to their high electrical conductivity, chemical stability, and low cost. As a result, graphite electrodes are commonly used in analytical procedures. Modified electrodes, through chemical changes on their surface, enhance the analytical efficiency [15]. The modification of graphite-based electrodes in determining copper ions is achieved using nanomaterials, bismuth, alloys, organic reagents and other variable elements [16,17]. The modified electrodes ensure high sensitivity and accuracy in copper ion

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determination. This modification helps improve the electrochemical properties of the electrode and creates optimal conditions for the determination of copper ions [18].

In addition, other methods are available for determining copper ions. Techniques such as Atomic Emission Spectroscopy (AES), Atomic Absorption Spectroscopy (AAS), and Inductively Coupled Plasma Optical Emission Spectroscopy (ICP-OES) provide high sensitivity but are costly and require large equipment. AES and AAS methods are mainly limited by their high cost, complex operation processes, and long analysis times. The ICP-OES method requires analysis at high temperatures, complicating the process further [19,20]. These methods are primarily used in laboratory settings and may be challenging to implement in smaller-scale analyses. Therefore, the SV method, particularly with modified electrodes, provides high portability, speed, and sensitivity, making it suitable for environmental monitoring and industrial quality control applications [21].

The advantages of the stripping voltammetric method for determining copper ions are clear. The effectiveness and convenience of this method allow for its widespread application in environmental monitoring, water and air quality control, as well as in the inspection of industrial waste and groundwater [22]. The primary advantages of the stripping voltammetry method include affordability, high sensitivity, rapid analysis capabilities, portability, and ease of use. Compared to other electroanalytical methods, this technique also offers the potential to enhance sensitivity and accuracy, ensuring high purity and not requiring excessive equipment [23,24].

This article explores the analytical methods used for determining copper ions with stripping voltammetry, utilizing graphite-based modified electrodes, and discusses their advantages. Additionally, by comparing these methods with other traditional and modern techniques, the efficiency and advantages of the SV method in environmental monitoring and industrial processes are highlighted

## 2. Materials and Methods

### 2.1. Chemicals and reagents

All reagents were of analytical grade and were used in this study without any additional purification. Carbon graphite powder and tritolyl phosphate oil were purchased from Sigma-Aldrich. All solutions were prepared using bidistilled water.

### 2.2. Apparatus

The analysis results were obtained using an electrochemical sensor based on graphite, connected to a voltammetric analyzer (ABC-1.1 OOO NTF “VOLTA” №0092184; Made in Russia), within an electrolysis cell consisting of a saturated potassium chloride reference electrode and a large-surface-area auxiliary graphite electrode. The pH of the solutions was monitored using a pH meter (pH Mettler-Toledo AG 8603; Made in China, №-B507604800). The masses of the substances were measured with an analytical balance (FA2204N; Made in China), and bidistilled water was obtained using a distillation unit (GFL_2104 D-30938; Made in Germany).

### 2.3. Working electrode

The electrode modified with Pyrocatechol violet (PV was prepared by hand-mixing the PV compound and graphite powder (GP) in various weight ratios, with the addition of tritolyl phosphate. Ethanol was added to the mixture as an inert, volatile solvent in the appropriate amount, and the resulting mixture was homogenized by thoroughly blending both materials. The mixture was then placed in open air to allow the solvent to evaporate. The obtained composite material (paste) was placed into a cylindrical teflon tube (the geometric surface area of the working electrode is 0.2 $cm^2$). Electrical contact was provided by a copper wire. Therefore, as shown in the following figure, the optimal percentage of PV for the study was found to be 1.5%.

### 2.4. Measurements and procedure

Before performing the analysis, sample collection and preparation must be carried out. For analysis, 2 mL of the water sample is taken and placed in a temperature-resistant beaker. Then, 0.02 mL of 0.1 M HCl and a solution prepared by mixing bidistilled water and 0.1 M $HNO_3$ in a 1:1 ratio are added, and the mixture is stirred with a glass rod. The solution is evaporated until no water droplets remain. After evaporation, the beaker is removed and cooled to room temperature, and 25 mL of 0.1 M $HNO_3$ supporting electrolyte solution is added, which is then thoroughly mixed with a glass rod. The resulting solution is placed into the electrochemical cell. Afterward, the analysis is performed. The standard solution of Cu(II) ions was prepared based on "Zolotoe runo" UzDSN, and interfering ions were removed by dissolving water-soluble salts in bidistilled water.

