

## Amperometric and potentiometric method for the determination of copper (II) in an aqueous medium in-situ

Mahaman Nazirou GARBA LABO <sup>1,\*</sup>, Oumarou Farroukou MOUSTAPHA BELLO <sup>2</sup> and Marou GOUROUZA <sup>2</sup>

<sup>1</sup> National Polytechnic Institute, Félix Houphouët-Boigny (INP-HP), BP 1093, Yamoussoukro, Côte d'Ivoire.

<sup>2</sup> Department of chemistry, Faculty of Sciences and Technology, Materials Water and Environment Laboratory, Abdou Moumouni University, BP 10662, Niamey, Niger.

World Journal of Advanced Research and Reviews, 2022, 14(02), 230–239

Publication history: Received on 10 April 2022; revised on 12 May 2022; accepted on 14 May 2022

Article DOI: <https://doi.org/10.30574/wjarr.2022.14.2.0437>

### Abstract

The objective of this work is to establish new amperometric and potentiometric methods for the determination of copper (II) in an aqueous medium. To achieve this goal, a device for measuring the current intensity and the potential difference as a function of the concentration of Cu (II) has been developed. The current intensity and the potential difference as a function of the concentration of Cu<sup>2+</sup> ions were measured. Correlation curves were established. The influence of the distance between the two electrodes, of the pH and that of the conductivity on the intensity of the measured current or on the potential difference was determined. The results obtained show a good correlation on the one hand, between the intensity of the current and the [Cu<sup>2+</sup>] and on the other hand between the potential difference and the [Cu<sup>2+</sup>] in the aqueous medium. Analysis of the results indicate that: pH and conductivity have no influence on the linearity of the correlation curves. Better linearity is obtained with a distance of 2 cm between the two electrodes. This study shows the possibility of measuring copper (II) in an aqueous medium by simple amperometry or potentiometry using a probe.

**Keywords:** Amperometric; Potentiometric; Copper (II); Determination

### 1. Introduction

The development of electrochemistry began at the end of the 18th century when Luigi Galvani (Italian physicist and physician 1737-1798) showed that the contraction of a frog's leg produces an electric current [1, 2]. Electrochemistry is a science that aims to study the chemical changes caused by the passage of an electric current between ionic and electronic conductors (electrodes) [3].

Electrochemical methods are based on oxidation-reduction reactions which are the site of an exchange of electrons between the oxidant and the reducer, the most commonly used of which are: amperometry, polarography, conductimetry, potentiometry, voltammetry, etc. [4]. These methods can be used in several fields such as the environment, the food industry, synthetic chemistry, industry, biomedical analysis, etc. [5]. Contamination of soil and water by metals is widespread throughout the world. Given their toxicity even at low concentrations, these metals, once ingested, can be very harmful to health.

Copper is naturally found in four oxidation states: elemental metallic copper Cu (0), monovalent ion Cu (I), bivalent cupric ion Cu (II) and more rarely trivalent copper ion Cu (III). It has two stable isotopes (<sup>63</sup>Cu et <sup>65</sup>Cu) and 27 less stable isotopes [6].

\* Corresponding author: Mahaman Nazirou GARBA LABO

National Polytechnic Institute, Félix Houphouët-Boigny (INP-HP), BP 1093, Yamoussoukro, Côte d'Ivoire.

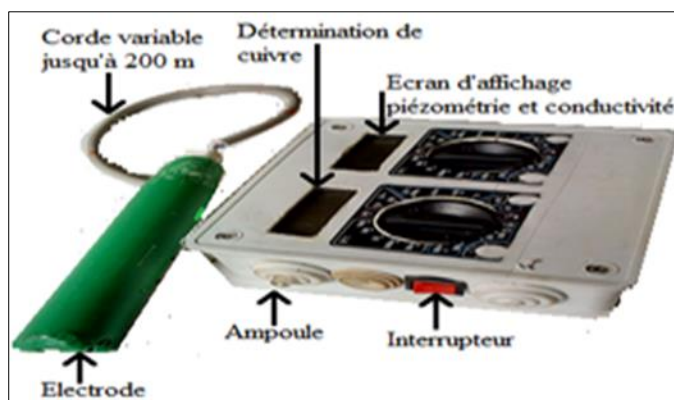
Copper is a transition metal essential for the development of biological processes such as the maintenance of immune functions, the cellular respiratory chain, etc. hence its role as a very important trace element in the body [7, 8]. However, it can be toxic, depending on the concentration and the nature of the organisms considered [9]. Excess administration of the water-soluble ionized form of copper in humans or animals over a long period can lead to progressive and irreversible degradation of their organisms, of varying severity depending on the species studied [10]. Thus, the extreme accumulation of copper in the liver in early childhood causes Native American childhood cirrhosis. In adults, it can cause disruption of the gastrointestinal tract [11]. The above shows the need to monitor the copper content in waters.

Several techniques (atomic absorption spectroscopy, atomic emission spectrometry, mass spectrometry with inductively coupled plasma, etc.) are used for the analysis or detection of metallic elements (Cu, Zn, Cd, etc.). These methods are on the one hand too expensive and require a lot of preparation time; and on the other hand, they require the use of chemicals [12]. The high cost of these methods, their lack of adaptation in the field and the seriousness of their impacts on environmental pollution, increase the need for new analytical tools for the detection and quantification of metals [13]. Some electrochemical methods offer interesting alternatives for portable and low-cost instrumentation. They offer the possibility of carrying out certain analyzes directly on site such as: quantitative chemical assays, analysis of metals under different oxidation numbers, working with low concentrations and in the presence of other non-electroactive species [14].

