# Chronoamperometric Cu(II) Analysis at Gold Ultramicroelectrodes in Concentrated Sulfuric Acid Solutions

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Chronoamperometric analysis of Cu (II) ion concentration at a gold ultramicroelectrode (UME) is reported. An appropriate potential/time program was selected after the analysis of the corresponding j *vs* t transients in order to establish a defined value in the limiting current for analytical purposes. Good linearity between Cu (II) concentration and the stationary stripping current was obtained in the concentration of 5 g dm$^{-3}$ to 150 g dm$^{-3}$ range. Moreover, interference effects from sulfuric acid in a wide concentration range and from additives such as thiourea and glue showed that they do not affect the linearity between the stationary current values and Cu(II) concentration. These results could be adapted for the chronoamperometric detection of Cu(II) in on-line measurements in industrial copper refining electrolytes.

## 1. INTRODUCTION

The control of Cu (II) concentration is a key parameter in different processes of copper recovering, as is the case for the copper electrorefining and copper electrowinning technologies [1]. Molar concentration of copper solutions are also used in HydroCopper processes for recovery of copper from chalcopyrite concentrates [2]. On the other hand, it is important to explore the possibility of on-line Cu (II) ion concentration analysis in order to automate the methodology employed in the quantification of this metal during the recovering process. However, analytical techniques such as atomic absorption spectrometry, inductively coupled plasma emission spectrometry and energy

dispersive X-ray fluorescence are limited in their use for on-line monitoring because of their dimensions, cost and time consuming. Besides, copper ion-selective electrodes alternative is not convenient because they usually present problems with some interference, mainly in the presence of iron at low pH values.

Electrochemical methods, such as stripping analysis, have been reported as an adequate analysis method, because they are well adapted for in-situ measurement of heavy metal ions [3-6]. Particularly, anodic stripping is a representative method where in a deposition step the analyte of interest is electroplated on a convenient working electrode, then stripped from the electrode and finally the oxidation current is measured. In anodic stripping voltammetry the oxidation of the analyte is recorded as a current peak related to the potential at which is oxidized [7]. Another approach is to use the chronoamperometric technique, consisting in recording the stationary stripping current extracted from the respective current-time transients obtained after applying a pre-determined potential step for the metal deposition [8].

The aim of current work is to use chronoamperometry for the analysis of copper in conditions prevailing in industrial refinery electrolytes at a gold ultramicroelectrode (UME) as working electrode. It is well established that when an electrode is miniaturized to the micrometer scale, new properties and improving of the electrochemical measurements are observed [9-12]. The following advantages can be highlighted: Non-planar diffusion increases mass transport rate, reduction of ohmic losses and the double layer capacitance decreases due to the small electrode area. UME is a well adapted tool in the studies of concentrated electrolytes as is the case of copper industrial electrolytes which present both, low current and ohmic drop values. Bard *et al.* demonstrated that voltammetry with an UME can also measure copper concentration with good precision even at 1 M Cu(II) concentrations in concentrated copper chloride complexes [2]. The influence of dc potential, temperature, Cu(II) ions and animal glue concentration on electrochemical impedance at UME has been also studied in detail [13]. In our case, we have studied the feasibility of determining Cu(II) concentration by chronoamperometry in a concentrated sulfuric acid synthetic electrolyte containing thiourea and glue, two additives usually present in copper electrorefining process. Results show a linear relationship between the initial stages of the limiting current at UME and Cu(II) concentration, in the range of 5 and 50 g dm$^{-3}$, in a wide range of sulfuric acid concentration.

## 2. EXPERIMENTAL

The determination of Cu(II) concentration ions was studied by the chronoamperometry technique. Chronoamperometric measurements were performed in a three electrodes configuration cell employing a gold UME (CH Instruments) with 25μm of nominal diameter as working electrode, a Ag/AgCl$_{(3 M)}$ as reference electrode and platinum wire as counter electrode. On the other hand, the voltammetric measurements were carried out using the same cell configuration and in all cases the scan rate was 0.01 V s$^{-1}$. These curves were recorded in the potential windows between +0.6 V and −0.4 V for the electrolyte without additives (glue and thiourea) and between +0.6 to −0.6 V for the electrolyte with additives. A Gamry Serie G750 potentiostat was used in both, chronoamperometric

and voltammetric measurements in order to control all the electrochemical parameters trough the Gamry Framework software whereas the data analyses were managed by the Echem Analyst software.