## 3. Results and Discussion

In the research work, infrared spectroscopy (IR) analysis of the working surface of the electrochemical sensor (MES) modified with the selected PV for the determination of copper ions was performed, and the obtained results are shown in Figure 1.

In the IR spectrum of the pyrocatechol violet reagent, absorption peaks corresponding to the -OH group were observed in the 3054–2962 $cm^{-1}$ region. At 1733 $cm^{-1}$, vibration spectra of the –C=O bond were detected. At 1042 $cm^{-1}$, absorption maxima related to $–SO_3H$ bonds were observed. The bonding mechanisms of the complex formed between Cu(II) ions and the Pyrocatechol violet organic reagent were studied using IR spectroscopy. Subsequently, the IR spectrum of the complex formed between Cu(II) ions and Pyrocatechol violet was obtained. The results are shown in Figure 2. From Figure 2, we can observe that the vibrations corresponding to the –OH groups have shifted compared to the reagent, appearing at 3197 cm$^{-1}$, which suggests the involvement of the metal in the binding with the –OH group near the carbonyl group. This shift indicates a reduction in hydrogen bonding, which led to the absorption peak shifting to the 3197 cm$^{-1}$ region. The retention of the spectrum at 1042 cm$^{-1}$ indicates that no bonding occurred with the $-SO_3H$ group. The appearance of a peak at 543 cm$^{-1}$ in the fingerprint region suggests the formation of an -O-Cu bond.

In conclusion, the binding of Cu(II) ions to the -C=O and nearby -OH groups was observed through IR spectroscopic analysis. In the subsequent work, standard solutions of organic reagents prepared with a solvent were subjected to optical density measurements relative to a reference solution using an auto-calibration method. Solutions were prepared in 50 mL volumetric flasks, and before measuring the wavelength, they were mixed using a magnetic stirrer. The optical densities were then measured using "EMC-30PC-UV, UV-5100 UV VIS" spectrophotometers, and the results are shown in Figure 3. From Figure 3, we can observe that the absorption spectrum of the selected Pyrocatechol violet modifier was observed at 447 nm. The absorption spectrum of the $Cu^{2+}$ solution was observed at 815 nm. The absorption spectrum of the complex formed between Pyrocatechol violet and Cu(II) in a pH=5.0 universal buffer solution was observed at 615 nm. Based on these results, it can be concluded that the absorption spectrum of the reagent shifted bathochromically by 168 nm upon complex formation, indicating the formation of the complex.

Based on the above experiments and information from the literature, the mechanism of complex formation between copper and the PV organic reagent is hypothesized to be as Figure 4.