The objective of this study is the development of new simple electrochemical methods for the determination of copper in an aqueous medium.

## 2. Material and methods

This work focuses on two methods (amperometric and potentiometric) for the determination of copper (II) in aqueous solution. These methods are based respectively on the measurement of the intensity of the current and that of the potential difference. The current intensity and the potential difference were measured using the probe below.



**Figure 1** Measurement probe

The electrodes of the probe used are made of copper and iron. They have the same surface and are immersed parallel in the analytical solution at the same depth. The intensity and the potential difference are measured after addition and total dissolution of the  $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$ .

The intensity is read after stabilization (30 seconds). Each measurement is repeated three times. The retained intensity value  $I$  is obtained by the average of three measured values while subtracting the value obtained with the blank. The influence of the distance between the two electrodes was evaluated. The distances between the electrodes used are: 0.5 ; 1 and 2 cm. The potential difference is read instantaneously. Each measurement is repeated three times. The retained ddp value is obtained by the average of three measured values while subtracting the value obtained with the blank.

To determine the detection limit by the amperometric method, five solutions of respective concentration ( $10 \times 10^{-7}$ ;  $5 \times 10^{-7}$ ;  $2.5 \times 10^{-7}$ ;  $1 \times 10^{-7}$ ;  $0.5 \times 10^{-7}$ ) were been used. After each measurement, the electrodes are washed and rinsed with distilled water. Three tests were carried out for each concentration. The retained intensity value  $I$  is obtained by the average of three measured values while subtracting the value obtained with the blank. The detection limit was calculated by a statistical method.

The influence of iron (II) ions on the variation of ddp ( $ddp = f([Cu^{2+}])$ ) was evaluated. Thus, in three beakers each containing a solution of copper (II) at 2 ppm,  $Fe^{2+}$  was added. In the three beakers the concentrations of  $Fe^{2+}$  at the end are respectively 1, 2 and 3 ppm in each beaker the measurement of the potential difference is repeated three times. The selected ddp value is obtained by the average of the three measured values. The same procedure was carried out with a concentration of copper (II) at 5 ppm in three beakers with respectively 1; 2 and 3 ppm of the  $Fe^{2+}$ .

pH can influence reactions electrochemical therefore on the intensity of the current. The pH was adjusted with 0.5 M HCl or NaOH.

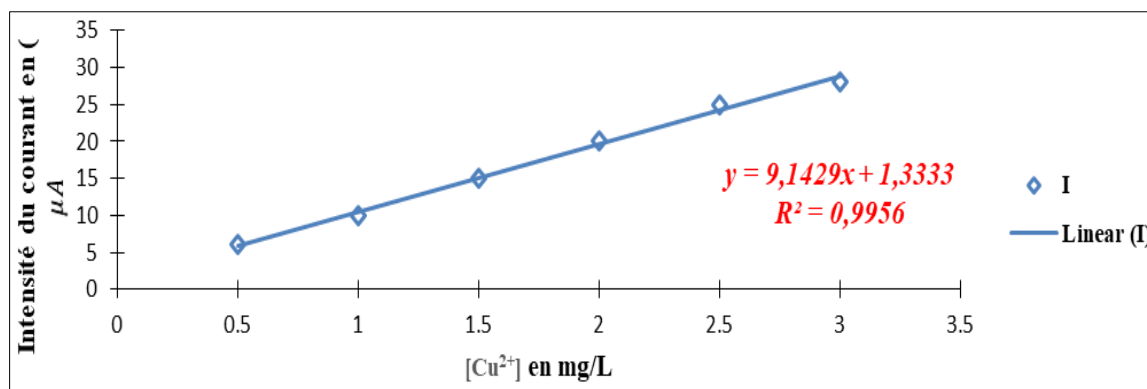
To determine the influence of pH on current intensity, solutions with a pH ranging from 5 to 11 were used. The pH was measured using a Crisson Basic 20 type pH meter.

It was also determined the influence of conductivity on the measured current intensity or on the potential difference. To vary the conductivity a solution of NaCl et MgSO4 was used. Conductivity was measured using a WTW 3430 model conductometric multimeter. Precision type 205A T159072

### 3. Results and discussion

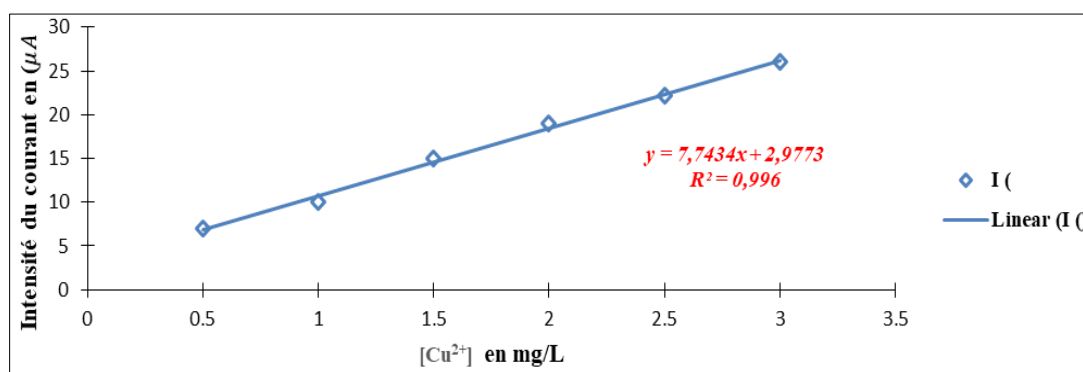
#### 3.1. Amperometric measurement and regression curves

