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Derivative Potentiometric Stripping Analysis of Cu(II) at Nanomolar Levels Exploiting the 4-[10,15,20-tris(4-sulfophenyl)-21,22-dihydroporphyrin-5-yl] Benzenesulfonic Acid Host Compound on Multi-Walled Carbon Nanotubes

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A new and simple electroanalytical method was developed for determination of Cu(II) by derivative potentiometric stripping analysis (dPSA). The method employed a basal plane pyrolytic graphite (BPPG) electrode modified with 4-[10,15,20-tris(4-sulfophenyl)-21,22-dihydroporphyrin-5-yl] benzenesulfonic acid (H_2TSPP) adsorbed onto multi-walled carbon nanotubes (MWCNT). The modified electrode showed excellent stability and was able to detect Cu(II) at nanomolar levels. The electrochemical method is based on simultaneous preconcentration/reduction of Cu(II) ions on the H_2TSPP/MWCNT/BPPG electrode at –0.25 V vs. Ag/AgCl(sat) in 0.1 mol/L phosphate buffer solution (pH 7.0), during 240 s, followed by subsequent chemical stripping. The analytical signal showed a linear response for Cu(II) concentrations in the range 5 to 1600 nmol/L (R = 0.9998), with a detection limit of 1.0 nmol/L. The sensor was successfully applied for Cu(II) determination in gasoline samples, and the results were in agreement with those obtained by graphite furnace atomic absorption spectroscopy (GFAAS).

Keywords: Potentiometry; Copper; 4-[10,15,20-tris(4-sulfophenyl)-21,22-dihydroporphyrin-5-yl] benzenesulfonic Acid; Multi-Walled Carbon Nanotubes

1. INTRODUCTION

Analytical techniques that have been proposed for determination of Cu(II) in different samples include spectrophotometric methods [1], atomic absorption spectrometry [2-4], inductively coupled plasma-optical emission spectrometry [5], inductively coupled plasma-mass spectrometry [6,7], liquid chromatography [8], coulometry [9,10], sorbent extraction [11,12], solid phase extraction [13,14], luminescence detection [15], fluorescence and luminescence measurements [16,17], and gravimetry [18]. However, these techniques often suffer from a variety of disadvantages related to cost, lack of selectivity, complex sample preparation procedures, and lengthy analysis times. As an alternative, electrochemical stripping analysis has been recognized as a powerful tool for analyzing metals [19-27], and offers several advantages including simple instrumentation and operation, low cost, high sensitivity [19-27] and miniaturization possibility [28] for application *in situ.* [19-26]. One of the disadvantages of electrochemical stripping methods is need of a time for pre-concentration of the analyte that in some cases can be slow.

PSA is a two-step technique consisting of an electrolysis step and a stripping step. The electrolysis step is a preconcentration during which metal ions are reduced to free metal, and are electrodeposited as an amalgam on the working electrode. The measurements are made during the stripping step, when the metal is re-oxidized. The re-oxidation can be a chemical or electrochemical process. During the stripping step in chemical oxidation, the electrical circuit is interrupted and a chemical oxidant, such as dissolved oxygen or mercury ions, is responsible for the re-oxidation. In electrochemical oxidation, an anodic current is applied to the electrode to re-oxidize the electrodeposited metals. The change in the electrode potential (E) with time (t) during the re-oxidation process is monitored, obtaining a stripping potentiogram of E vs. t [29]. The derivative potentiometric stripping analysis (dPSA), is a variant of PSA developed by Jagner and Aren [30] in order to facilitate evaluation of the analytical signal (by using its derivative).

