



## Elucidation of Cu-AMT Structure by Voltammetric Method

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**Abstract:** The long-term anthropogenic release of metals has increased their distribution and concentration in ecosystems, leading to sustained interest in their behavior and impact. Metals are not biodegradable and are converted from one chemical state to another. Even in low concentrations, heavy metals carry high danger. Therefore, the need for continuous control of trace metals in the environment is increasing. In this technique, the metal to be analyzed is deposited on the electrode surface in the form of metal complexes, and determinations are made using the peak currents obtained by potential scanning in the cathodic or anodic direction. The sensitivity and selectivity of the assay are increased by the choice of the ligand used as the complexing agent. In the study carried out to elucidate the structure of the complex formed by Cu(II) with 5-amino-1,3,4-thiadiazole-2-thiol (AMT), it was estimated that the complex structure could probably be in the ratio of 1:1. In addition, studies have been carried out to determine the stability of the complexes to be formed in various environments since the stability of the complex is related to the species in the solution comprising the medium, its concentration and the pH of the solution.

**Keywords:** 5-amino-1,3,4-thiadiazole-2-thiol, Trace element, Adsorptive stripping voltammetry (AdSV), Mercury drop electrode, Stoichiometry.

**Submitted:** December 7, 2023. **Accepted:** July 23, 2024.

**Cite this:** Gençdağ Şensoy K, Karagözler AE. Elucidation of Cu-AMT Structure by Voltammetric Method. JOTCSA. 2024;11(3): 1313-20.

**DOI:** <https://doi.org/10.18596/jotcsa.1401623>

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### 1. INTRODUCTION

Environmental control is one of the main applications of electroanalytical chemistry, and its importance in the determination of pollutants is increasing day by day. Electrochemical measuring devices are of great importance in controlling contaminants in situ, as they allow the instrument to be taken to the sample rather than to the laboratory. Progress in miniaturization technology has allowed the development of sensitive and sensitive electrochemical devices for in situ and instant measurement (1). Electrochemical sensors and detectors are well suited for on-site control of primary pollutants. These devices meet most of the requirements of on-site environmental analysis.

Copper is critical in environmental studies due to its widespread occurrence, potential toxicity, and ecological significance. Its presence in environmental samples can indicate pollution from various sources, including industrial processes, agriculture, and urban runoff.

Several analytical techniques are used to determine copper in environmental samples, each offering different levels of sensitivity, selectivity, and precision. When the literature studies in recent years are examined, spectroscopic methods (inductively coupled plasma-optical emission spectrometry, inductively coupled plasma mass spectrometry, flame atomic absorption spectroscopy (2-4), electrochemical techniques (voltammetry) (5), and portable analytical tools (X-ray fluorescence) are widely used.

The voltammetric determination of copper has undergone significant advancements, driven by the increasing demand for precise, rapid, and cost-effective analytical techniques. Voltammetry, known for its high sensitivity and selectivity in detecting trace metal ions, has been enhanced through various innovations, making it a vital tool in environmental monitoring, industrial applications, and biomedical research.

One key innovation is the development of advanced electrode materials. Traditional mercury-based

electrodes, which pose environmental and health risks, are being replaced by eco-friendly alternatives such as bismuth, carbon nanotubes, and graphene-based electrodes. These materials not only mitigate health and environmental concerns but also improve detection limits and analytical performance (5).

Another significant advancement is the integration of microfluidic systems and the miniaturization of voltammetric devices. These portable and on-site systems enable real-time monitoring of copper levels in various environmental matrices, providing critical data for timely decision-making in pollution control and remediation efforts (6).

Additionally, improvements in software and computational methods have revolutionized data analysis and interpretation in voltammetry. The incorporation of machine learning algorithms and advanced signal processing techniques has enhanced the accuracy and reliability of copper determination, allowing for better handling of complex datasets (7).

These innovations, ranging from advanced electrode materials to portable devices and sophisticated data analysis tools, have significantly expanded the capabilities of voltammetric techniques. They play a crucial role in addressing contemporary challenges in environmental science, public health, and industrial quality control, ensuring precise and efficient monitoring of copper in diverse settings.