##### 3.1.1. Influence of the distance between the 2 electrodes on the linearity



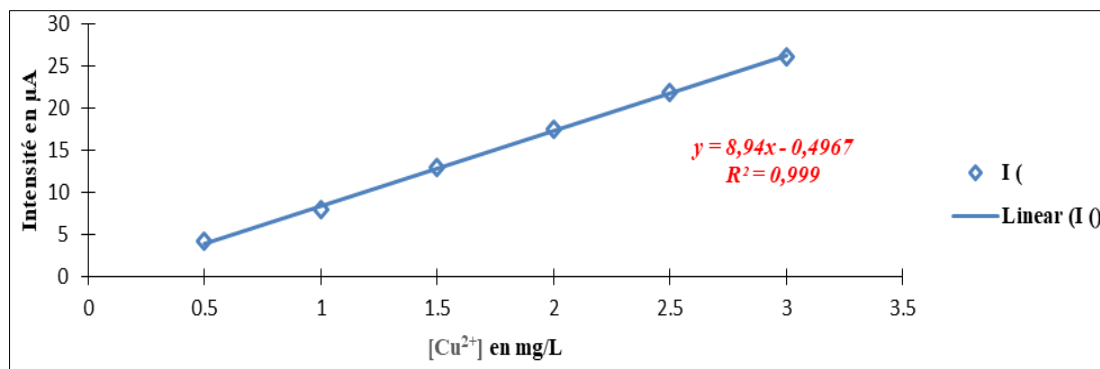
**Figure 2** Regression curve of the current intensity measured as a function of the concentration of  $Cu^{2+}$  in the medium at  $d = 0.5$  cm

The regression curve in Figure 2 shows good linearity between the concentration of copper (II) ions in the aqueous medium and the intensity of the current measured at  $d = 0.5$  cm. It also shows a strong correlation above the guide value ( $R^2 > 0.95$ ) for quantitative assays [15]



**Figure 3** Regression curves of the current intensity measured as a function of the concentration of  $Cu^{2+}$  in the medium at  $d = 1$  cm

The regression curve in Figure 3 shows good linearity between the concentration of copper (II) ions in the aqueous medium and the intensity of the current measured at  $d = 1$  cm. This figure also shows a strong correlation which is beyond the guideline value ( $R^2 > 0.95$ ) for quantitative assays [15].

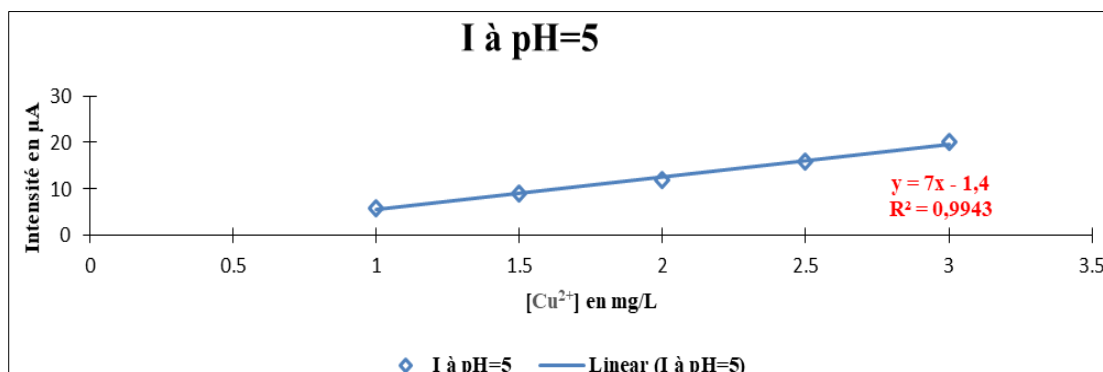


**Figure 4** Regression curves of the current intensity measured as a function of the concentration of Cu<sup>2+</sup> in the medium at  $d = 2$  cm

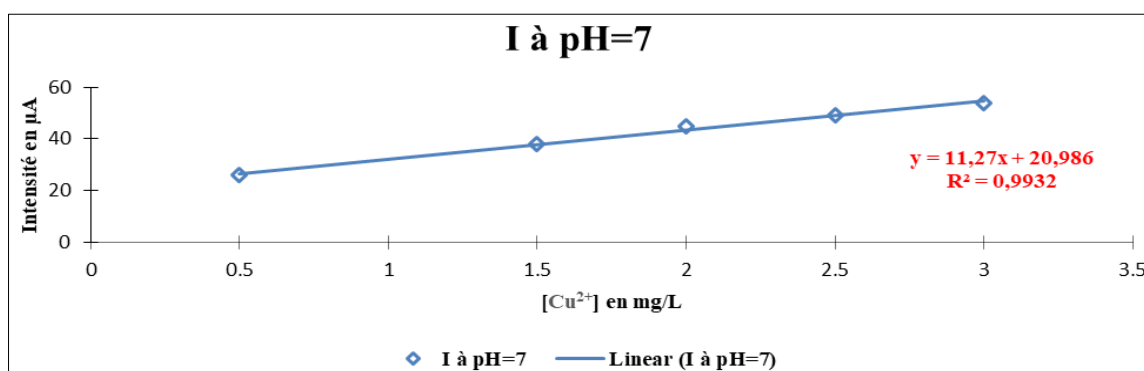
The regression curve in Figure 4 shows good linearity between the concentration of copper (II) ions in the aqueous medium and the intensity  $I$  of the current measured at  $d = 2$  cm. This curve also shows a strong correlation which is equal to  $R^2 > 0.99$  between the concentration of copper (II) ions and the intensity of the current.