Prior to running the chronoamperometric experiments, a clean UME surface is required in order to obtain reproducible responses. Thus, the UME was thoroughly rinsed with deionized water and then chemically treated during 30 seconds in a concentrated nitric acid solution. Finally, the electrode was again rinsed with deionized water.

The cell temperature was maintained at 25°C by thermostated water. The synthetic electrolyte was prepared from dissolution in deionized water containing $CuSO_4$ and $H_2SO_4$ of analytical grade (Merck P.A.). The concentration of Cu(II) ions varied from 5–50 g dm$^{-3}$ and that of sulfuric acid from 180–250 g dm$^{-3}$. Thiourea (Merck, between 2.4 mg dm$^{-3}$ – 3.6 mg dm$^{-3}$) and animal glue (between 1.25 mg dm$^{-3}$ – 1.88 mg dm$^{-3}$) were added for studying the influence of these additives in copper deposition. In chronoamperometry experiments the potential was stepped from 0.5 V to the potential at which the deposition of copper occurs, which was adjusted according the composition of the electrolytic solution.

All data used in the construction of the calibrate curves in both electrolytes, with and without additives, were obtained in triplicate. The summary of these results is shown in the corresponding Tables with their respective statistical analyses (mean value and standard deviation, SD).

## 3. RESULTS AND DISCUSSION

The first stage of current work was to study the potential range of copper electrodeposition at UME following the guidelines described by Lumkoska et al. [14], who performed a detailed analysis of this process in copper refinery electrolytes containing some impurities, but in absence of thiourea and glue as additives employed for improving the quality of copper electrodeposits at industrial scale. Figure 1 shows that, instead of the characteristic current peak present in the voltammograms of macro electrodes, such as platinum and gold disks, for copper electrodeposition a limiting diffusion current is observed when a gold UME is used as working electrode. The anodic peak in the inverse scan is associated to the stripping of the deposited copper and is quite similar to that observed in gold macroelectrodes. Notwithstanding, the charge related to copper electrodeposition is higher than the corresponding electrooxidation charge. This behavior can be attributed either to the participation of a parallel reduction process, *i.e.* hydrogen evolution in strong acid medium, or to a partial stripping of the electrodeposited copper. The first possibility can be discarded because the difference between cathodic and anodic charges is still present, even at potential intervals where the hydrogen discharge contribution is negligible. Therefore, it is necessary to implementing a rigorous protocol procedure for a complete electrode surface cleaning before each Cu(II) chronoamperometric analysis. To avoid this problem, after the partial copper stripping, the electrode was removed from the cell, rinsed with deionized water, followed by 30 s immersion in concentrated nitric acid, and then rinsed again with deionized water. Following this protocol the UME area remains practically unchanged and clean, allowing getting reproducible voltammograms.
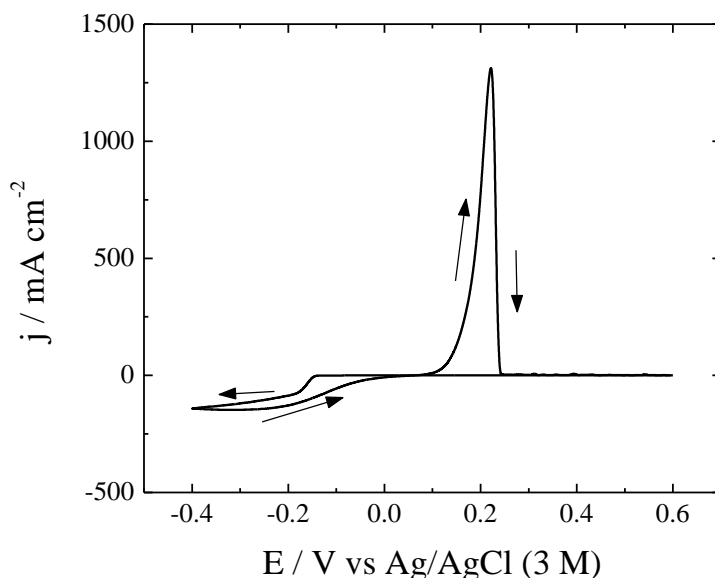
**Figure 1.** Cyclic voltammogram of a 15 g dm$^{-3}$ Cu(II) and 180 g dm$^{-3}$ H$_2$SO$_4$ solution at a gold UME (25 μm diameter). Scan rate: 0.01V s$^{-1}$.
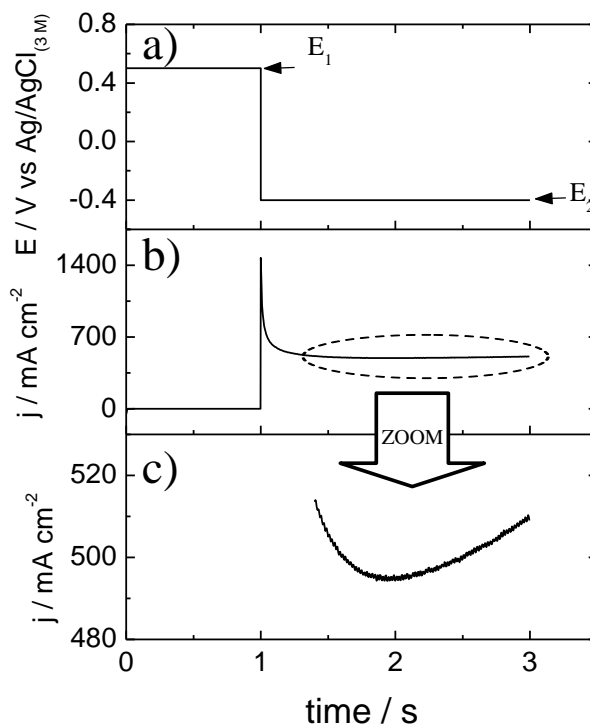