The interaction between AMT (5-amino-1,3,4-thiadiazole-2-thiol) and  $\text{Cu}^{2+}$  (copper (II) ion) generally occurs in the form of a complex formation. AMT interacts with copper (II) ions as a strong complexing agent and forms complexes with high stability.

AMT contains a triazole compound, and the nitrogen and sulfur atoms in this ring connect coordinative bonds with copper (II) ions. Copper (II) ions are generally systems of four- or six-coordinated complexes. Depending on the structure of AMT, these complexes can be four-coordinated, and coordinative bonds occur between the nitrogen and sulfur atoms of AMT and copper (II) ions.

In recent years, electrochemical techniques based on stripping analyses have attracted attention for the in situ determination of selected metals (8–10). For example, a method based on stripping potentiometry (for traces of copper, cadmium, lead, and zinc) and adsorptive stripping voltammetry (for traces of chromium) has been used successfully to study metal contamination in soils and sediments at hazardous waste sites (11). In these in situ measurements, the concentration values measured by stripping analyses were found to be close to those obtained by the Environmental Protection Agency (EPA). The very low detection limits achieved by anodic stripping voltammetry (ASV) are due to the concentration of the analyte in the sample solution during the deposition step. Unlike techniques such as atomic absorption spectrometry and inductively coupled plasma emission spectrometry, which determine only the total metal concentration, ASV detects not only

the total metal concentration but also the reactive metal, which is a fraction of the total metal concentration. High sensitivity, portability, and low cost make stripping analyses attractive for the identification of contaminated sites and in situ analysis of selected metals during their remediation. There are not many examples in the literature of the use of AMT in the study for analytical purposes. Three of these few studies are about immobilizing AMT on silica gel and removing heavy metals from water with immobilized particles (11–13).

Other studies demonstrate the electrocatalysis, selectivity, and signal-enhancing effects of 5-amino-1,3,4-thiadiazole-2-thiol thin-film electrodes, which are generally formed by electropolymerization on carbon electrodes (14–20).

In this study, using the adsorptive stripping voltammetry (AdSV) technique, trace levels of the Cu element were complexed with 5-amino-1,3,4-thiadiazole-2-thiol (AMT), deposited on the mercury drop electrode, and then applied in the appropriate direction. The aim was to determine the amount of the trace element by stripping it from the electrode and performing a potential scan. To avoid the interference effect of other metals, pH, accumulation potential, and accumulation time were adjusted during voltammetric analysis to increase the selectivity of  $\text{Cu}^{2+}$  detection. These parameters are optimized to support the formation and detection of  $\text{Cu}^{2+}$  complexes relative to other metals. The fact that 5-amino-1,3,4-thiadiazole-2-thiol has been used for the first time in stripping voltammetry in the determination of Cu will contribute to the emergence of a new field of study in this field.

## 2. EXPERIMENTAL SECTION

### 2.1. Reagent and Solutions

All reagents used were analytical reagent grade, and all solutions were prepared using ultrapure water.  $10^{-2}$  M  $\text{Cu}^{2+}$  stock solution: It was prepared by dissolving 0.1705 g  $\text{CuCl}_2 \cdot 2\text{H}_2\text{O}$  in 100 mL ultrapure water.

5-amino 1,3,4-thiadiazole 2-thiol (AMT): This was prepared daily at a concentration of  $10^{-2}$  M. 0.0133 g of AMT was dissolved in 10 mL of dimethylformamide (DMF).

Preparation of 0.1 M Britton-Robinson buffer solution: Ultrapure water by mixing 6.1830 g  $\text{H}_3\text{BO}_3$ , 6.75 mL  $\text{H}_3\text{PO}_4$  (85%,  $d=1.71$  g/mL), 5.75 mL  $\text{CH}_3\text{COOH}$  (100%,  $d=1.05$  g/mL) and 7.45 g KCl made up to 1000 mL. The pH was adjusted to the desired value by adding dropwise 2 M NaOH solution onto 250 mL portions of the prepared stock buffer solution. pH=2.0, 5.0, 7.0, and 9.0 Britton-Robinson (BR) buffer solutions were obtained, and studies were carried out on these pHs.