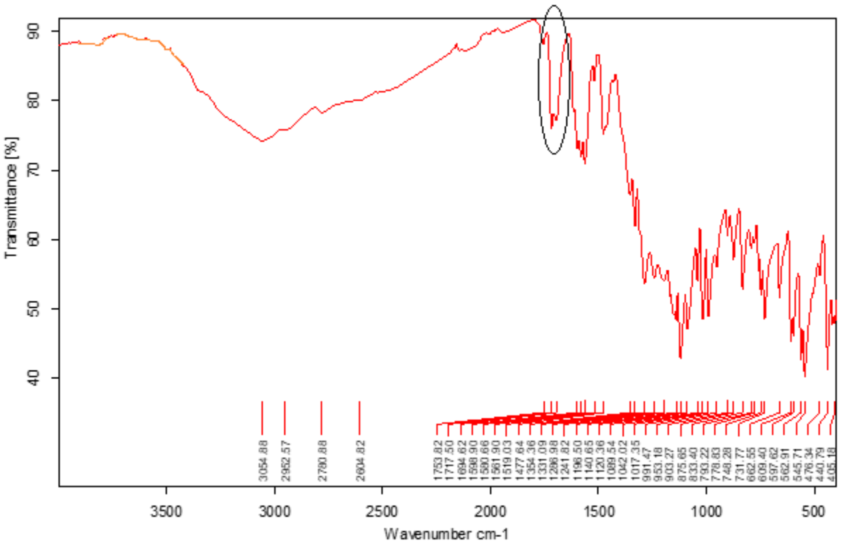


**Fig. 1**. IR spectrum of pyrocatechol violet reagent.

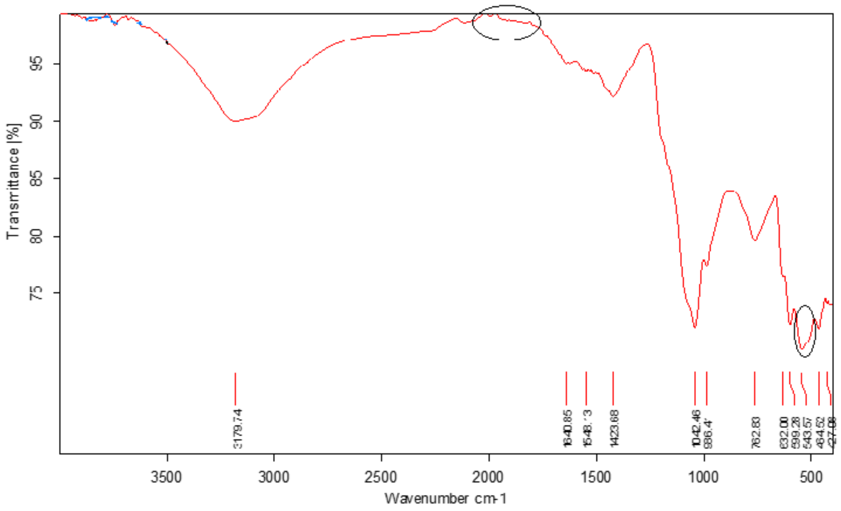


**Fig. 2.** IR spectrum of the complex formed between Cu(II) ion and pyrocatechol violet reagent.

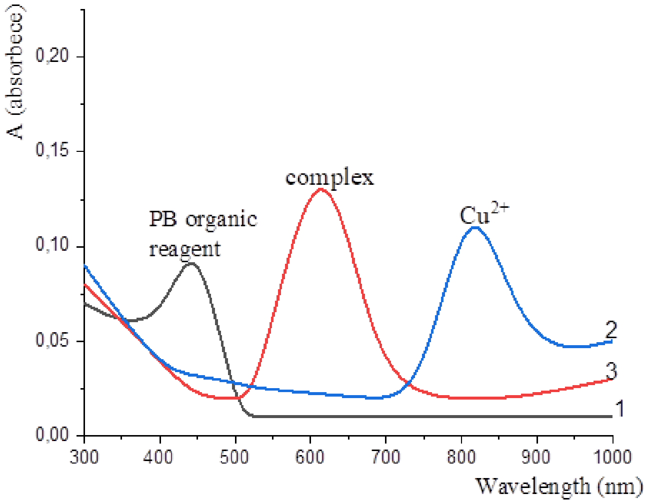


**Fig. 3.** Absorption spectra of pyrocatechol violet and its complex with Cu(II) Ion: 1.Absorption spectrum of PV; 2.Absorption spectrum of Cu(II) ion; 3.Absorption spectrum of the complex formed between PV and Cu(II).

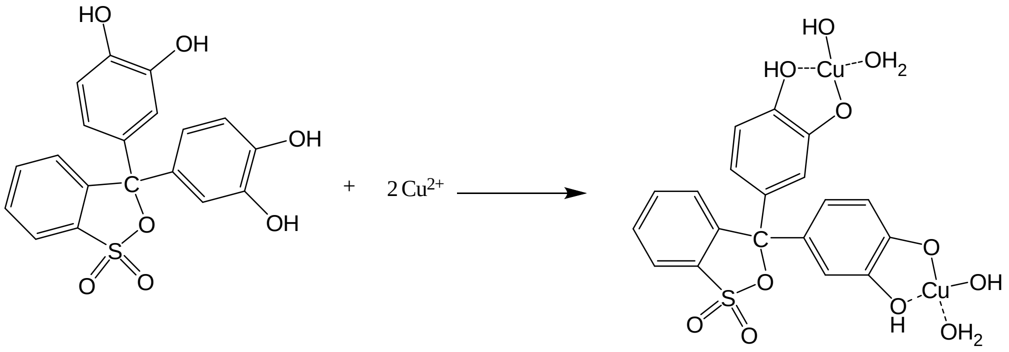


**Fig. 4.** The proposed ptructure of the complex formed between Cu(II) ion and the selected organic reagent.

After selecting the PV organic reagent for the Cu(II) ions, the electrochemical sensor (MES) was prepared using the following method: Spectral grade graphite particles of specific mesh size were initially ground in a porcelain mortar (the powder was passed through a sieve of known diameter), and the exact mass of each sample was weighed using an analytical balance. A suspension of pre-cleaned wax was heated in a porcelain crucible using a sand bath to its melting point (75-85°C). The graphite powder was then added to the molten wax mixture while continuously stirring. The weight ratio of wax to graphite was 1:1. The obtained mixture was heated at 90°C for 90 seconds and, while continuously stirring, was slowly filled into polyethylene tubes with a hollow interior, 60 mm long and 0.3 mm in diameter, using a syringe. Copper or silver wire with a diameter of 0.05 mm and a length of 90 mm was used as the conductor. To stabilize the paste components and prevent the sensor surface from being damaged during the mechanical renewal of the electrode surface, the paste should be left to harden completely for 7-10 days.