**Figure 2.** a) Potential/time program for the chronoamperometric measurements at gold UME electrode. E$_1$= Pre-treatment potential (no electrochemical process takes place). E$_2$=copper electrodeposition potential. b) j *vs* t transient at gold UME: 35 g dm$^{-3}$ Cu(II), 180 g dm$^{-3}$ sulfuric acid solution according to potential/time program depicted in a). c) Zoom corresponding to the potential range where the electrodeposition current initially decays and its further increasing due to the increasing in the UME surface area.

The chronoamperometric measurements were performed applying the potential time program depicted in Figure 2a), where $E_1 = 0.5$ V is the initial pre-treatment step (1 s) and $E_2 = -0.4$ V is the copper deposition potential at different times (5 – 30 s depending on a particular condition. Figure 2b) shows a typical j *vs* t transient for copper electrodeposition from concentrated sulfuric acid solution. The initial current decay corresponds to the electric double layer discharge, followed by an apparent limiting current but a zoom in this region reveals that there is a current increasing after 2 s (Figure 2c)). It can be assumed that this behavior obeys to the formation of hemispheric nuclei at the UME surface [14], a process that involves a remarkable electrode area increasing. Under these circumstances, it would be difficult to establishing a defined value in the limiting current for analytical purposes. This drawback can be faced assuming that the current minimum in the j *vs* t transients, just before its increasing, can be considered as equivalent to the limiting current value that the system would reach if it were a macro electrode. Figure 3 shows the different j *vs* t curves obtained in Cu(II) solutions of different concentration (5 – 50 g dm$^{-3}$) in 180 g dm$^{-3}$ H$_2$SO$_4$ media.

As can be observed, the current minimum in the recorded j *vs* t transients presents a direct relationship with Cu(II) concentration in sulfuric acid solutions in the 5–50 g dm$^{-3}$ interval, validating thus the proposed methodology (inset Figure 3). These results are summarized in Table 1.
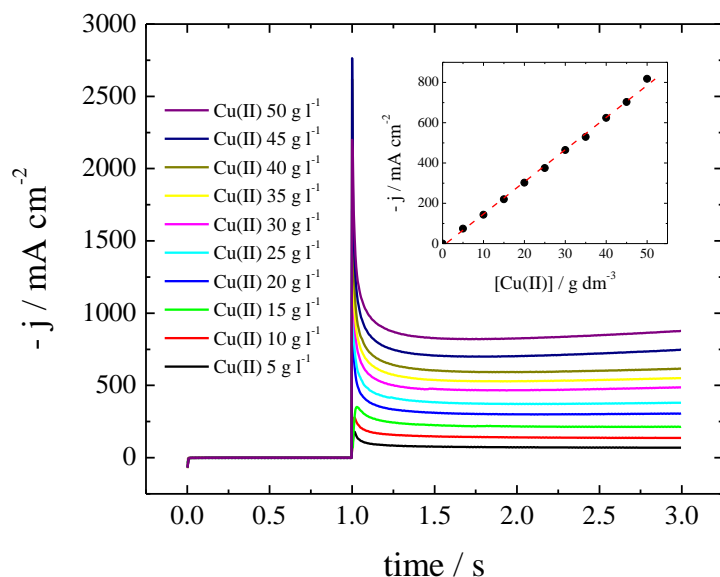


**Figure 3.** j *vs* t transients of a gold UME recorded at different Cu(II) concentrations with 180 g dm$^{-3}$ sulfuric acid solution, without additives. Inset: Plot of –j *vs* Cu(II) concentration in the range 5 g dm$^{-3}$ – 50 g dm$^{-3}$, 180 g dm$^{-3}$ H$_2$SO$_4$ solutions. Values extracted from Table 1.