### 2.2. Apparatus

Voltammetric measurements were carried out by using the IVIUM Compact Stat Plus Module. The three-electrode system consisted of a mercury drop electrode working electrode (Bioanalytical Systems, Inc.), an Ag/AgCl/KCl reference electrode (BAS,

Model RE-5B, W. Lafayette, USA), and a platinum wire as the auxiliary electrode.

Fourier transform infrared (FT-IR, Measurement mode: ATR, Resolution:  $4\text{ cm}^{-1}$ , four scans) spectroscopy was employed to characterize liquid Cu, AMT, and Cu-AMT complex within the range of  $4000\text{-}450\text{ cm}^{-1}$  (Perkin Elmer, spectrum two, USA).

### 2.3. Removal of Mercury

Dirty mercury was taken into falcon tubes, approximately 5 mL each. Up to 40 mL of tap water was added and vortexed. This process was repeated at least five times. The mercury fractions through which the tap water was passed were collected in a single tube and vortexed again (to ensure homogeneity). The same procedures were repeated by adding 2 M  $\text{HNO}_3$ . The mercury fractions vortexed with  $\text{HNO}_3$  were vortexed with distilled water until their acidity was removed. The deacidified mercury was taken into a clean beaker and dried on filter paper at  $50\text{ }^\circ\text{C}$  in the oven. It was checked voltammetrically whether the mercury taken into the mercury chamber contained impurities.

### 2.4. Removal of Dissolved $\text{O}_2$ from Analysis Solutions

Oxygen creates the following problems in voltammetric studies because it gives a wide range of reduction waves and is a strong oxidant;

- Reduction of  $\text{O}_2$  creates an additional faradaic current.
- $\text{O}_2$  reduction waves interfere with analyte waves because they cover a wide potential range.
- Some analytes can react with oxygen. For example, in the presence of heavy metal ions, metal oxides are formed or cause oxidation of the metal collected in anodic stripping voltammetry.

For these reasons, it is necessary to remove dissolved  $\text{O}_2$  from the analysis solutions. The most convenient method for removing oxygen is by bubbling pre-purified nitrogen gas through the analysis solution. For solutions with high analyte concentration, nitrogen directly from the tank can be used. However, direct use of tank nitrogen is not suitable for solutions with low analyte concentration. With the oxygen cleaning system, the oxygen in the nitrogen gas must also be removed beforehand.

There are different methods for this final purification process, with varying levels of ease of use. The most common of these methods is the use of vanadium chloride solution, which was applied in this study.

This solution consists of boiling two grams of ammonium metavanadate with 25 mL of concentrated hydrochloric acid, then diluting it with water to 250 mL and reducing it by adding a few grams of zinc amalgam. When nitrogen gas containing traces of oxygen is passed through the blue or green vanadium solution obtained, it is reduced to the vanadium (II) stage, and the solution becomes clear purple.

Once depleted (as evidenced by the disappearance of the purple color), vanadium chloride solutions can be reconstituted by adding a few mL of concentrated hydrochloric acid or zinc powder mixed with more mercury.

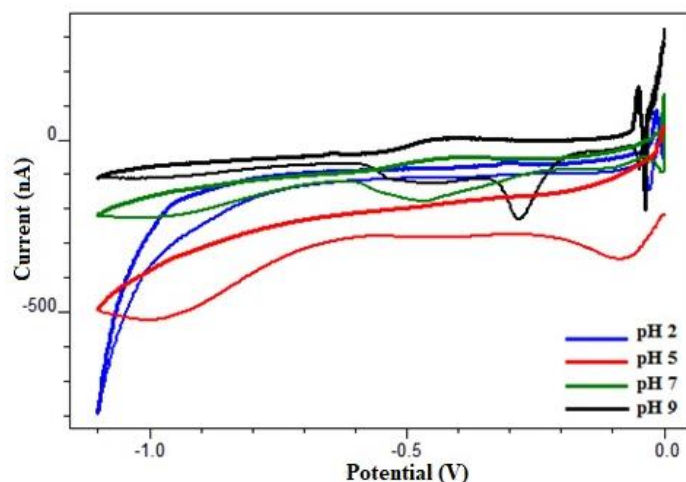
## 3. RESULTS AND DISCUSSION

Classically, the most common method used for the voltammetric determination of trace metals is anodic stripping voltammetry. In this method, metals are deposited on the mercury drop to form an amalgam with mercury at a potential more negative than the reduction potential and then oxidized from the electrode by an anodic scan. The differential pulse technique is generally used as the scanning technique. Metals can also be determined by scanning in the cathodic direction. Since there is no accumulation step in this approach, the detection limit of the method is higher than that of ASV.

