

# Electrode Modified with 1,3-bis(4-butyl-1H-1,2,3-triazol-1-yl)propan-2-ol for Electrochemical Determination of Cu(II) Ions in Cabbage Cultivated with Bordeaux Syrup

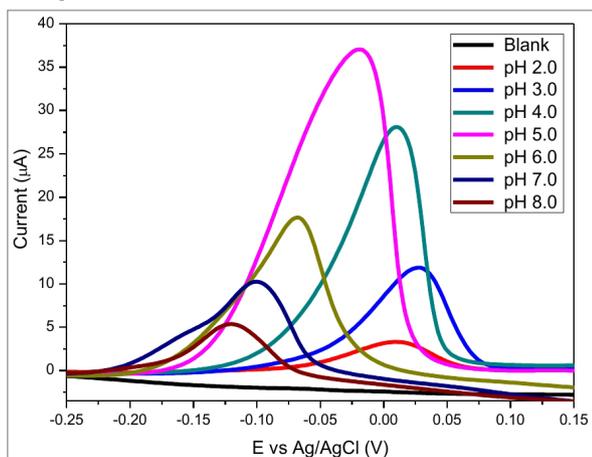
Jonatas de Oliveira S. Silva<sup>1</sup>, Jéssica B. S. Lima<sup>3</sup>, Sanny W. M. M. de Carvalho<sup>1,2</sup>, Mércia V. S. Sant'Anna<sup>1,2</sup>, José C. S. Júnior<sup>1,2</sup>, Ravir R. Farias<sup>3</sup>, Maurício M. Victor<sup>3</sup>,  Eliana Midori Sussuchi<sup>1,2\*</sup>

<sup>1</sup>Corrosion and Nanotechnology Laboratory/NUPEG, Federal University of Sergipe, São Cristóvão, SE, 49100-000, Brazil. \*esmidori@gmail.com

<sup>2</sup>Postgraduate Program in Chemistry, Department of Chemistry, Federal University of Sergipe, Av. Marechal Rondon, S/N, São Cristóvão, SE, 49100-000, Brazil.

<sup>3</sup>Department of Organic Chemistry, Chemistry Institute, Federal University of Bahia, Salvador, BA, 40170-115, Brazil.

## Graphical Abstract



The modified electrode with 1,3-bis(4-butyl-1H-1,2,3-triazol-1-yl)propan-2-ol ligand (CPE/BT) was applied to determinate Cu(II) ions in cabbage cultivated with the use of Bordeaux syrup.

The modified electrode with 1,3-bis(4-butyl-1H-1,2,3-triazol-1-yl)propan-2-ol ligand (CPE/BT) was applied to determinate Cu(II) ions in cabbage cultivated with the use of Bordeaux syrup. The parameters optimization resulted in better analytical signals in B-R buffer solution at pH 5.00, potential of -0.4 V for 900 s on preconcentration, scan rate of 10 mV s<sup>-1</sup> and amount of modifier of 5%. Under the electroanalytical method obtained linear behavior in the range of 1.00 x 10<sup>-8</sup> to 1.30 x 10<sup>-7</sup> mol L<sup>-1</sup>, with a correlation coefficient of 0.994. The limit of detection (LOD) and the limit of quantification (LOQ) for determination of copper were with 1.67 x 10<sup>-9</sup> mol L<sup>-1</sup> and 5.05 x 10<sup>-9</sup> mol L<sup>-1</sup>, respectively. The electrode was successfully applied in the determination of Cu<sup>2+</sup> on cabbage (“couve”) cultivated with Bordeaux syrup and the quantity of copper found was 8.05 µg kg<sup>-1</sup>, which is within the standards stipulated by ANVISA.

**Keywords:** Modified electrode, bistriazoles ligand, copper(II), Bordeaux syrup.

## INTRODUCTION

The development of technologies to improve organic crops, in order to produce healthy foods, has been scientifically and socioeconomically important over the years [1,2]. Phytoprotective syrups, such as the Bordeaux blend (Bordeaux syrup), has as main objective the diseases' control and pests at the farms. Discovered in France in 1882, consists in the mixture of calcium oxide and copper(II) sulphate and has fungicidal and bactericidal actions [3]. Although they provide an improvement in agricultural production, excessive copper accumulation in plants may cause adverse effects on the human body representing risks to the kidneys, liver, and central nervous system, beyond increased blood pressure and respiration rate [4]. The Brazilian National Health Surveillance Agency (ANVISA) delimits the maximum limit for copper ions in 10 mg kg<sup>-1</sup> per vegetable [5], and its determination has

been investigated by several analytical techniques such as atomic absorption spectroscopy, coupled plasma-mass spectrometry, UV spectrophotometry, fluorescence and electrochemical techniques [6-12]. Analyzes using the electrochemical techniques present advantages when compared to others analytical techniques. According to Skoog [13], the main advantage of electrochemical procedures is the possibility to determinate the concentration of same element's metal ions with different oxidation states. Besides, they are more accessible due its low costs. The electrochemical techniques have a high application in the monitoring of metals ions employing adsorptive stripping voltammetry as a powerful technique for determination of metals. The low limits of detection are determined by stripping techniques which is based on the adsorption accumulation of metal ions and suitable complexing agent (ligand) on the electrode's surface [14-16].

The use of chemical species as a surface modifier of the conventional carbon, silver, gold, platinum electrodes, among others, provides greater selectivity and reactivity when in contact with the desired analyte [17]. The carbon paste electrodes (CPEs) are an alternative to replace the electrodes containing toxic metals, such as mercury. CPEs are produced from powdered graphite and mineral oil, acting as a binder and promoting the immiscibility of the electrode in the solution. In addition, the development of chemically modified carbon paste electrodes presents ease in the preparation, modification and renewal of their surface [18].

A sensitivity's increase and a lower detection limit can be achieved with the use of voltammetric detectors along with a preconcentration step for the deposition of electroactive species on the electrode's surface prior to its electroanalytical determination. An important tool to preconcentrate an analyte and to study the electrochemical behavior of the species is Stripping Voltammetry. Anodic Stripping Voltammetry of copper(II) ions involves preconcentration of the metal at the electrode's surface by the application of a sufficiently negative potential for the copper to reduce at it. Then the potential sweep is carried out in the anodic direction, oxidizing the previously deposited copper. The current recorded in the anodic stage is used as analytical signal, as long as the peak current be proportional to the concentration of the species in solution.