In order to consider the possible influence of the additives (thiourea and glue) on the voltammetric and chronoamperometric behavior of Cu(II) solutions at gold UME, they were added to the electrolytic solution. The cyclic voltammogram presents a similar response to that previously observed in absence of the additives, excepting that the limiting current condition appears slightly shifted towards negative potentials values (Figure 4). In this way, the chronoamperometric measurements were performed at –0.5 V instead of at –0.4 V. The corresponding j *vs* t transients and

the linear relationship between copper concentration and the current minimum plot are depicted in Figures 5. It is seen that the presence of glue and thiourea don't alter the linear relationship found when they are not present in the electrolytic solution, besides there is a better correlation between the experimental points. Therefore, it is concluded that the proposed method is suitable for the direct analysis of copper in concentrated sulfuric acid solutions containing both additives.

**Table 1.** Statistical results of data obtained from chronoamperometric measurements (in triplicate) like those shown in Figure 3. The corresponding plot $-j$ *vs* Cu(II) concentration is shown in the inset in Figure 3.

| [Cu(II)] / g dm$^{-3}$ | 5.00 | 10.00 | 15.00 | 20.00 | 25.00 |
|---|---|---|---|---|---|
| Mean Current / mA cm$^{-2}$ | 73.34 | 143.08 | 216.14 | 300.48 | 372.67 |
| SD / mA cm$^{-2}$ | 1.43 | 0.77 | 2.65 | 1.63 | 3.06 |

| [Cu(II)] / g dm$^{-3}$ | 30.00 | 35.00 | 40.00 | 45.00 | 50.00 |
|---|---|---|---|---|---|
| Mean Current / mA cm$^{-2}$ | 468.55 | 527.36 | 626.09 | 695.49 | 817.86 |
| SD / mA cm$^{-2}$ | 4.50 | 2.41 | 25.63 | 6.18 | 13.32 |
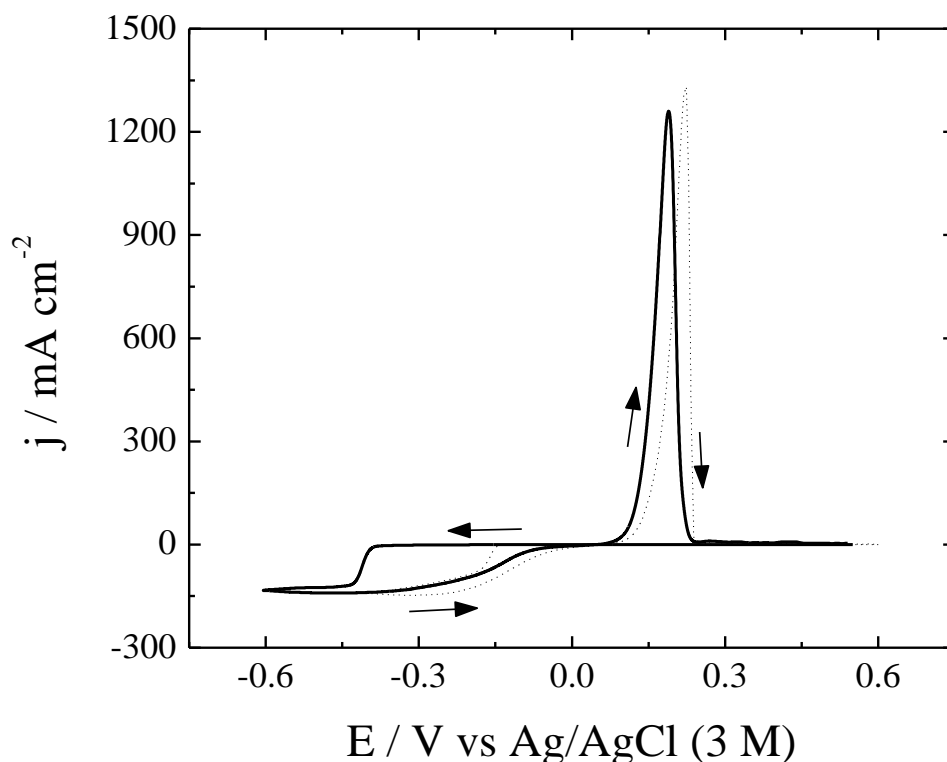