Adsorptive stripping voltammetry is an alternative detection approach used for the determination of trace metals whose detection limit is not low enough or which are outside the potential window of the electrode used in the determination of redox potential or at potentials close to the anodic/cathodic potential limits. The concentration of the metal is determined by the voltammetric peaks observed as a result of the anodic or cathodic scans of the complex, which is formed in the solution or on the electrode surface, with the metal to be determined and adsorbed on the electrode surface.

### 3.1. Cyclic Voltammetric Behaviors of AMT and Cu-AMT Complexes

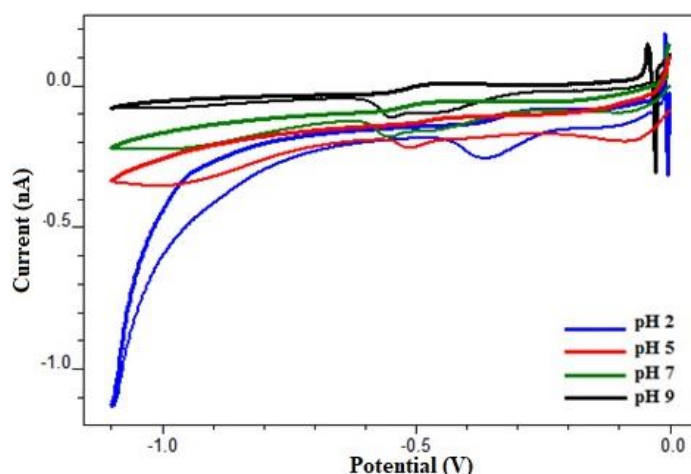
The voltammograms obtained on the suspended mercury drop electrode of  $10^{-5}\text{ M}$  AMT solution in four different pH environments are shown in Figure 1. While anodic and cathodic peaks are not observed at low pH, especially cathodic peaks that occur at  $\text{pH}=7$  and 9, with an increase in pH ( $\text{pH}=9$ ), the cathodic peak becomes more pronounced and shifts to more positive potentials.



**Figure 1:** Comparison of cyclic voltammograms of  $10^{-5}$  M AMT taken in pH=2.0, 5.0, 7.0, and 9.0 BR buffer.

Figure 2 shows the cyclic voltammetric behavior of solutions containing  $10^{-6}$  M Cu and  $10^{-5}$  M AMT (1:10 Cu: AMT mole ratio) obtained at different pHs on a suspended mercury drop electrode. At this stage, it is not possible to determine precisely whether the

small peaks that appear in the cathodic scanning, depending on the pH of the environment in four different pH environments, are caused by AMT itself or a possible Cu: AMT complex.