It can be seen that the best linearity is obtained at  $d = 2$  cm.

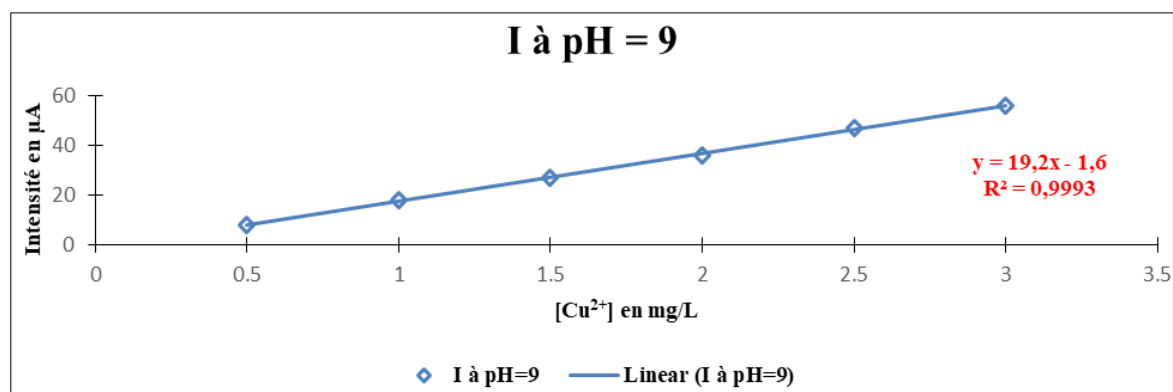
### 3.2. Influence of the pH of the medium on the regression curve $I = f [Cu^{2+}]$



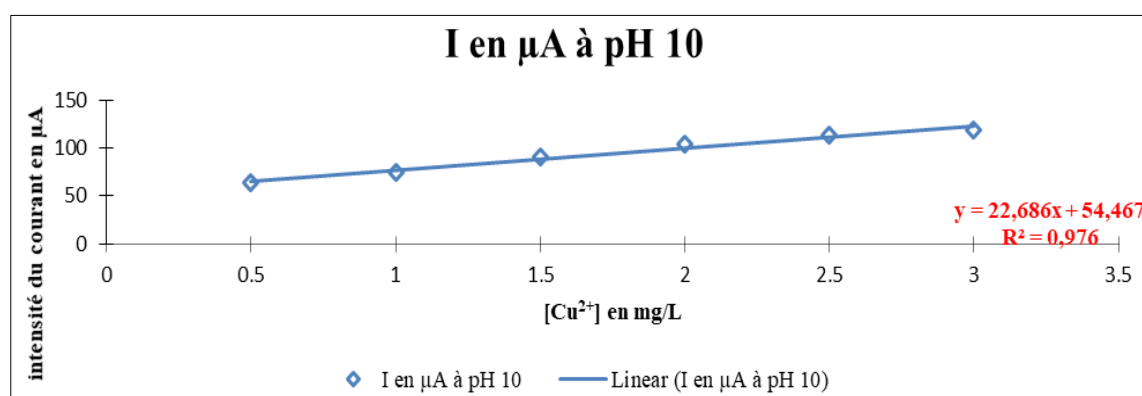
**Figure 5** Regression curves of  $I = f ([Cu^{2+}])$  at pH = 5



**Figure 6** Regression curves of  $I = f ([Cu^{2+}])$  at pH = 7



**Figure 7** Regression curves of  $I = f([Cu^{2+}])$  at pH = 9



**Figure 8** Regression curves of  $I = f([Cu^{2+}])$  at pH = 10

The regression coefficient between the intensity of the current and the concentration of copper (II) ions at pH= 5 is  $R^2 = 0.9943$  (figure 5). This coefficient shows a good correlation in the measurement of  $[Cu^{2+}]$  at pH= 5. Similarly, the regression coefficient between the copper (II) ion concentration and the current intensity at pH = 7 is  $R^2 = 0.9932$  (figure 6). This strong regression coefficient shows that, at pH = 7, good results can be obtained for the concentrations of copper (II) ions in the aqueous medium with the amperometric method. Also, figure 7 shows a good correlation ( $R^2 = 0.9993$ ) between the intensity of the current and the  $[Cu^{2+}]$  in aqueous medium. This strong correlation shows the possibility of measuring  $[Cu^{2+}]$  in an aqueous medium with the same method. Similarly, Figure 8 shows a good correlation between current intensity and  $[Cu^{2+}]$  at pH = 10. Indeed, these results indicate that the strongest correlations between current intensities and copper (II) ion concentration were obtained at pH between 5 and 9. Therefore, the measurements should be made at a pH between 5 and 9.

### 3.3. Limit of detection of the amperometric method

The limit of detection is the smallest amount of an analyte that produces a signal detectable with defined reliability and statistically different from that produced by a blank under the same conditions [4]. In this study the detection limit was determined to know the smallest concentration of copper (II) ions that can give a detectable current signal.

The detection limit obtained from Long and Winefordner formula is 0.016 mg/L. This result is slightly higher than that of Souleymane TRAOURE which is 0.02 ppm (mg/L) for the same compound with atomic absorption spectrometry in 2007.