**Figure 4.** Cyclic voltammogram of gold UME: 15 g dm$^{-3}$ Cu(II), 180 g dm$^{-3}$ H$_2$SO$_4$, 1.25 mg dm$^{-3}$ glue, 2.40 mg dm$^{-3}$ thiourea. Scan rate 0.01V s$^{-1}$. Dotted line represents the voltammogram of the same solution but in the absence of additives (glue and thiourea).
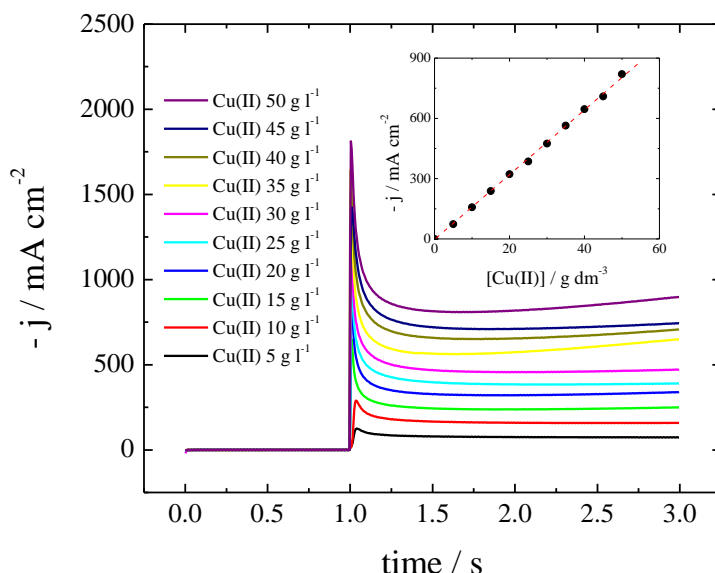
**Figure 5.** j *vs* t transients recorded at gold UME with different Cu(II) concentrations in 180 g dm$^{-3}$ , 1.25 mg dm$^{-3}$ glue, 2.40 mg dm$^{-3}$ thiourea. Inset: Plot of –j *vs* Cu(II) concentration in the range 5 g dm$^{-3}$ – 50 g dm$^{-3}$, 180 g dm$^{-3}$ H$_2$SO$_4$, 1.25 mg dm$^{-3}$ glue and 2.40 mg dm$^{-3}$ thiourea solutions. Values extracted from Table 2.

**Table 2.** Statistical results of data obtained from chronoamperometric measurements (in triplicate) like those shown in Figure 5. The corresponding plot –j *vs* Cu(II) concentration is shown in the inset in Figure 5.

| [Cu(II)] / g dm$^{-3}$ | 5.00 | 10.00 | 15.00 | 20.00 | 25.00 |
|---|---|---|---|---|---|
| Mean Current / mA cm$^{-2}$ | 73.75 | 157.27 | 237.67 | 317.80 | 385.71 |
| SD / mA cm$^{-2}$ | 0.20 | 1.62 | 3.11 | 4.07 | 1.18 |

| [Cu(II)] / g dm$^{-3}$ | 30.00 | 35.00 | 40.00 | 45.00 | 50.00 |
|---|---|---|---|---|---|
| Mean Current / mA cm$^{-2}$ | 456.33 | 560.22 | 651.90 | 708.94 | 810.80 |
| SD / mA cm$^{-2}$ | 2.04 | 2.04 | 14.26 | 8.15 | 15.38 |

In order to further validate the procedure, it was necessary to study the effect of possible variations in sulfuric acid and additives concentration as is usually the case in the industrial copper electrorefining process. For this purpose, from the Cu(II) calibration curve were selected two points: one was 15 g dm$^{-3}$, which is the frequent value present in the electrorefining electrolyte, and the other 45 g dm$^{-3}$ which considers the extreme case of an eventual concentration Cu(II) increasing. For each one of these points the concentrations of all the components were kept fixed, except the studied variable that were sulfuric acid and additive concentrations, respectively. In the former case the concentration varied between 140 and 240 g dm$^{-3}$ and in the second one between 1.25 and 1.88 mg dm$^{-3}$ for glue, and 2.4 to 3.6 mg dm$^{-3}$ for thiourea. Figures 6 and 7 reveal that the linear relationships between these points remain practically without changes that could be attributed to these concentration