**Figure 2:** Comparison of cyclic voltammograms of Cu-AMT (1:10) complex taken in BR buffer pH=2.0, 5.0, 7.0, and 9.0.

### 3.2. Effect of Cu and Cu-AMT Complex on Cathodic Scanning, Anodic Scanning and Anodic Stripping Peaks

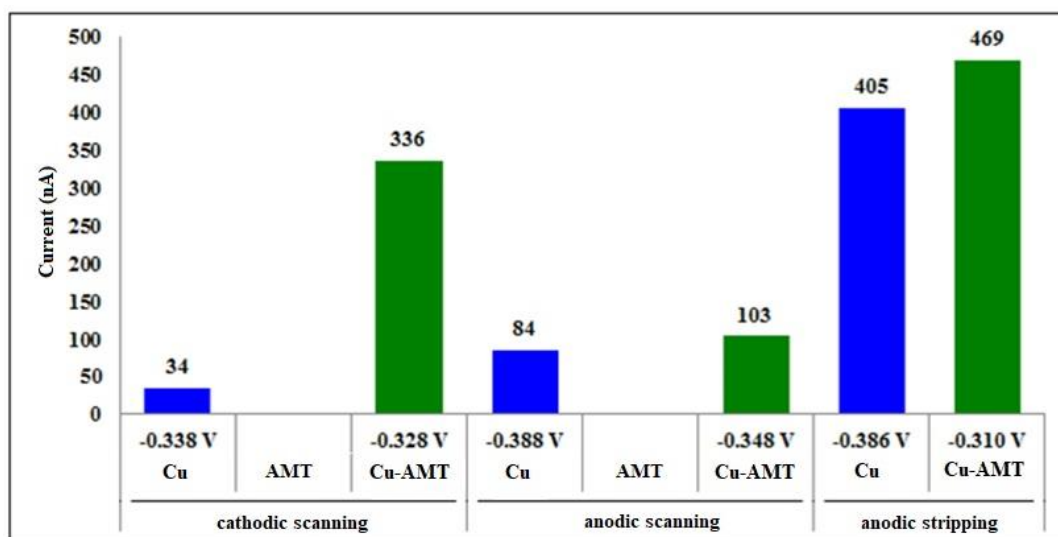
When the peak heights and positions in voltammograms taken with pure AMT, Cu, and Cu: AMT (1:10) complex solutions at four different pHs were examined, it was observed that  $\text{Cu}^{2+}$  formed a complex with AMT only in pH 2 BR buffer.

When Figure 3 is examined,  $\text{Cu}^{2+}$  at pH=2 gives a small (34 nA) reduction peak in the cathodic scan. In the anodic scans, the copper peaks are higher (84 and 405 nA). It is expected that the anodic stripping peak (405 nA) is this high, as  $\text{Cu}^{2+}$  is concentrated by forming amalgam on the mercury drop for 60 seconds in the stripping mode. The fact that the  $\text{Cu}^{2+}$  peak in the anodic direction is larger than the peak in the cathodic direction (84 nA > 34 nA), without precipitation step, is  $\text{Cu}^{2+}$  with the negative potential effect applied to the electrode in a short time from -

1.1 V, which is the beginning of the anodic scanning until the  $\text{Cu}^{2+}$  peak appears (-0.388 V). This can be explained by the accumulation of mercury on the electrode surface.

The histogram drawn for the copper metal clearly shows that the Cu-AMT complex is formed at this pH, and the peak of this complex causes a peak of about ten times ( $336/34 \sim 10$  times) size compared to the pure copper peak in the cathodic scan. On the other hand, the peak obtained by the anodic stripping technique in the presence of AMT is higher than the peak obtained in the absence of ligand in the medium ( $469 \text{ nA} > 405 \text{ nA}$ ).

The results in the pH=2 environment of copper metal clearly show that the presence of AMT allows the obtaining of higher peak currents by both cathodic scanning and anodic stripping voltammetry.