3.3.1. Influence of the ions ( $Mg^{2+}$ ,  $Na^+$  and  $Cl^-$ ) of the medium on the linearity  $I = f([Cu^{2+}])$

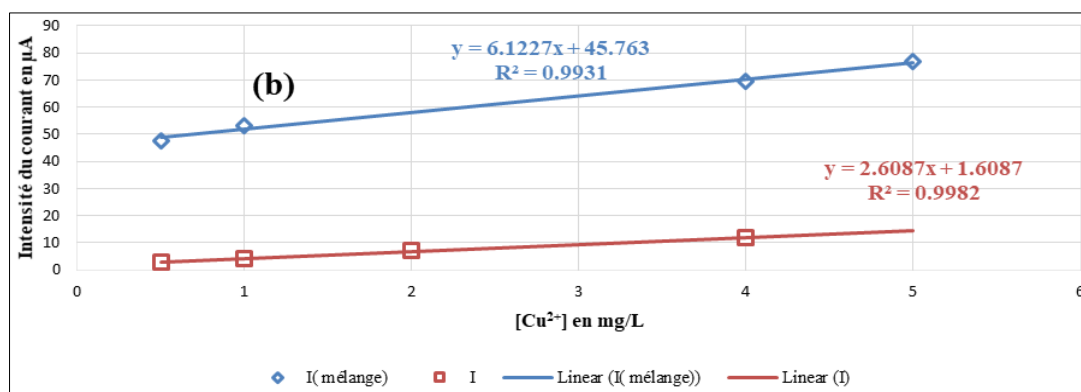


Figure 9 Regression curves  $I = f([Cu^{2+}])$ : (a) without addition of ions and (b) with addition of ions

The regression curves (a) and (b) show that, for each concentration of  $Cu^{2+}$  ions, the intensity measured after addition is greater than that measured without addition. However, in both cases (with addition and without addition) the correlation coefficients obtained ( $R^2$  and  $R$ ) are greater than 0.99; which indicates that the presence of ions ( $Mg^{2+}$ ,  $Na^+$  and  $Cl^-$ ) has no influence on the concentration of  $Cu^{2+}$  ions [15].

3.4. Potentiometric measurement and regression curve

3.4.1. Regression curve  $ddp = f(C)$

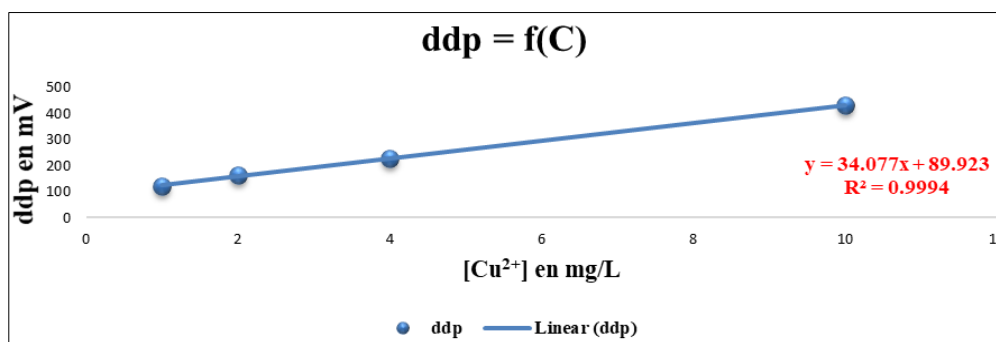


Figure 10 Regression curve of the measurement of  $ddp = f([Cu^{2+}])$

The regression coefficient obtained ( $R^2 = 0.9994$ ) in Figure 10 shows that there is an excellent correlation between the measured potential difference and the concentration of copper (II) ions in the aqueous medium.

3.4.2. Influence of  $Mg^{2+}$  ion content;  $Na^+$ ; Middle  $Cl^-$  on linearity ( $ddp = f([Cu^{2+}])$ )

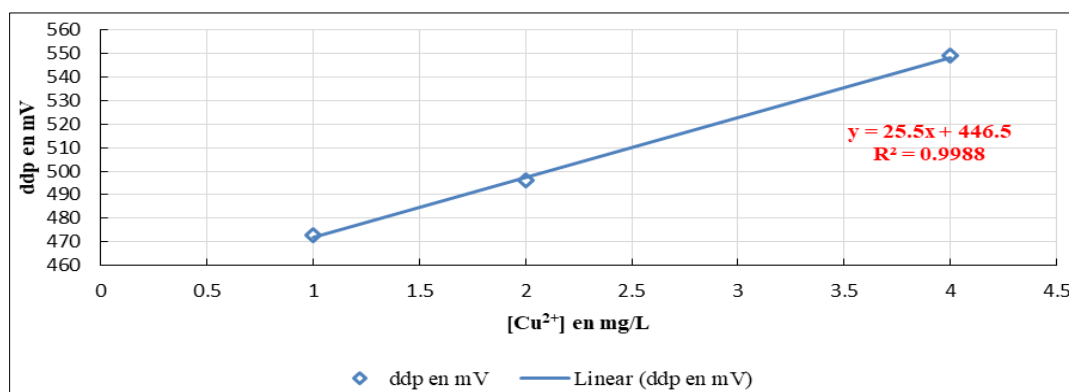
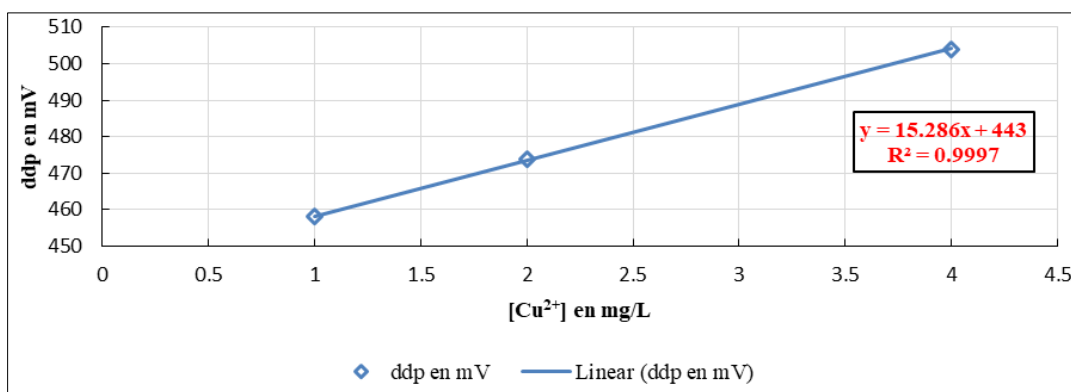