In this context, the triazolic compounds were used as modifier of carbon paste electrodes, due to their ability to complexation with copper(II) ions [19-20]. In this work, to enhance the Cu(II) ions detection, the differential pulse stripping voltammetry technique was proposed based on the complexation of 1,3-bis(4-butyl-1H-1,2,3-triazol-1-yl)propan-2-ol (BT) ligand with Cu(II) ions on the carbon paste electrode. The peak currents of Cu(II) ions were evaluated within a wide concentration range, with high selectivity and sensitivity suitable for investigation of real samples in cabbage cultivated with Bordeaux syrup and produced on the irrigated perimeter of the Piauí city, located in the Sergipe state's countryside.

## MATERIALS AND METHODS

### Materials

Graphite powder (C), cadmium chloride ( $\text{CdCl}_2$ ), zinc(II) acetate dihydrate ( $\text{Zn}(\text{CH}_3\text{COO})_2 \cdot 2\text{H}_2\text{O}$ ), epichlorohydrin, sodium azide ( $\text{NaN}_3$ ), copper(II) sulphate ( $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$ ) and mineral oil were purchased from Sigma-Aldrich. Sodium phosphate monobasic monohydrate ( $\text{NaH}_2\text{PO}_4 \cdot \text{H}_2\text{O}$ ), copper(II) nitrate trihydrate ( $\text{Cu}(\text{NO}_3)_2 \cdot 3\text{H}_2\text{O}$ ), sodium phosphate dibasic anhydrous ( $\text{Na}_2\text{HPO}_4$ ) and phosphoric acid ( $\text{H}_3\text{PO}_4$ ) were purchased from Synth. Sodium hydroxide ( $\text{NaOH}$ ) was purchased from IMPEX. Potassium hexacyanoferrate(III) ( $\text{K}_3\text{Fe}(\text{CN})_6$ ) was purchased from Baker. Glacial acetic acid ( $\text{CH}_3\text{COOH}$ ), lead(II) acetate trihydrate ( $\text{Pb}(\text{CH}_3\text{COO})_2 \cdot 3\text{H}_2\text{O}$ ), iron(II) chloride tetrahydrate ( $\text{FeCl}_2 \cdot 4\text{H}_2\text{O}$ ), manganese(II) acetate tetrahydrate ( $\text{Mn}(\text{CH}_3\text{COO})_2 \cdot 4\text{H}_2\text{O}$ ) were purchased from Vetec. Sodium acetate trihydrate ( $\text{Na}(\text{CH}_3\text{COO}) \cdot 3\text{H}_2\text{O}$ ) and Boric acid ( $\text{H}_3\text{BO}_3$ ) were purchased from Reagen. Acetonitrile was used in HPLC grade. Analytical thin layer chromatography (TLC) and TLC plates pre-coated with silica gel 60 F254 (250  $\mu\text{m}$  thickness) were performed on E. Merck. Ultrapure water was in-laboratory produced from deionized water using an ultrapure water generator device (Millipore). The melting points were uncorrected and determined on a MQAPF-302 apparatus. Nuclear Magnetic Resonance spectra was

recorded on Varian spectrometer model Inova-500 in deuterated solvents (Figures S1–S2). Electrospray high-resolution mass spectra (HR-MS) was obtained using an Agilent 6550 Q-TOF MS instrument in the positive mode (Figure S3). IR spectra was measured using a Shimadzu IR-Affinity spectrophotometer (Figure S4).

### **Synthesis of 1,3-bis(4-butyl-1H-1,2,3-triazol-1-yl)propan-2-ol**

The synthesis of ligand BT was reached in two steps from epichlorohydrin according to literature described proceedings [20-21].

### **Synthesis of 1,3-diazide propan-2-ol**

To a stirred solution of epichlorohydrin (2.00 mL, 25.5 mmol) in a mixture of acetonitrile and water (7:3) sodium azide (4.00 g, 61.6 mmol) was added at room temperature and the mixture was refluxed overnight at 90 °C. The solvent was removed under reduced pressure and the aqueous layer was extracted with dichloromethane (3 X 10 mL). The combined organic layer was dried over anhydrous sodium sulphate. The pure compound (2.97 g, 20.9 mmol) was obtained after removing the solvent under reduced pressure as a transparent viscous liquid. The compound shows single point in ethyl acetate by thin layer chromatography at  $r_f$  0.8. Yield: 82%.

### **Synthesis of 1,3-bis(4-butyl-1H-1,2,3-triazol-1-yl)propan-2-ol**

1,3-Diazide propan-2-ol (0.5 mmol) and hex-1-yne (1.5 mmol) were suspended in a 1:1 mixture of water and *tert*-butyl alcohol (2 mL). Sodium ascorbate (0.2 mmol, 200  $\mu$ L of freshly prepared solution in water) was added, followed by copper(II) sulfate pentahydrate (0.02 mmol in 67  $\mu$ L of water). The heterogeneous mixture was stirred vigorously overnight at 40 °C, which in that point it cleared and TLC analysis indicated complete consumption of the reactants. The reaction mixture was diluted with water (8 mL), cooled in ice, and the white precipitate was collected by filtration. After washing the precipitate with cold water (2 x 4 mL), it was dried under vacuum and recrystallized with EtOAc:hexanes mixtures furnishing ligand BT as a white solid. Yield: 85%. Mp 153.0-154.5 °C; FTIR (KBr)  $\nu_{\max}$  (cm<sup>-1</sup>) 3284, 3140, 3115, 3064, 1550; <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>)  $\delta$  0.94 (t, 6H,  $J$  = 7.4 Hz), 1.39 (sex, 4H,  $J$  = 7.4 Hz), 1.65 (quint, 4H,  $J$  = 7.5 Hz), 2.68 (t, 4H,  $J$  = 7.7 Hz), 4.34 (dd, 2H,  $J$  = 6.4 and 14.1 Hz), 4.47 (dd, 2H,  $J$  = 4.3 and 14.1 Hz), 4.54-4.62 (m, 1H), 5.11 (s, 1H), 7.47 (s, 2H); <sup>13</sup>C NMR (125 MHz, CDCl<sub>3</sub>)  $\delta$  13.8, 22.3, 25.3, 31.4, 53.0, 68.8, 122.7, 148.4; ESI-HRMS  $m/z$  329.20663 (observed), 329.20658 (required for [M<sup>+</sup>Na]<sup>+</sup>).