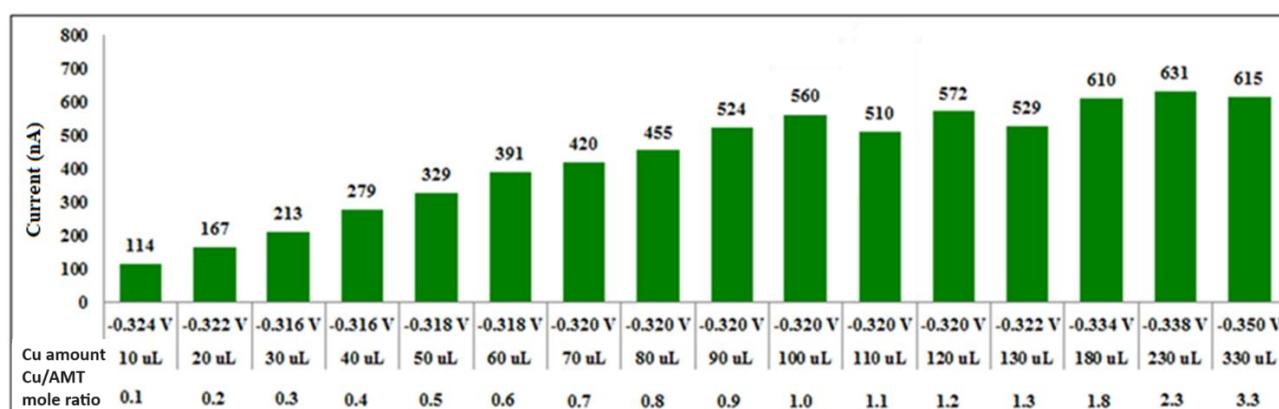


**Figure 3:** Peak heights measured from differential pulse voltammograms taken in pH 2 BR buffer of  $\text{Cu}^{2+}$  ( $10^{-6}$  M), AMT ( $10^{-5}$  M), and Cu: AMT 1:10 ( $10^{-6}$  M  $\text{Cu}^{2+}$  and the solution containing  $10^{-5}$  M AMT) and comparison of their location.

### 3.3. Elucidation of the Structure of the Complex

To elucidate the Cu-AMT complex structure, cathodic scans were carried out in a series of solutions in which the mole ratios of Cu-AMT were changed systematically. The peak heights measured from the cathodic scanning voltammograms obtained by adding at least 10  $\mu\text{L}$  of  $10^{-6}$  M Cu solution to the  $10^{-5}$  M AMT solution each time were plotted in Figure 4 on a bar chart.

Both the volumes of  $\text{Cu}^{2+}$  solution added, and the mole ratios of Cu-AMT are shown on the horizontal axis of the graph. When the graph is examined, it is seen that the Cu-AMT complex peak increases regularly until the mole ratio of Cu-AMT is roughly 1. Therefore, it can be said that the resulting complex is a 1:1 complex.



**Figure 4:** Histogram giving the responses of cathodic scanning voltammograms taken in pH 2 BR buffer after each addition of at least 10  $\mu\text{L}$  of  $10^{-6}$  M Cu solution to  $10^{-5}$  M AMT solution.

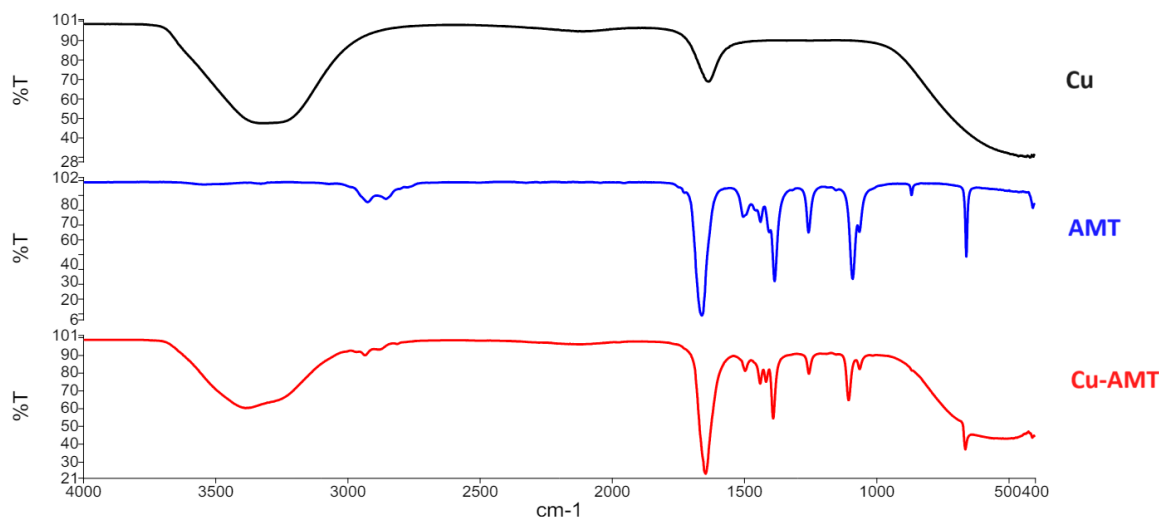
### 3.4. Characterization of Cu, AMT, and Cu-AMT complex by FT-IR

The chemical characterization was investigated using FT-IR. The FTIR spectra were recorded in the range of  $4000\text{--}450\text{ cm}^{-1}$ .