As is known, the properties of the modified solid MES are primarily dependent on the ratio of the components that make up the graphite paste. Therefore, mixtures with different weight ratios of graphite powder, wax, and the modifier were prepared. The optimal amount of modifier incorporated into the graphite paste was selected based on the experimental data obtained. Based on optimized conditions, MES was prepared with the following amounts of modifier: 0.1, 0.2, 0.3, 0.4, 0.5, 0.6, 0.7, 0.8, and 0.9 mg. The results obtained from testing sensors developed using this method are presented in Table 1 and Figure 5.

From the above figure and table, it can be seen that the effective amount of the modifier in the paste for determining copper was achieved when 0.4 mg of the modifier was added, which resulted in an increase in the peak height. Beyond this point, higher amounts of the modifier led to a decrease in the analytical signal. The mixture of graphite and wax in the paste not only ensures the conductivity of the electrochemical sensor (ES) but also enhances its selectivity. If the amount of either component is increased or decreased, the conductivity of the ES is reduced.

If too much or too little modifier is added to the paste, the sensitivity of the sensor's active surface decreases, which negatively affects the electrical conductivity of the ES. Therefore, the amounts mentioned above should be used when designing electrochemical sensors. When the mass of the modifier in the ES is 0.4 mg, the slight decrease in electrical conductivity is compensated by the increase in selectivity and sensitivity, making this concentration ideal for applying the modifier with different characteristics and concentrations.

The developed MES were used to determine Cu(II) ions in standard samples using the stripping voltammetric method, yielding satisfactory results. When using MES with PV reagent, an intense analytical signal for copper was observed, and the detected amount of copper was found to match the amount added. Additionally, when comparing voltammograms obtained with ES and MES, it was observed that the analytical signal for copper in the MES shifted from the -250 mV range to the -140 mV range. This shift indicates that the interference from elements like Cd, Pb, and Sn during the determination of Cu(II) ions in natural samples is minimized. In many cases, the analytical signals of Sn(IV) and Pb(II) ions have interfered with the copper signal, negatively affecting the accuracy of copper determination in natural samples. The results obtained are presented in Figure 6.

### 3.1. Selection of the optimal working temperature for modified carbon paste electrodes:

The test results of the developed electrochemical sensor (ES) samples showed that the properties of the ES are highly dependent on the temperature of the carbon paste placed inside the polyethylene tube during fabrication.

Furthermore, it is important to note that the temperature should not exceed 100°C when heating the mixture of graphite powder, modifier, and wax, as higher temperatures could lead to the thermal decomposition of the organic modifier. Following these guidelines, the prepared carbon paste should be slightly cooled before being introduced into the polyethylene tubes, otherwise, the electrode’s working surface would become unsuitable for mechanical renewal, losing the essential active sites required for the electrochemical sensor’s surface recovery. However, to prevent air gaps inside the tube, the carbon paste is inserted into the plastic tube and left in an upright position for 10-15 days to ensure the paste settles tightly within the tube. Cu(II) ion determination was carried out using ES fabricated at various temperatures, and the results are provided in Table 2.

From the data in Table 2, we can conclude that electrochemical sensors made at temperatures between 60-70°C provide the best analytical signal and accuracy compared to those made at other temperatures and conditions. The best analytical signal (peak height, reliability, and correct results) in the stripping-voltammetric method for determining Cu(II) ions was observed in sensors made at 60-70°C. Based on this, further research was carried out using sensors made under the conditions mentioned above.

Cu(II) ions were detected on the working surface of the MES modified with PV from the solution. The results, shown in the following figures, demonstrate that Cu(II) ions were uniformly adsorbed on the surface of the PV-modified sensor (Figure 7).