### **Modified electrodes**

Unmodified carbon paste electrodes containing 7:3 m/m (solid:liquid) of graphite powder:mineral oil per weight were used for the sake of comparison. The modified carbon paste electrodes containing 1,3-bis(4-butyl-1H-1,2,3-triazol-1-yl)propan-2-ol (CPE/BT) were prepared by mixing graphite powder:BT:mineral oil (6.5:0.5:3 ratio). The carbon paste mixture holder was constructed using a thick-walled glass tube with 0.40 cm internal diameter. A copper sleeve equipped with a copper wire plunger was mounted at the top of the glass tube. By rotating the sleeve, the plunger extruded a used paste layer which was sliced off to form a fresh surface and was made by hand-polishing on a weighing paper. The electrodes used in the experiments were stored in a refrigerator at 5 °C and the measurements were performed at room temperature.

### **Instrumentation**

The electrochemical measurements were carried by using an Autolab 100N Potentiostat/Galvanostat. Cyclic and differential pulse voltammetrics experiments were performed in a one-compartment cell using a carbon paste working electrode, a platinum wire auxiliary electrode and Ag/AgCl/KCl (3.00 mol L<sup>-1</sup>) reference electrode. The differential pulse voltammetry parameters used were: 5 mV step potential,

50 mV modulation amplitude, 0.01 s pulse modulation and 0.1 s interval times. Experiments were performed at  $25 \pm 1$  °C in B-R buffer, acetate or phosphate buffer solution. The B-R buffer ( $\mu = 2.0$  mol L<sup>-1</sup>) was obtained as described in the literature and pH was adjusted adding sodium hydroxide. The preconcentration step of the system was maintained under stirring all the time. The Scanning Electron Microscopy (SEM) images were obtained using a SEM of the HITACHI model TM 3000. Using a sample holder by means of a carbon tape, the samples were adhered and gold-plated and subsequently subjected to equipment.

### Stock Solutions

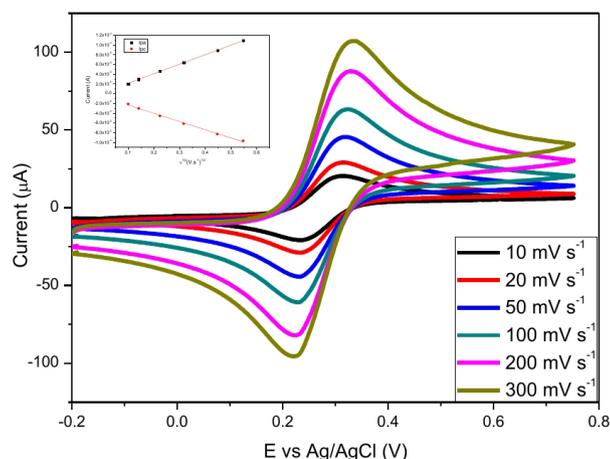
A stock solution of hydrate cooper(II) nitrate (0.01 mol L<sup>-1</sup>) was prepared and aliquots were diluted with B-R buffer solution pH = 5.0 ( $\mu = 2.0$  mol L<sup>-1</sup>) to obtain the concentration range of  $1.00 \times 10^{-8}$  -  $1.30 \times 10^{-7}$  mol L<sup>-1</sup>. The Cu<sup>2+</sup> determinations were carried out by stripping voltammetric analysis. All measurements were performed at room temperature.

### Real samples

In this work, two methods of preparation were used to prepare cabbage samples: a) the samples (59.8810 g) were ground in 70.00 mL of ultrapure water, then the mixture was centrifuged in two 1200 s cycles at 4000 rpm s<sup>-1</sup> and the solution obtained was analyzed; and b) the cabbage samples were ground and stirred for 24 hours in B-R buffer solution pH 5.0 ( $\mu = 2.0$  mol L<sup>-1</sup>). After stirring, the obtained mixture was centrifuged for 1200 s cycles at 4000 rpm s<sup>-1</sup> and, after filtered, the solution was analyzed. However, this later method of preparation did not present reproducible results, being discarded.

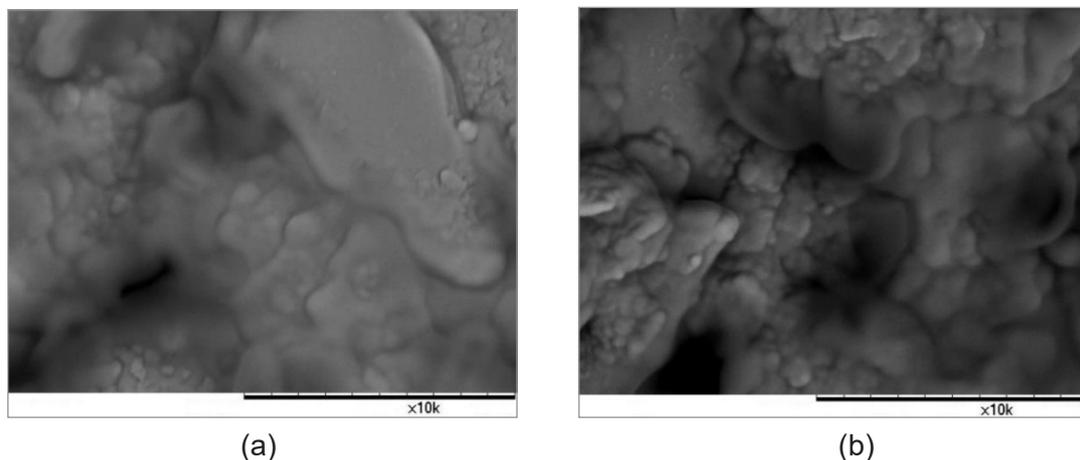
## RESULTS AND DISCUSSION

The electrochemical behavior of the modified carbon paste electrode was evaluated in K<sub>3</sub>Fe(CN)<sub>6</sub> (1.0 mmol L<sup>-1</sup>) in KCl. The cyclic voltammograms revealed a linear correlation between the scan rates ( $v^{1/2}$ ), anodic and cathodic peak currents ( $I_{pa}$  and  $I_{pc}$ ), typical behavior of reversible electrochemical processes presenting diffusional control (Figure 1). Using the Randles-Sevcik equation, it was possible to determine the effective electrode's area [22]. The modified electrode presented a response surface of 0.27 cm<sup>2</sup>, higher than its geometric area (0.12 cm<sup>2</sup>).