Figure 11 Regression curves of the influence of ions on the linearity  $ddp = f([Cu^{2+}])$  before adding the ions ( $Mg^{2+}$ ;  $Na^+$ ;  $Cl^-$ )

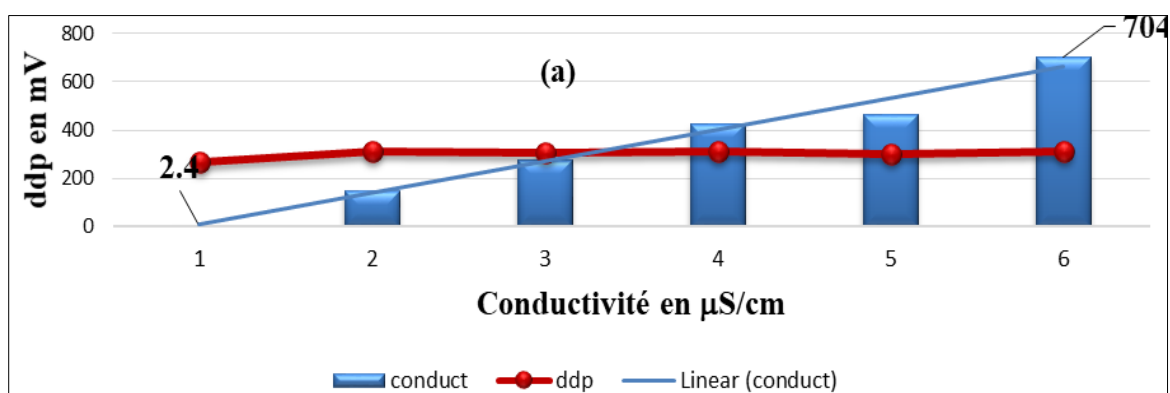


**Figure 12** Regression curves of the influence of ions on the linearity  $ddp = f([Cu^{2+}])$  after adding the ions ( $Mg^{2+}$ ;  $Na^+$ ;  $Cl^-$ )

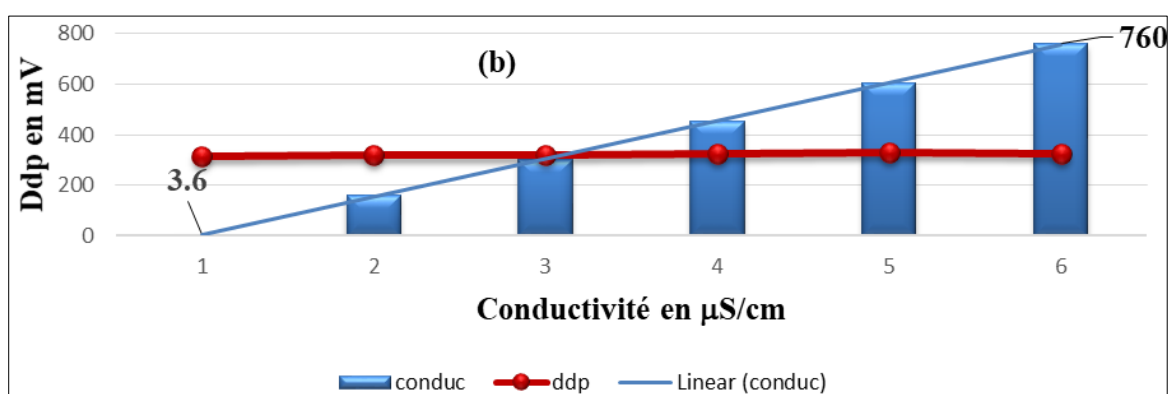
The regression coefficients  $R^2$  (figure 11) equal to 0.9988 and  $R^2$  (figure 12) equal to 0.9997

show that the presence of ions ( $Mg^{2+}$ ;  $Na^+$ ;  $Cl^-$  and  $SO_4^{2-}$ ) in the medium practically does not affect the linearity between the ddp and the concentration of copper (II) ions in this aqueous.