**Table 1**. Selection of the amount of modifier to be added in the development of modified electrochemical sensors.

| Amount of modifier, mg | 0,1 | 0,2 | 0,3 | 0,4 | 0,5 | 0,6 | 0,7 | 0,8 | 0,9 |
|---|---|---|---|---|---|---|---|---|---|
| I, µA | | | | | | | | | |
| MES with Pyrocatechol violet organic reagent | 15 | 20 | 25 | 27 | 22 | 17 | 12 | 8 | 4 |

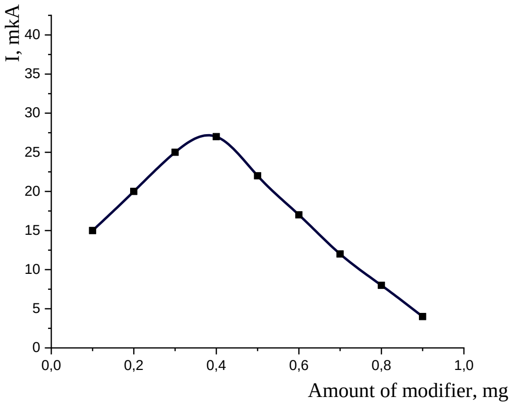


**Fig. 5.** The relationship between the amount of modifier added to the electrochemical sensor and the analytical signal.

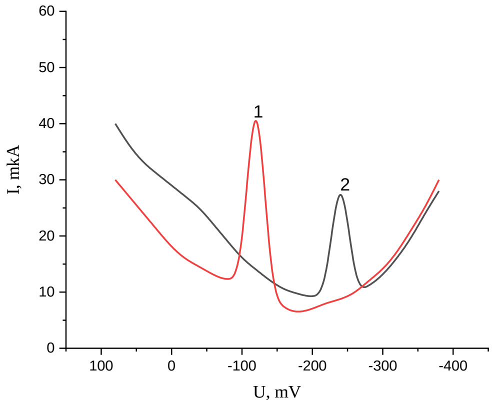
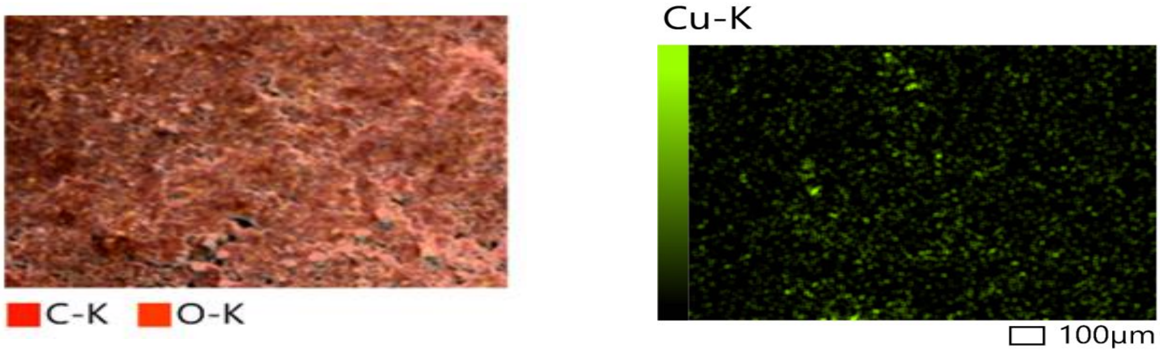


**Fig. 6.** Stripping-voltammetric determination of Cu(II) ion: 1.Voltamperogram obtained with the modified electrochemical sensor; 2.Voltamperogram obtained with the graphite-based electrochemical sensor.

**Table 2.** The results of the effect of temperature on the intensity of the analytical signal for Cu(II) determination using modified carbon paste electrochemical sensors at different temperatures are shown. (n=5; $C_{Cu(II)}$=2,5 μg $L^{-1}$)

| **Temperature during the modification process, °C** | **E, mV** | **Found Cu(II), μg $L^{-1}$ ($\bar{X}$ ±ΔX; P = 0,95)** | **I, μA** | **S** | **$S_r$** |
|---|---|---|---|---|---|
| 90 | -120 | 1.0±0.35 | 32 | 0.220 | 0.222 |
| 80 | -120 | 2.15±0.22 | 40 | 0.180 | 0.083 |
| 70 | -120 | 2.45±0.20 | 68 | 0.160 | 0.065 |
| 65 | -120 | 2.49±0.14 | 64 | 0.090 | 0.036 |
| 60 | -120 | 2.53±0.13 | 64 | 0.110 | 0.043 |
| 55 | -120 | 2.44±0.17 | 42 | 0.140 | 0.057 |
| 50 | - | 1,50±0.36 | - | 0.230 | 0.153 |



(1) (2)

**Fig. 7.** Micrographs of the distribution of various elements (1) and copper (2) on the surface of the modified electrochemical sensor.