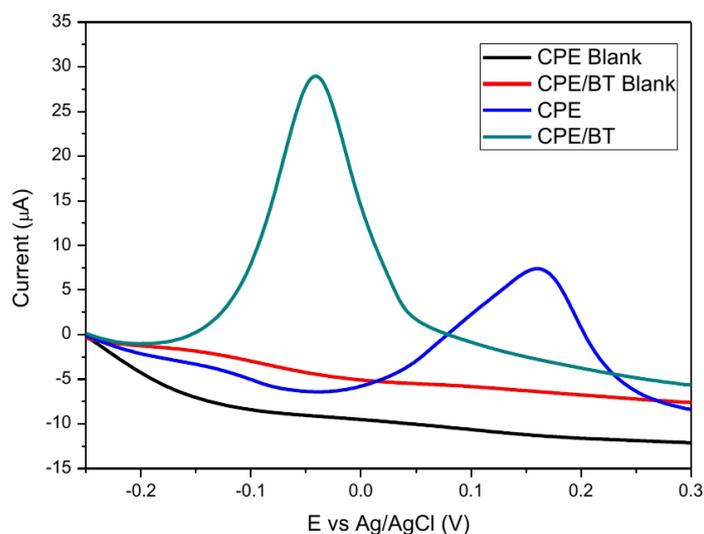
**Figure 1.** Cyclic voltammograms of CPE/BT in K<sub>3</sub>Fe(CN)<sub>6</sub> solution (1.0 mmol L<sup>-1</sup>) in 1.0 mol L<sup>-1</sup> KCl, scan rate range 10 - 300 mV s<sup>-1</sup>.

Confirming, along with the results shown in cyclic voltammograms, the scanning electron microscopy (SEM) images (Figure 2) corroborate with the data obtained through the cyclic voltammograms. When compared to that of the carbon paste electrode without modifier (a), the modified surface electrode (b) presents greater roughness and porosity, such characteristics can provide a greater surface area, causing the rapid diffusion of the analyte in the support solution which generates the increase of the analytical signal.



**Figure 2.** SEM images of CPE (a) and CPE/BT (b).

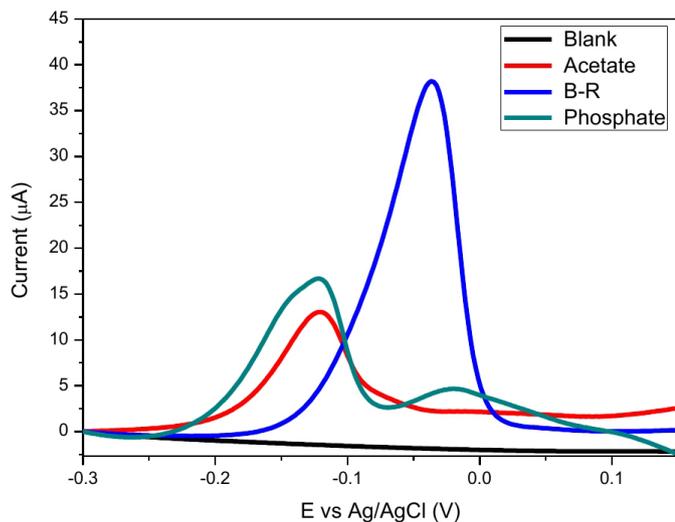
The CPE's electrochemical behavior (absence of modification) and CPE/BT (Figure 3) in presence of a fixed amount of copper(II) were performed to determine the variation in the anodic peak currents and the method's sensitivity. The presence of the -OH group and triazoles rings of the ligand's molecular structure contribute to their ability to complexate with copper(II) ions, increasing the intensity of the anodic peak current and a shift to lower potential value.



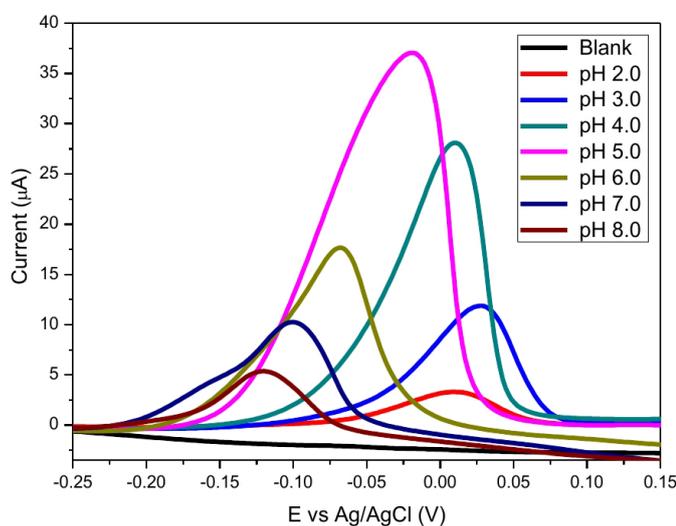
**Figure 3.** Differential pulse voltammograms of CPE in  $\text{Cu}^{2+}$  absence (black line), CPE/BT in  $\text{Cu}^{2+}$  absence (red line), CPE (blue line) and CPE/BT (green line) in the presence of  $\text{Cu}^{2+}$   $1.0 \times 10^{-5} \text{ mol L}^{-1}$ . Conditions: preconcentration potential  $-0.5 \text{ V}$  for  $300 \text{ s}$  in phosphate buffer ( $\text{pH} = 6.0$ );  $v = 10 \text{ mV s}^{-1}$ .