In PSA, the most widely used working electrodes are either mercury film deposited onto a glassy carbon electrode [26] or a static mercury drop [29], which are efficient for metal accumulation during the deposition step. A major advantage of the mercury drop is that each drop has a smooth and uncontaminated surface free from any adsorbed analyte or impurity and since the drops are produced predictably the changing surface area can be accounted for or even used advantageously [29]. However, these electrodes require meticulous experimental precautions regarding the stability of the mercury drop and its recovery after each experiment, as well as careful manipulation of the mercury solutions used for film deposition. Hence, much effort has been devoted to the development of alternative new electrodes [31]. To this end, it appears that combining the excellent characteristics of this technique with the properties of carbon nanotubes (CNTs) and 4-[10,15,20-tris(4-sulfophenyl)-21,22-dihydroporphyrin-5-yl] benzenesulfonic acid (H_2TSPP) host compound could enable the development of a highly sensitive methodology for metal determination. CNTs present a number of attractive features, such as high surface area, high adsorption capacity for metal complexes, chemical inertness, metallic properties, low cost, and a more positive potential window than the mercury traditionally used in electrodes [31]. On the other hand, the 4-[10,15,20-tris(4-sulfophenyl)-21,22-

dihydroporphyrin-5-yl] benzenesulfonic acid (H_2TSPP) host compound display high affinity toward copper ions.

Although many studies on the electrochemical oxidation of Cu(II) using various modified electrodes have been reported, to our knowledge there are no reports concerning modification of the basal plane of a pyrolytic graphite electrode with H_2TSPP and multi-walled carbon nanotubes (MWCNT), for electrochemical determination of Cu(II). This modification aims to develop materials with improved properties. For this purpose, H_2TSPP was initially adsorbed onto MWCNT and then immobilized onto the BPPG surface by non-covalent π–π stacking, to obtain a new interface to stimulate electron transfer with Cu(II). In the analysis we employed dissolved oxygen as the oxidizing agent, thus reducing the contamination risk arising from the application of some externally added oxidizing agent.

2. EXPERIMENTAL

2.1. Reagents and solutions

All chemicals used were of analytical grade. Multi-walled carbon nanotubes (>90% purity, 110-170 nm diameter, 5-9 μm length) were purchased from Sigma-Aldrich. Cu(II) sulfate standard and 4-[10,15,20-tris(4-sulfophenyl)-21,22-dihydroporphyrin-5-yl] benzenesulfonic acid were obtained from Merck. Dimethyl sulfoxide, hydrochloric acid, sodium hydroxide, and monobasic sodium phosphate were acquired from Vetec. PIPES (piperazine-N,N′-bis(2-ethanesulfonic acid), HEPES (4-(2-hydroxyethyl)-1-piperazineethanesulfonic acid) and Tris (tris(hidroximetil)aminometano) were obtained from Sigma. All solutions were prepared with water (resistivity >18 MΩ cm) purified using a Master P&D system (Gehaka, São Paulo). The pH of the buffer solutions was determined using a Digimed DM-20 pH meter, and was adjusted with solutions of 0.1 mol/L HCl or 0.2 mol/L NaOH.

2.2. Electrochemical measurements

Electrochemical measurements were performed using a three-electrode electrochemical cell and an Autolab PGSTAT 128N potentiostat/galvanostat (Eco Chemie), coupled to a microcomputer running GPES (v. 4.9) software. The working electrode was a BPPG disk with a geometric area of *ca*. 0.28 cm^2, mounted in a Teflon body. The auxiliary and reference electrodes were a platinum wire and an Ag/AgCl, 3 mol/L KCl electrode, respectively. All potentials in this work are reported with respect to this reference electrode. Aliquots of stock solution of copper, were added into the electrochemical cell containing 0.1 mol/L phosphate buffer solution (pH 7.0). Under optimized conditions, the potential was first held at -0.25V for 240 s at stirred solution, where the metal ions were electrochemically deposited onto the working electrode at unstirred solution and the corresponding transients analytical signals (dt/dE) (Sec/V) versus E (V) were recorded.

2.3. Preparation of the modified electrode

Prior to electrode modification, the BPPG electrode was prepared by renewing the electrode surface with cellotape [32]. This procedure involves polishing the BPPG surface with polishing paper, pressing cellotape onto the cleaned BPPG electrode surface, and then removing the cellotape together with several surface layers of graphite. The electrode was rinsed in acetone to remove any adhesive. After cleaning the electrode, 20 µL of a dispersion prepared by sonication of MWCNT (0.5, 1.0, 2.0, 3.0, or 4.0 mg/mL) and H_2TSPP (1.0, 1.5, 2.0, 2.5, or 3.0 mg/mL) in DMSO was placed directly onto the BPPG electrode surface. The electrode was allowed to dry at 60 °C for 90 minutes to form the H_2TSPP/MWCNT composite on the BPPG surface. Finally, the modified electrode was thoroughly rinsed with distilled water and placed into the electrochemical cell.