From the microscopic images, it can be seen that the Cu(II) ions, for which PV was added, provide the MES with a large and developed working surface, as well as active centers that lead to higher sensitivity and selectivity compared to the ions detected without additives. Furthermore, by adding the modifier in correct proportions, it can be observed that copper is evenly distributed on the surface of the MES.

For voltammetric methods, it is necessary to reduce the solution resistance and ensure the migration of current during the process. To do this, a neutral (inert) electrolyte solution, known as the supporting electrolyte, should be added to the solution. The supporting electrolyte must not participate in oxidation and reduction processes under electrolysis conditions. When selecting a supporting electrolyte, the cathodic or anodic nature of the electrode process is taken into account.

At the same time, controlling the electrochemical reaction involves monitoring the proton-donating activity of the environment, the role of the supporting electrolyte and buffer mixture, and maintaining the concentration of the ion being detected within strictly defined limits throughout the entire electrolysis process. During the experiments, several different solutions were used as supporting electrolytes for the determination of zinc: 0.1 M $H_3PO4$; 0.2 M HCl; 0.1 M $HNO_3$; 1.0 M KSCN; 0.1 M $H3PO_4$ + 0.1 M $KNO_3$; 1.0 M KCl + 0.2 M $HNO_3$; 1.0 M LiCl; 1.0 M $KNO_3$ and 1.0 M $NaNO_3$ + 1.0 M HF. Various volumes and concentrations of these supporting electrolytes and buffer mixtures were used, and the obtained results are presented in Table 3 and Figure 8.

As seen from the results in Table 3 and Figure 8, the best results were observed when Cu(II) ions were detected using a 0.1 M $HNO_3$ supporting electrolyte. Therefore, all subsequent experiments were carried out with this supporting electrolyte at its optimal concentration.

It is impossible to determine the accuracy and reliability of the experimental results without conducting experiments on the determination of Cu(II) ions at different concentrations. To evaluate the accuracy of the developed method for determining the studied metal, the results obtained from parallel comparisons are shown in Figure 9.

From the results, it is observed that the accuracy of the Cu(II) ion determination by the ASV method is high, with a correlation coefficient of 0.9926, close to 1.

To assess the possibility of determining the studied metals in real objects, it is necessary to have information about the ratio of elements and their interactions, as the accuracy and repeatability of the results will be significantly influenced by the effects of neighboring cations. Therefore, the influence of several ions that commonly appear alongside Cu(II) ions in natural objects has been studied. According to literature reviews and our research findings, it is known that several elements such as nickel, cobalt, lead, cadmium, and tin influence the analytical signal of the target metal.

**Table 3.** The effect of supporting electrolyte in the determination of copper ions using the stripping voltammetric method (current = 2.0 μA; t=100 s; $C_{Cu(II)}$= 10,0 μg $L^{-1}$)

| **Supporting electrolyte behavior and concentration** | **Cu(II)** | |
|---|---|---|
| | **E, mV** | **I, μA** |
| 0.1 M $NH_4OH$+0.1 M $NH_4CI$ | -100.0 | 25.0 |
| 0.1 M HCl | -250.0 | 45.0 |
| 0.1 M $H_3PO_4$+0.1 M $KNO_3$ | -200.0 | 31.0 |
| 0.1 M $HClO_4$ | -180.0 | 27.0 |
| 0.1 M $H_3PO_4$ | -190.0 | 22.0 |
| 0.1 M $HNO_3$ | -120.0 | 55.0 |
| 0.1 M $KNO_3$ | -220.0 | 32.0 |
| 0.1 M HCOOH | -230.0 | 35.0 |

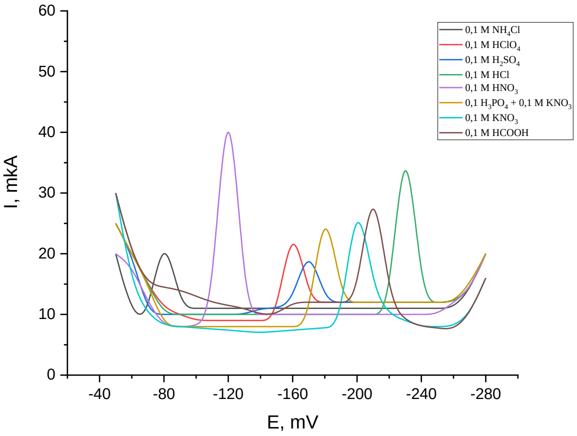


**Fig. 8.** The effect of supporting electrolyte in the determination of Cu(II) ions using the stripping voltammetric method.