The optimization of an electrochemical parameter is very important in order to improve the analytical response profile, furnishing better results for application in real samples. The electrolyte evaluation was performed using B-R, acetate and phosphate buffer solutions at  $\text{pH} 5.0$ , with a higher signal intensity when the analyzes were performed in B-R buffer solution (Figure 4). The study of the behavior by  $\text{pH}$  variation was obtained in B-R buffer solutions ( $\mu = 2.0 \text{ mol L}^{-1}$ ) with  $\text{pH}$  range from  $2.00$  to  $8.00$ . Figure 5 shows the displacement of the copper anodic peak potential to negative potential values indicating that oxidation is facilitated with increasing  $\text{pH}$ . However, the highest intensity of anodic peak current

was observed at pH 5.0. This behavior may be explained by the presence of protons and its influence on the triazole ligand's chelating ability. At pH 5.0 favors the desorption of copper in the oxidation stage, while the excess of  $H^+$  ( $pH < 5$ ) leads to the competition of  $H^+$  and  $Cu^{2+}$  ions during the adsorption step, reducing the detection of copper ions. The decrease of the anodic peak currents obtained in alkaline media is justified by the presence of hydroxyl ions in solution, leading to the formation of  $Cu(OH)_2$ , which decreases its availability in solution for its determination [23,24].



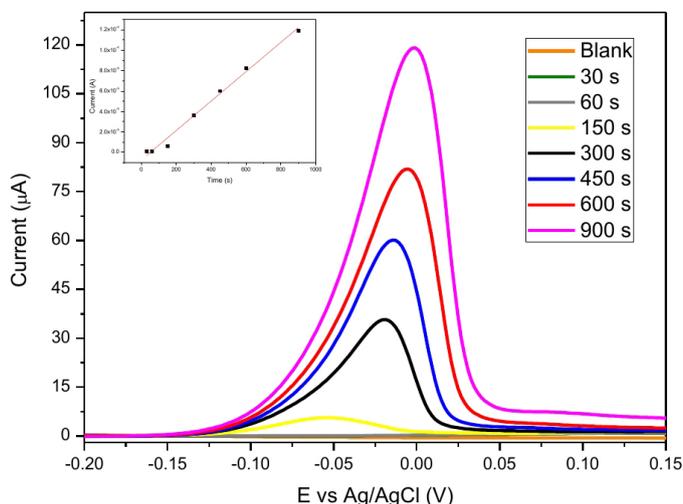
**Figure 4.** Differential pulse voltammograms of CPE/BT in the detection of  $1.0 \times 10^{-5} \text{ mol L}^{-1} \text{ Cu}^{2+}$  in different buffer solutions pH 5.0. Conditions: preconcentration time 300 s;  $v = 10 \text{ mV s}^{-1}$  and preconcentration potential -0.5 V.



**Figure 5.** Differential pulse voltammograms of CPE/BT in the detection of  $1.0 \times 10^{-5} \text{ mol L}^{-1} \text{ Cu}^{2+}$  in B-R buffer pH 2.0 – 8.0 range ( $\mu = 2.0 \text{ mol L}^{-1}$ ). Conditions: preconcentration time 300 s;  $v = 10 \text{ mV s}^{-1}$  and preconcentration potential -0.5 V.

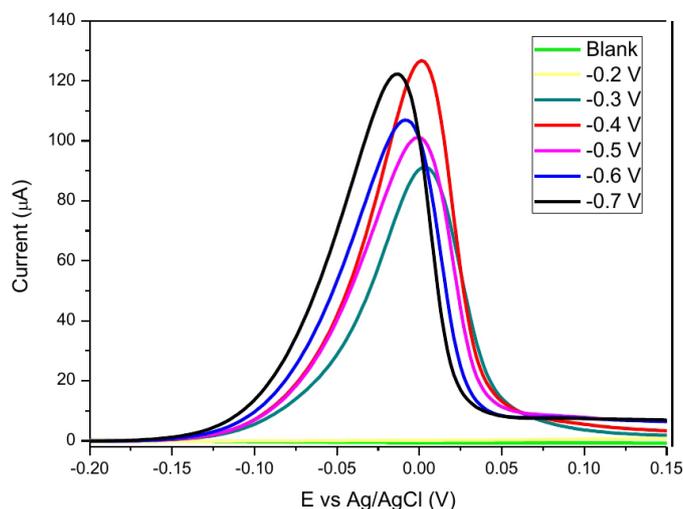
The effect of the modifier on the CPE/BT composition was studied by varying the modifier's proportion from 2.5 to 7.5% (w/w) in the electrode composition. The highest response was obtained using 5% (w/w) modifier and values above 5% were responsible for noticeable the reduction in current intensity. This effect could be attributed to the decrease in the presence of graphite (that is conductive) and the addition of modifier, which decreases the conductivity of the electrode. The influence of the preconcentration time on the electrochemical sensor response in times between 30 and 900 s, revealed

a greater intensity of anodic peak current in 900 s (Figure 6). The system also showed a linear behavior between the anodic peak currents and the preconcentration time.



**Figure 6.** Differential pulse voltammograms of CPE/BT in the detection of  $1.0 \times 10^{-5} \text{ mol L}^{-1} \text{ Cu}^{2+}$  at different preconcentration times. Conditions: B-R buffer solution pH 5.0 ( $\mu = 2.0 \text{ mol L}^{-1}$ );  $\nu = 10 \text{ mV s}^{-1}$  and preconcentration potential  $-0.4 \text{ V}$ . Inset: Current anodic peak ( $I_{pa}$ ) versus preconcentration time.

The data obtained to study the influence of preconcentration potential (Figure 7) revealed a better signal when applied a potential of  $-0.4 \text{ V}$  (vs. Ag/AgCl). The study of scan rate was performed from  $5$  to  $30 \text{ mV s}^{-1}$  scan rate range. The differential pulse voltammograms showed a better analytical response to  $30 \text{ mV s}^{-1}$ , which caused a widening of the signal that could evidence the presence of possible contaminants. Therefore, the scan rate of  $10 \text{ mV s}^{-1}$  was chosen for future studies.



**Figure 7.** Differential pulse voltammograms of CPE/BT in the detection of  $1.0 \times 10^{-5} \text{ mol L}^{-1} \text{ Cu}^{2+}$  in different preconcentration potentials. Conditions: B-R buffer solution pH 5.0 ( $\mu = 2.0 \text{ mol L}^{-1}$ );  $\nu = 10 \text{ mV s}^{-1}$  and preconcentration time  $900 \text{ s}$ .