The peak seen in the Cu and Cu-AMT spectra around  $3400\text{ cm}^{-1}$  belongs to O-H stretching vibrations. O-H stretching is generally a vibration that gives a wide and intense signal. In the AMT spectrum, the bands between  $3000$  and  $2800\text{ cm}^{-1}$  indicate  $\text{NH}_2$  stretching vibration. Bands in the range of  $1500\text{--}1000\text{ cm}^{-1}$  can

be assigned to CN, CN, NN, and CS stretching vibrations, respectively. When the band between  $700\text{--}400\text{ cm}^{-1}$  in all three spectra is examined, the change in AMT suggests that Cu forms a complex with AMT.

In the previous study in the literature, the structure of the complex was elucidated with IR, and its stoichiometry was found to be 1:1 (21). It is consistent with our study.

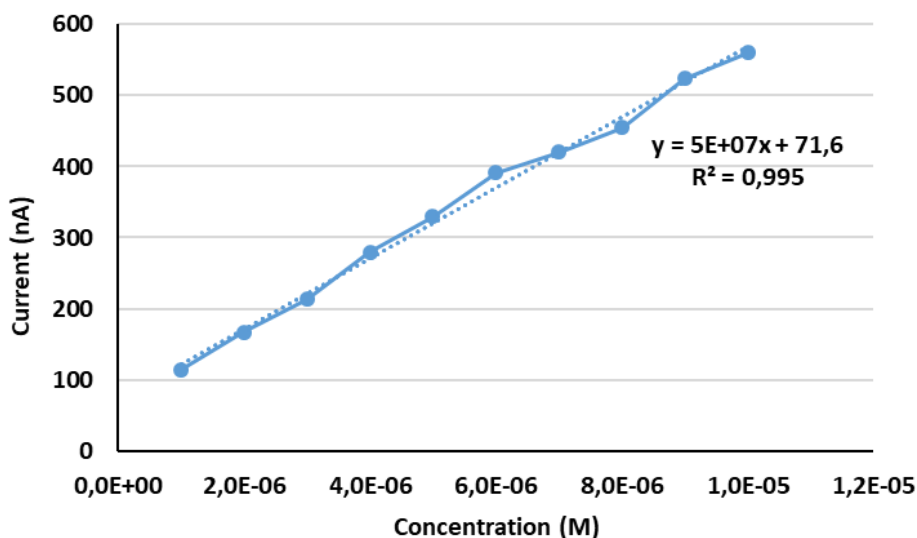


**Figure 5:** FT-IR spectra taken for characterization of Cu, AMT, and Cu-AMT complex.

### 3.5. Detection Limit of Cu Determination

The limit of detection (LOD) and quantification (LOQ) for electrochemical Cu determination was calculated by measuring the signal of Cu at different concentrations ranging from  $1 \times 10^{-6}$  to  $1 \times 10^{-5}$  M (Figure 6). According to the procedure reported by

Miller and Miller (22), the LOD and LOQ of Cu were calculated using the regression equations ( $y = 5E+07x + 71,6$ ,  $R^2 = 0,995$ ), and it was found to be  $0,68 \mu\text{M}$  and  $2,2 \mu\text{M}$  respectively.



**Figure 6:** The calibration graph illustrates the oxidation signal of Cu obtained at various concentrations from 1 to 10  $\mu\text{M}$ .

## 4. CONCLUSION

When designing an electrochemical sensor for copper determination, the detection mechanism plays a crucial role in ensuring sensitivity, selectivity, and reliability. One of the most widely used and effective detection mechanisms is anodic stripping voltammetry (ASV).

ASV is particularly suitable for detecting trace levels of copper due to its high sensitivity and low detection limits. The mechanism involves a two-step process: first, copper ions are pre-concentrated onto the electrode surface by applying a negative potential, causing the ions to be reduced and deposited as a metallic layer. In the second step, the potential is swept in the positive direction, causing the copper to oxidize and strip back into the solution. The current produced during this stripping process is directly

proportional to the concentration of copper in the sample.

In the study carried out to elucidate the structure of the complex formed by Cu(II) with AMT, it was estimated that the complex structure could probably be in the ratio of 1:1.

## 5. CONFLICT OF INTEREST

The authors possessed no relevant financial or non-financial interests.

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