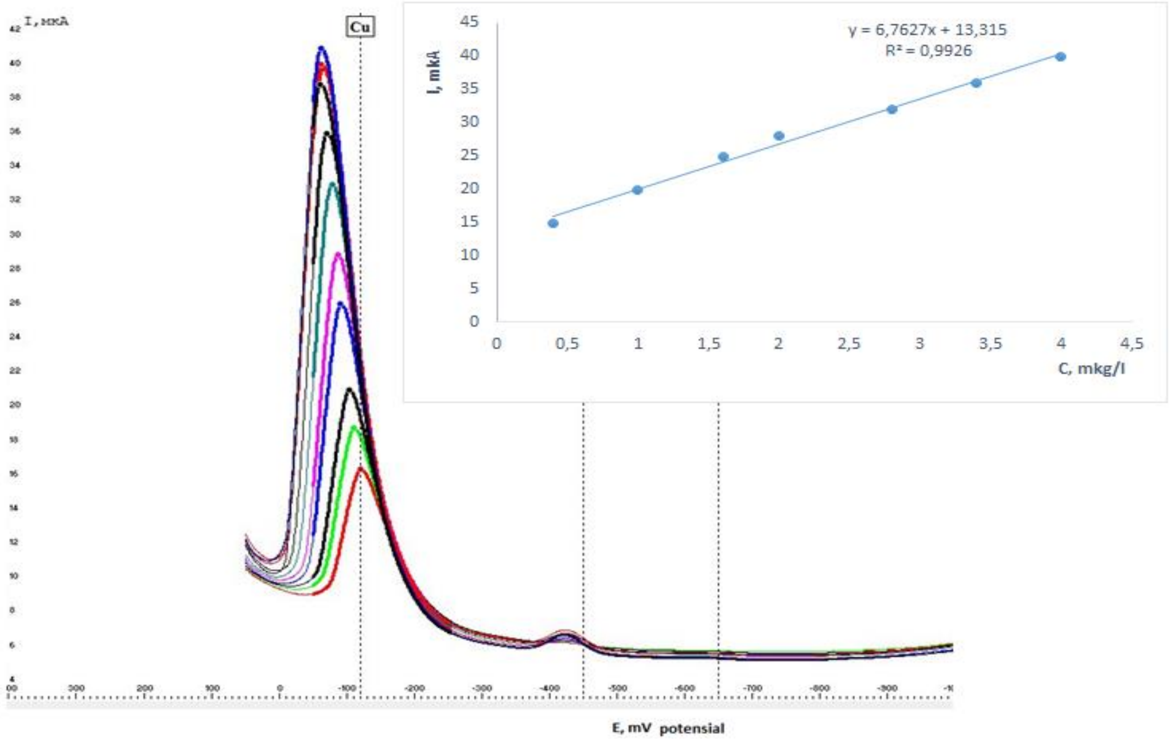


**Fig. 9.** Determination results of Cu(II) ions in individual solutions of different concentrations using the stripping-voltammetric method.

In this case, the overlap of voltammograms or the incorrect determination of concentrations of elements with similar half-wave potentials may occur. Therefore, the impact of neighboring cations on Cu(II) ion determination using the ASV method was studied. Some of the experimental results obtained by us are presented in Table 4, where the effect of neighboring cations on the accuracy and selectivity of Cu(II) ion determination at a concentration of 5.0 µg L$^{-1}$ using the ASV method in a 25 mL sample is shown. From the data in Table 4, it can be observed that among the coexisting ions commonly found with Cu(II) in natural objects, Sb at a mass ratio of 1:12, Hg(II) at 1:2, and Se(IV) at 1:3 interfere with the determination of Cu(II) ions using the ASV method. However, the other ions listed in the table do not cause interference at the given ratios.

The obtained results indicate that the determination of Cu(II) ions in the presence of coexisting cations is not significantly affected by the interfering cations mentioned above. The analytical data obtained serve as the basis for the feasibility of determining Cu(II) ions in the presence of foreign cations, confirming that these do not hinder the determination of Cu(II). This suggests that Cu(II) ions can be determined even when coexisting with other cations in both natural objects and industrial materials.