### Interference study

The selectivity of the proposed method was investigated in a range of  $0.1:1$ ,  $1:1$ ,  $10:1$  ( $M^{2+}:\text{Cu}^{2+}$ ) proportions (Table I). The anodic peak currents were monitored and compared to those from pure  $\text{Cu}^{2+}$  solution, revealing the interference of the ions following the order  $\text{Cd}^{2+} > \text{Zn}^{2+} > \text{Mn}^{2+} > \text{Fe}^{2+} > \text{Pb}^{2+}$ . The higher interference of  $\text{Cd}^{2+}$  and  $\text{Zn}^{2+}$  ions can be justified by competition with copper ions and their preference to coordinate to triazole ligand. In order to measure the magnitude of the interference ions

on a real sample, aliquots of the ion (1:1) were added to the electrochemical cell containing 10% (w/w) of the cabbage. Differential pulse voltammograms revealed a decrease in the anodic peak current in all the evaluated ions, being the reduction of 25.04%, 17.37% and 27.36%, for Cd<sup>2+</sup>, Fe<sup>2+</sup> and Zn<sup>2+</sup>, respectively, demonstrating that the interference in the real sample is smaller and the method can be applied in the presence of other metal ions.

**Table I:** Variation of the anodic peak currents using the fixed concentration of Cu<sup>2+</sup> ions and varying the interferents' concentration according to the proportions

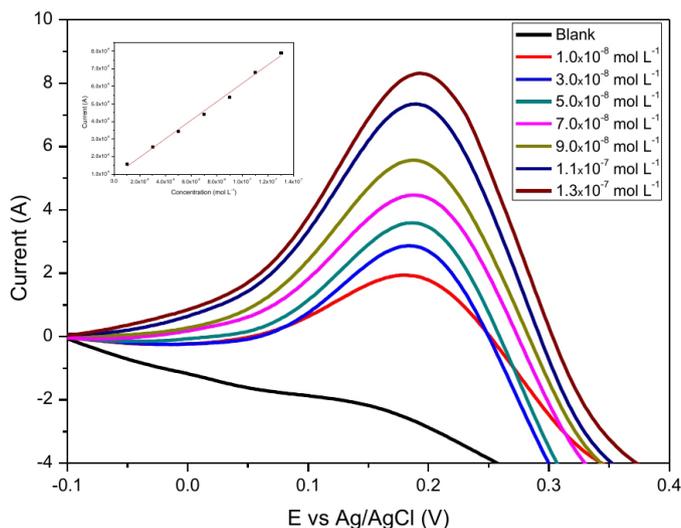
M <sup>2+</sup> :Cu <sup>2+</sup> (mol L <sup>-1</sup> )	Variation of anodic peak current (%)				
	Cd <sup>2+</sup>	Fe <sup>2+</sup>	Mn <sup>2+</sup>	Pb <sup>2+</sup>	Zn <sup>2+</sup>
0:1	0	0	0	0	0
0.1:1	+52.33	+10.02	-15.19	+12.90	+4.42
1:1	+78.00	+5.25	-17.81	-12.36	+14.75
10:1	+109.01	-20.04	-23.48	-18.81	+71.54

The repeatability of the method was evaluated in six analyses at concentration 0.10 μmol L<sup>-1</sup> of copper(II) solution under the optimized conditions. The relative standard deviation (RSD) was 4.3% (n= 6) indicating good repeatability of the modified electrode (CPE/BT). The reproducibility study was performed in three modified electrodes, prepared separately on the same day and the analyses were obtained in triplicate. The results obtained showed a standard deviation of 3.3% demonstrating the viability of the proposed method for the determination of Cu<sup>2+</sup> ions.

### Detection of Cu<sup>2+</sup> in real sample

The analytical curve obtained by the standard addition method under optimized conditions (Figure 8) revealed a linear relationship between the anodic peak currents and Cu<sup>2+</sup> concentrations ranging from 1.0 x 10<sup>-8</sup> to 1.3 x 10<sup>-7</sup> mol L<sup>-1</sup>. The linear regression equation is described by  $I_{pa} = 52.50 [Cu^{2+}] - 9.14 \times 10^{-7}$ , where  $I_{pa}$  is the anodic peak current and  $[Cu^{2+}]$  is concentration of copper(II) ions, with a correlation coefficient of 0.994 (n=7), and showing detection limit at 1.67 x 10<sup>-9</sup> mol L<sup>-1</sup> and quantification limit at 5.05 10<sup>-9</sup> mol L<sup>-1</sup> (LOD = 3.3 σ /α, LOQ = 10 σ /α, where σ is standard deviation, α is slope of the line). Therefore, the LOD and LOQ values of copper(II) ions using the modified electrode demonstrate that it is possible to detect this metal in real samples. Additionally, the results obtained here were comparable to other modified electrodes (Table II).

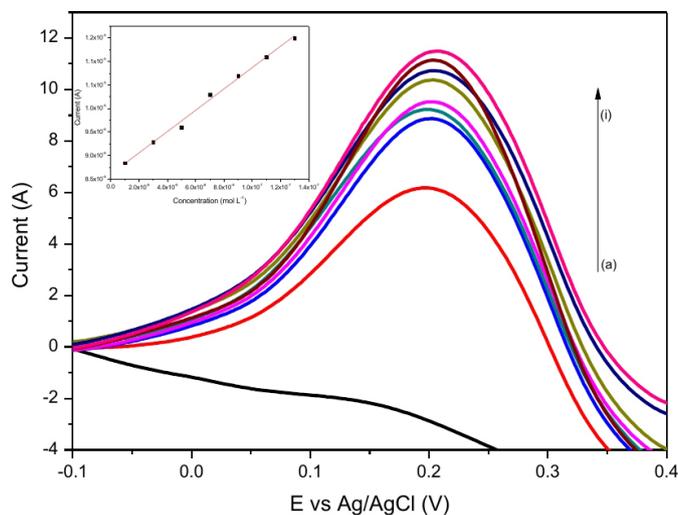
The electrochemical signal of Cu<sup>2+</sup> in cabbage cultivated with the use of Bordeaux syrup was observed by the increase of the anodic peak currents around -0.19 V (E vs Ag/AgCl) and its quantification was performed by the standard addition method. An amount of 6.89 μmol L<sup>-1</sup> of Cu<sup>2+</sup> was determined by extrapolating the calibration curve (Figure 9), described by  $I_{pa} = 22.68 [Cu^{2+}] - 8.60 \times 10^{-6}$ , R<sup>2</sup>= 0.992. The method using modified electrode CPE/BT indicated that the analyzed sample contains 8.05 μg kg<sup>-1</sup> of copper(II), which is lower than the limit established by the Brazilian resolution (10.0 mg kg<sup>-1</sup>).