changes. These results demonstrate that the methodology described in this study is suitable for copper analysis in electrolytes with variable concentration of both, sulfuric acid and additives (thiourea and glue)
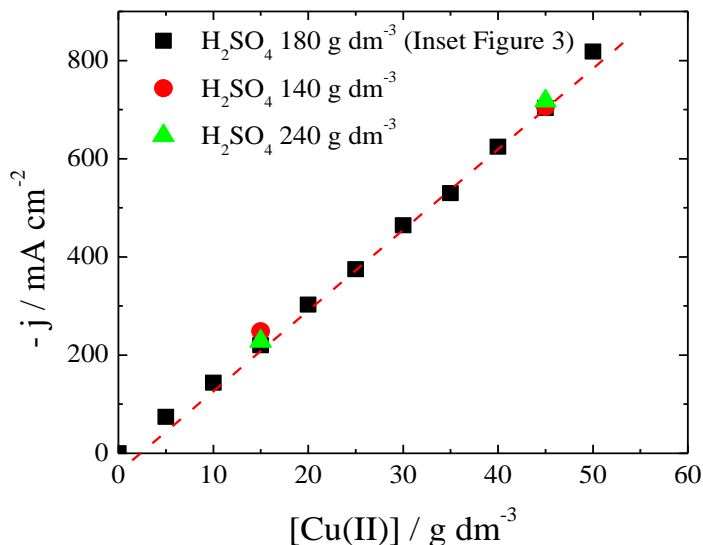


**Figure 6.** Effect of sulfuric acid concentration on the Cu(II) calibration curve. Cu(II) concentration: 15 g dm$^{-3}$ y 45 g dm$^{-3}$. Additives concentration: 1.25 mg dm$^{-3}$ glue, 2.40 mg dm$^{-3}$ thiourea. Sulfuric acid concentration: 140 g dm$^{-3}$ and 240 g dm$^{-3}$.
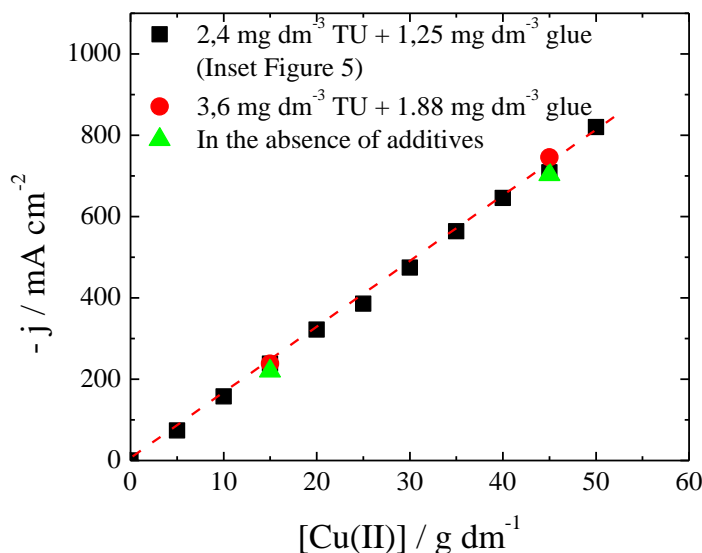


**Figure 7.** Effect of additives concentration in the Cu(II) calibration curve. Additives concentration were: glue 0, 1.25 and 1.88 mg dm$^{-3}$; thiourea (TU) 0; 2.4 and 3.6 mg dm$^{-3}$. Sulfuric acid concentration: 180 g dm$^{-3}$. Cu(II) selected for the study: 15 g dm$^{-3}$ and 45 g dm$^{-3}$.

# 4. CONCLUSIONS

Although ultramicroelectrodes are usually useful for the electrochemical analysis of cupric ions in low concentration ranges, current results demonstrate that they can be successfully employed in the

analysis of solutions containing higher concentrations such as those found in copper electrorefining electrolytes. Combined with chronoamperometry measurements it is possible to obtain good linearity between the stationary current and copper ions concentration in the 5 g dm$^{-3}$ – 50 g dm$^{-3}$ range. The linearity is not affected by variations in sulfuric acid concentration between 140 g dm$^{-3}$ to 220 g dm$^{-3}$ neither by the presence of thiourea and glue, which foresees the possibility of adapting the methodology for on-line determination of Cu(II) in the electrolytes of the industrial electrorefining processes.

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