Using the developed ASV method, the concentration of Cu(II) ions in various water samples representing real natural objects was determined, and the results are presented in Table 5.

The data presented in the tables indicate the effectiveness of the developed method for determining Cu(II) ions in various technogenic, river, and wastewater samples.

To assess the accuracy of the developed method, water samples were analyzed using the X-ray fluorescence method, and the results were compared with those obtained using the proposed approach. The comparison results are presented in Table 6.

From the obtained X-ray fluorescence analysis results, it can be observed that the concentration of copper ions in the four analyzed samples closely matches the values determined using the developed method. This confirms the accuracy and competitiveness of the new approach. The fact that the obtained results and relative standard deviation (Sr) do not exceed 0.080 in any case further demonstrates the precision and reproducibility of the method.

**Table 4.** The influence of interfering cations on the determination of Cu(II) ions by stripping voltammetry (supporting electrolyte=0.1 M HNO$_3$; current=2,0 µA; E=-120 mV; C$_{Cu(II)}$=5,0 µg L$^{-1}$)

| **[Cu(II)]:[X]** | **Found Cu(II), µg L$^{-1}$** | **n (Number of experiments)** | **S** | **S$_r$** |
|---|---|---|---|---|
| Cu:Zn 1:100 | 4.98±0.08 | 5 | 0.070 | 0.014 |
| Cu:Pb(II) 1:80 | 4.95±0.11 | 5 | 0.097 | 0.020 |
| Cu:Cd 1:70 | 4.98±0.15 | 4 | 0.132 | 0.027 |
| Cu:Ni(II) 1:110 | 5.14±0.52 | 5 | 0.456 | 0.089 |
| Cu:Cr(III) 1:30 | 5.01±0.23 | 5 | 0.198 | 0.040 |
| Cu:Co(II) 1:20 | 4.98±0.27 | 5 | 0.239 | 0.048 |
| Cu:Sb(V) | | | | |
| 1:5 | 4.99±0.33 | 5 | 0.284 | 0.057 |
| 1:12 | 4.40±1.92 | 4 | 1.673 | 0.380 |
| Cu:Hg(II) 1:2 | 4.60±1.74 | 5 | 1.517 | 0.310 |
| Cu:Se(IV) 1:3 | 4.60±1.74 | 4 | 1.517 | 0.340 |

**Table 5**. Determination of copper ions in industrial and groundwater samples using the developed stripping voltammetric method (P=0,95; n=5)

| **Sample** | **Concentration of Cu(II) ion, µg L$^{-1}$** | | |
|---|---|---|---|
| | $\bar{x} \pm \Delta X$ | **S** | **S$_r$** |
| Navoiy technogenic water | 3.01±0.17 | 0.055 | 0.050 |
| Olmaliq city groundwater | 3.63±0.20 | 0.078 | 0.047 |
| Groundwater (Navoiy) | 0.30±0.02 | 0.104 | 0.067 |
| "Olmaliqsoy" canal water | 2.65±0.24 | 0.205 | 0.080 |

**Table 6.** Results of X-ray fluorescence analysis of water samples of various natures.

| **Metal ion** | **Sample** | **Developed Method** | | **X-ray Fluorescence** | |
|---|---|---|---|---|---|
| | | **Found µg $L^{-1}$** | **$S_r$** | **Found µg $L^{-1}$** | **$S_r$** |
| Cu(II) | Navoiy technogenic water | 3.01±0.17 | 0.050 | 3.09±0.20 | 0.038 |
| | Olmaliq city groundwater | 3.63±0.20 | 0.047 | 3.75±0.30 | 0.037 |
| | Groundwater (Navoiy) | 0.30±0.02 | 0.067 | 0.30±0.01 | 0.082 |
| | "Olmaliqsoy" canal water | 2.65±0.24 | 0.080 | 2,87±0,20 | 0.062 |

## 4. Conclusion

For the first time, an electrochemical sensor modified with the pyrocatechol violet organic reagent was developed and applied for the determination of Cu(II) ions in wastewater down to a concentration of 0.04 µg $L^{-1.}$ The electrochemical sensor modified with PV exhibited high selectivity towards Cu(II) ions and showed negligible sensitivity to $Na^+$, $K^+$, $Ni^{2+}$, $Zn^{2+}$, and $Cd^{2+}$ ions. Additionally, it was found that PV-modified electrochemical sensors could be cleaned by rotating at 2000 revolutions per minute in bidistilled water and remained stable for reuse for up to 110 days.

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