**Figure 8.** Differential pulse voltammograms of CPE/BT in the detection of different  $\text{Cu}^{2+}$  concentrations. Conditions: B-R buffer solution pH 5.0 ( $\mu = 2.0 \text{ mol L}^{-1}$ );  $\nu = 10 \text{ mV s}^{-1}$ , preconcentration potential  $-0.4 \text{ V}$  for 900 s. Inset: analytical curve.

**Table II:** Efficiency comparison of some modified electrodes used in the determination of  $\text{Cu}^{2+}$

Modified electrodes	Linear range ( $\text{mol L}^{-1}$ )	Limit of detection ( $\text{mol L}^{-1}$ )	References
MS4/QD	$5.0 \times 10^{-8} - 2.3 \times 10^{-6}$	$6.4 \times 10^{-8}$	[25]
FMC	$5.0 \times 10^{-7} - 1.7 \times 10^{-6}$	$8.2 \times 10^{-8}$	[26]
MCPE-CNT	$6.3 \times 10^{-8} - 3.1 \times 10^{-5}$	$1.7 \times 10^{-8}$	[27]
Cu-DPABA-NA/GCE	$15 \times 10^{-8} - 5.6 \times 10^{-5}$	$8.9 \times 10^{-8}$	[15]
BTPSBA-MCPE	$8.0 \times 10^{-7} - 1.0 \times 10^{-5}$	$2.0 \times 10^{-7}$	[16]
CPE/BT	$1.0 \times 10^{-8} - 1.3 \times 10^{-7}$	$1.67 \times 10^{-9}$	This work



**Figure 9.** Differential pulse voltammograms of CPE/BT in different  $\text{Cu}^{2+}$  concentrations. a) blank; b) 5% real sample. Conditions: 5% sample, 95% B-R buffer solution pH 5.0 ( $\mu = 2.0 \text{ mol L}^{-1}$ ),  $\nu = 10 \text{ mV s}^{-1}$ , preconcentration potential  $-0.4 \text{ V}$  for 900 s. Inset: variation of the anodic peak currents as a function of the  $\text{Cu}^{2+}$  concentrations.

## CONCLUSIONS

The new modified carbon paste electrode with 1,3-bis(4-butyl-1H-1,2,3-triazol-1-yl)propan-2-ol ligand was successfully applied for Cu<sup>2+</sup> determinations in cabbage cultivated with the use of Bordeaux syrup. Optimizations of the analysis parameters enabled the elaboration of an analytical curve with linear coefficient within the ANVISA standards for  $n \geq 5$ . Finally, the new methodology application in real samples showed its validity by evaluating it within the standards for human consumption.

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## Supplementary Material

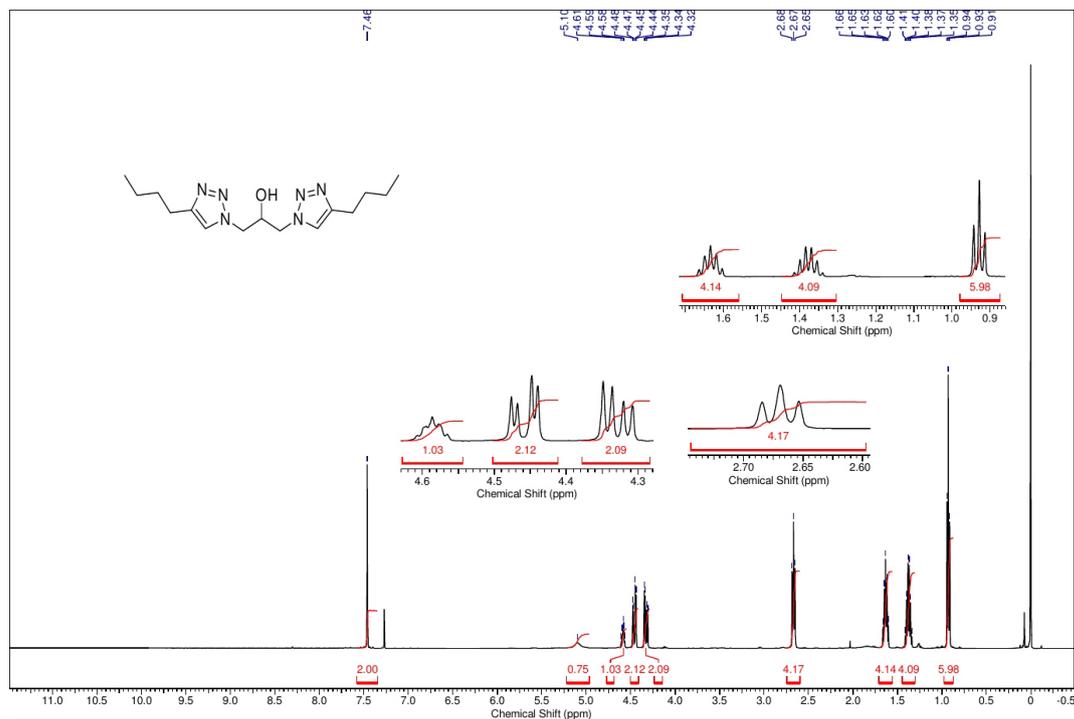


Figure S1.  $^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ ) of 1,3-bis(4-butyl-1H-1,2,3-triazol-1-yl)propan-2-ol.