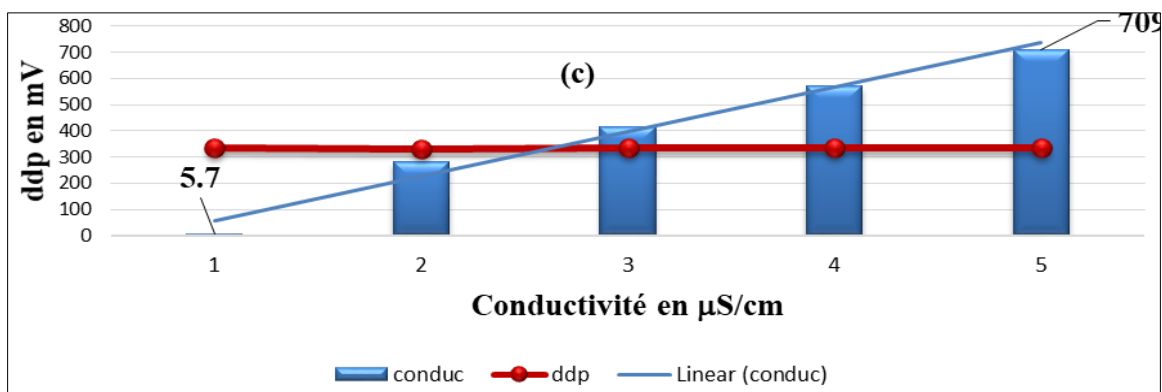
### 3.5. Influence of the conductivity of the medium on the ddp at $[Cu^{2+}]$ fixed



**Figure 13** Curves of variation of potential difference as a function of conductivity with 1 mg/L of Cu (II)



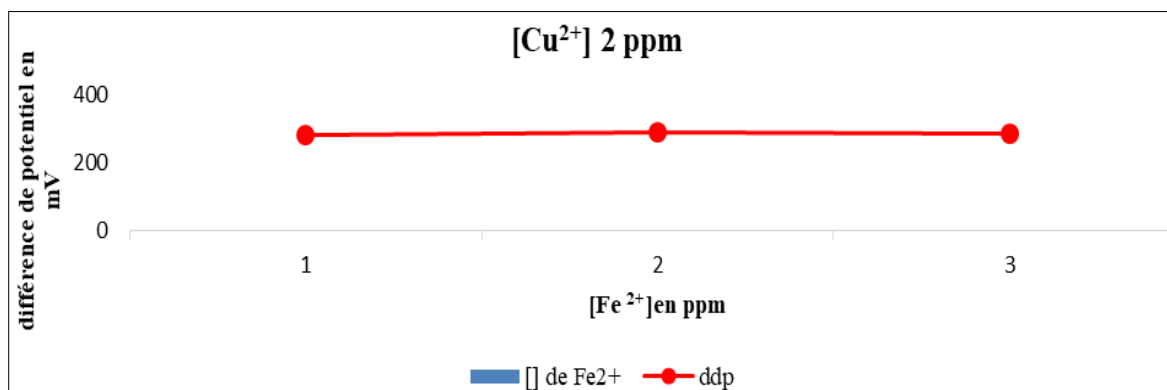
**Figure 14** Curves of variation of the potential difference as a function of the conductivity with 2 mg/L of Cu(II)



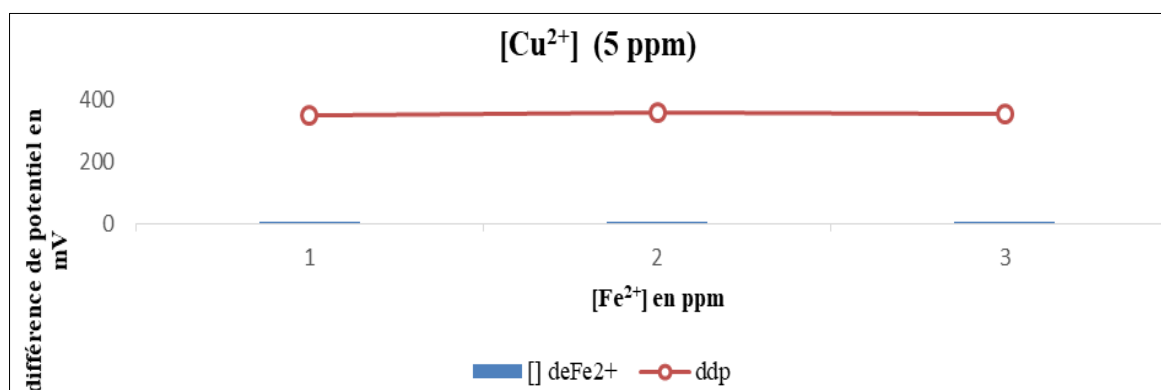
**Figure 15** Curves of variation of the potential difference as a function of the conductivity with 4 mg/L of Cu (II)

The curves of variation of the potential difference as a function of the conductivity of figures 13; 14 and 15 above show that the conductivity has practically no influence on the measurement of the potential difference between the two electrodes. This indicates that the mineralization of the medium does not practically affect the measurement of the ddp as a function of the concentration of copper (II) ions in the medium.

### 3.6. Influence of the iron (II) ion content on the fixed copper (II) ion concentration of an aqueous medium



**Figure 16** Curves of variation of the potential difference between the iron electrode and the copper electrode with a concentration of 2 mg/L in Cu (II)



**Figure 17** Curves of variation of the potential difference between the iron electrode and the copper electrode with a concentration of 5 mg/L in Cu (II)

The ddp measured is the difference between the potential of the copper electrode and the potential of the iron electrode. According to Nernst's law, the electrode potential is obtained from the following formula:



$$E = E^0 + \frac{RT}{nF} \ln \frac{(a_{Ox})^\alpha}{(a_{Red})^\beta}$$

The ddp is calculated using the following formula:  $\Delta E = E(\text{Cu}^{2+}/\text{Cu}) - E(\text{Fe}^{2+}/\text{Fe})$  [16-17].

Theoretically the potential of the iron electrode is a function of the concentration of  $\text{Fe}^{2+}$ . This indicates that the concentration of  $\text{Fe}^{2+}$  can influence the ddp. This is why it was determined the influence of  $\text{Fe}^{2+}$  ions on the potential difference.