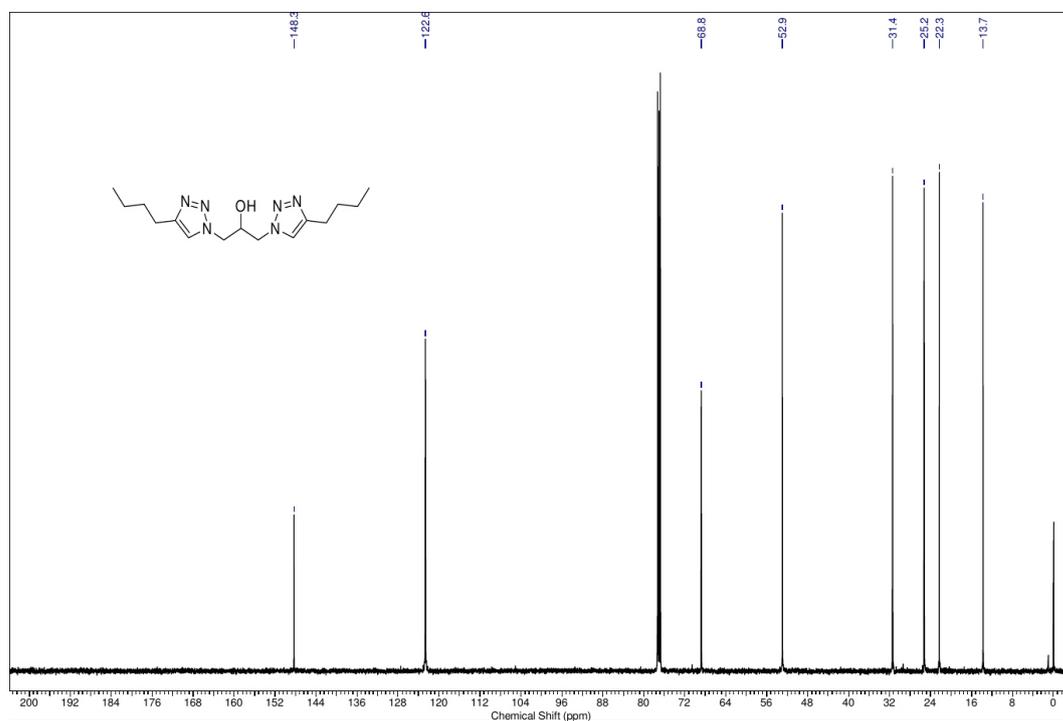


Figure S2.  $^{13}\text{C}$  NMR (125 MHz,  $\text{CDCl}_3$ ) of 1,3-bis(4-butyl-1H-1,2,3-triazol-1-yl)propan-2-ol.

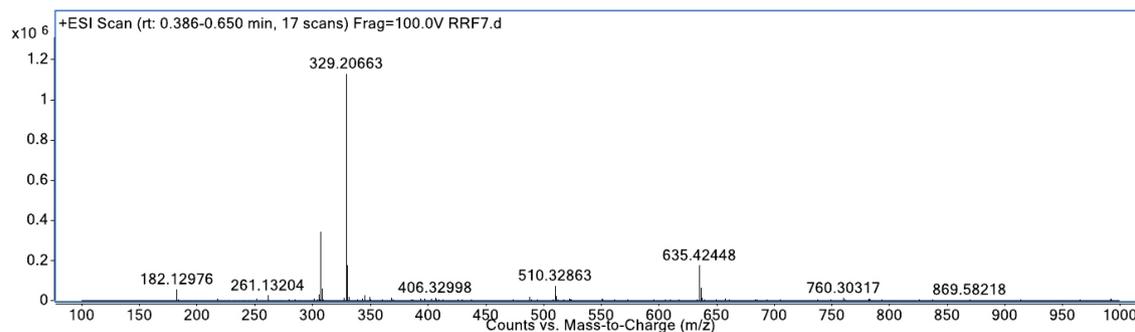


Figure S3. ESI-HRMS of 1,3-bis(4-butyl-1H-1,2,3-triazol-1-yl)propan-2-ol.

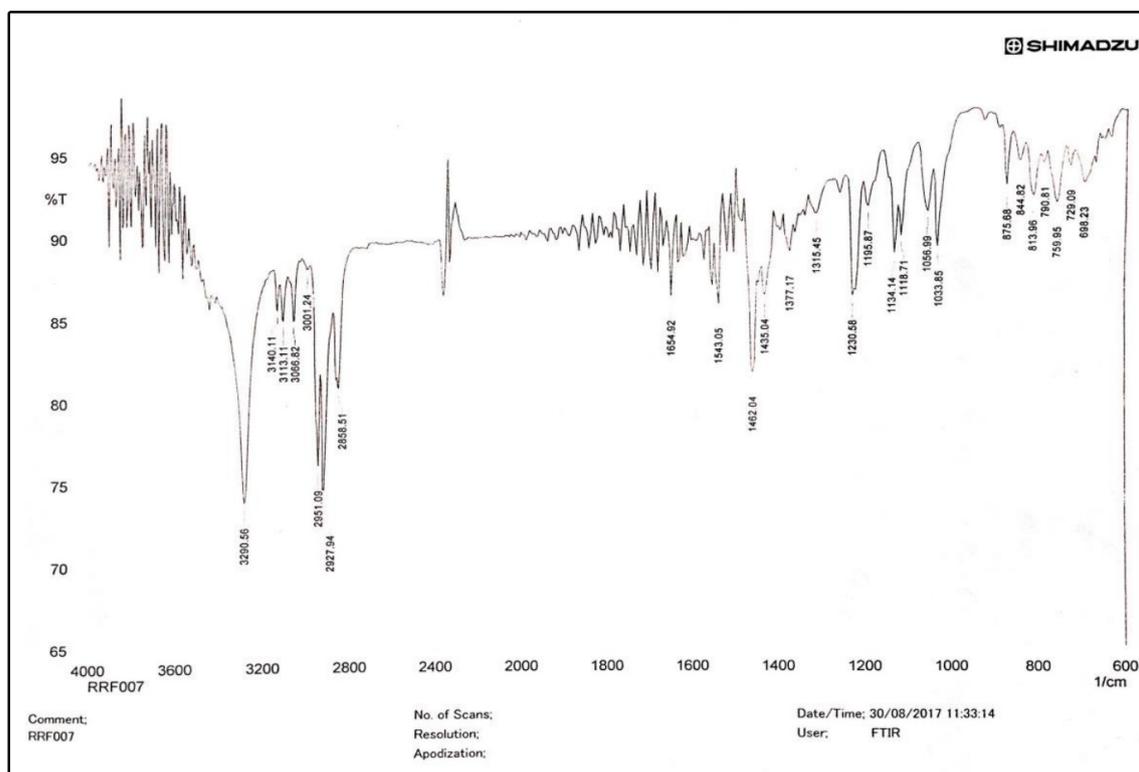


Figure S4. FTIR (KBr) of 1,3-bis(4-butyl-1H-1,2,3-triazol-1-yl)propan-2-ol.