The curves in figure 16 and 17 above show that the concentration of  $\text{Fe}^{2+}$  ions has practically no influence on the potential difference. This shows that the copper (II) ions of an aqueous medium could be well and truly measured by calibration between the measured potential difference (between the iron electrode and the copper electrode) and the concentration of the  $\text{Cu}^{2+}$  ions.

#### 4. Conclusion

In this study, a method for measuring copper in an aqueous medium by amperometry and potentiometry was developed. The regression coefficient ( $R^2 = 0.99$ ) obtained during the amperometric study shows the possibility of assaying copper in an aqueous medium in situ and without the use of chemicals. Similarly, the regression coefficient ( $R^2 = 0.999$ ) obtained during the study potentiometer shows the possibility of copper dosage in an aqueous medium in situ and without the use of chemicals. In both cases the best results are obtained with a distance between the two electrodes equal to 2 cm. The amperometric dosage must be carried out at a pH between 5 and 9. The pH has no influence on the potentiometric dosage. Ions ( $\text{Fe}^{2+}$ ,  $\text{Na}^+$ ,  $\text{Cl}^-$ ,  $\text{Mg}^{2+}$ , and  $\text{SO}_4^{2-}$ ) do not interfere with potentiometric dosing. On the other hand, they Compliance with ethical standards (WJS-I-Heading no numbering) influence the amperometric dosage but have no effect on the linearity. The amperometric detection limits is 0.016 ppm.

#### Compliance with ethical standards

##### *Disclosure of conflict of interest*

The authors declare that they have no competing interests.

#### References

- [1] Quavorie, Mc DA. general chemistry, 4th Edition, University science books, P931. ISBN: 978-2-8041-7127-8. 2011
- [2] Aboubakre B. Anodic redissolution determination of some heavy metals in drinking water. Physical and analytical chemistry. Département of chemistry. University Aboubekr Belkaid. 44P. Available at <http://dspace.univtlemcen.dz/bitstream/112/12351/Determination-per-redissolution-anodique.pdf>.
- [3] Isabel M. Development of electrochemical sensors based on current sampling voltammetry on electrode array. [Online]. Chemistry. Rennes: University of rennes 1. 190P. French. < NNT: 2016REN1S139> <tel-01660122> available at: <https://www.google.com/url?sa=t&rct=j&q=&esrc=s&source=web&cd=1&cad=rja&uact=8&ved=2ahUKEwiqin formation.v7VzjDgAhVKGt8KHUGAB9cQFjAAegQIAxAC&url=https%3A%2F%2Ftel.archivesouvertes.fr%2Ftel-01660122%2Fdocument&usg=AOvVaw2xzDCaVIRrsoVi6XHCon1X>
- [4] Jean LB. Electrochemical methods of analysis. Available at sur <http://editions.lavoisier.fr/chimie/methodes-electrochimiques-d-analyse/burgot/tecetdoc/livre/9782743014445>.
- [5] Fakhry A. Electrochemical synthesis of conductive polymer nanostructures without using a support matrix: applications to (bios) sensors. Materials. Université Pierre et Marie Curie - Paris VI, 2014.
- [6] Franch. < NNT: 2014PA066296>. <tel-01127179> Disponible sur <https://tel.archives-ouvertes.fr/tel-01127179/file/2014PA066296.pdf>
- [7] Copper in drinking water: health Canada (2018) In: EFSA NDA panel (EFSA panel on dietetic products, nutrition and allergies). Scientific opinion on dietary reference values for copper. EFSA journal, 13(10): 4253, 51pp. 2015.

- [8] Anaïs P. Synthesis and study of new selective copper(I) chelators for Wilson-type diseases. Inorganic and Bioinorganic Chemistry. University of Grenoble. French. <tel-00598705> available at <https://tel.archivesouvertes.fr/tel-00598705>. 2010
- [9] Buffle J, Tercier ML, Waeber. Voltammetric environmental trace metal analysis and speciation: from laboratory to in situ measurements available on <http://citeseerx.ist.psu.edu/viewdoc/download?doi=10.1.1.516.5890&rep=rep1&type=pdf>
- [10] PICO A. Association toxicology chemistry, fact sheet #3, copper: from benefits to risks. Available at <http://atctoxicologie.free.fr> accessed on 10/02/2019.
- [11] Copper in drinking water: health Canada : Copper toxicity induced hepatocerebral and neurodegenerative diseases: An urgent need for prognostic biomarkers. Neurotoxicology, 40: 97-101. 2018.
- [12] Imane A, Aziz A. Electrochemical determination of heavy metals. Review article. Available on <<https://revues.imist.ma/index.php?journal=technolab&page=article&op=download&path%5B%5D=333&path%5B%5D=310%3Fjournal%3Dtechnolab>> . 2007.
- [13] L. Marc-Andre L. In: A.W. BOTT, Current Separations, 14, 64. 1995.
- [14] Electrochemical methods of analysis PPT available at [http://www.educnet.education.fr/rnchimie/chi\\_gen/dossiers/bencheikh/methodes\\_electrochimiques.ppt](http://www.educnet.education.fr/rnchimie/chi_gen/dossiers/bencheikh/methodes_electrochimiques.ppt)
- [15] Dominique B. Validation of an analytical method. University of Montpellier: Max Mousseron Biomolecules Institute. 2010.
- [16] Gourouza M. Electrochemical L3 chimie fondamentale. Université Abdou Moumouni de Niamey. 2015.
- [17] Mohamed N. Electrochemistry course. Process engineering and environment. Université Dr Yahia Feres de Médéa. Faculty of Science and Technology. 99. 2013.