2.4. Fuel sample preparation

In order to determine total copper in gasoline samples, it was necessary to destroy the organic matrix of the sample by oxidation with a strong oxidizing acid. This process consisted of digestion using nitric acid, followed by the addition of hydrogen peroxide to eliminate any residual nitric acid and complete the oxidation process. Approximately 2.6 mL of gasoline sample was accurately placed into a microwaveable Teflon vessel, followed by the addition of 20 mL of nitric acid (65% v/v) and 10 mL of hydrogen peroxide (30% v/v). The sample vessel was then sealed, and submitted to microwave digestion. Microwave digestion was performed in Mars 5 CEM microwave furnace. After the digestion of the sample, the same was added in a balloon of 50 mL and the volume was completed with water deionized. Then, 500 µL of the sample was added in a cell electrochemistry of 10 mL containing the electrolyte supports.

3. RESULTS AND DISCUSSION

3.1. Electrochemical behavior of BPPG and modified BPPG electrodes

In order to determine the electrochemical behavior of the modified BPPG electrodes, potentiometric stripping curves were recorded in the presence of 1.0 µmol/L Cu(II) (Figure 1). The modified electrodes were prepared with 20 µL of the dispersion containing 2.0 mg/mL H_2TSPP and 2.0 mg/mL MWCNT in DMSO. As shown in Figure 1 (curve a), there was an enhancement in the analytical signal with the H_2TSPP/MWCNT/BPPG electrode, when compared to the curves obtained for the H_2TSPP/BPPG, MWCNT/BPPG, and unmodified BPPG electrodes (Figure 1, curves b-d). This increase of the analytical signal may have been due to the dispersion and immobilization of the ionophore on the MWCNT [31], as well as the H_2TSPP host capability toward copper ions.

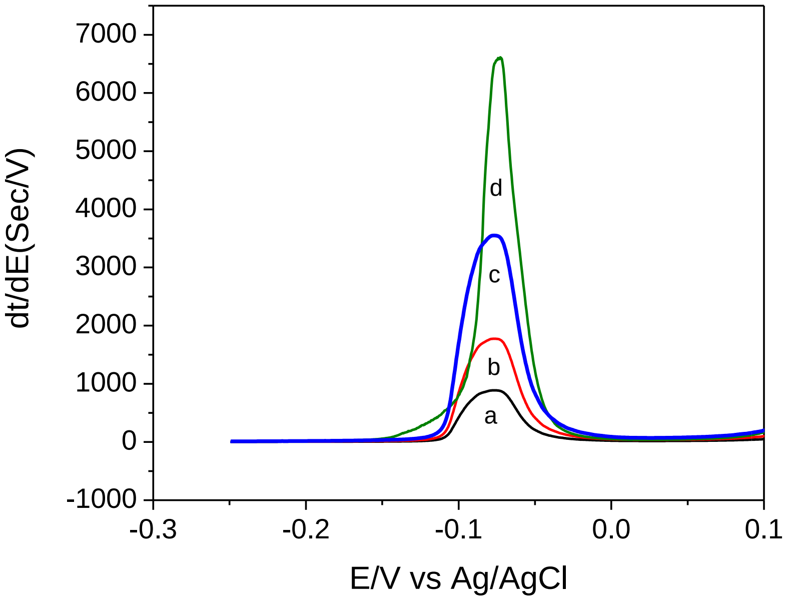

Figure 1. Stripping potentiograms for H_2TSPP/MWCNT/BPPG electrode (a); for H_2TSPP/BPPG electrode (b); for MWCNT/BPPG electrode (c) and for unmodified BPPG electrode (d) in the presence of 1.0 μmol/L Cu(II). The potentiograms were obtained using 0.1 mol/L phosphate buffer solution (pH 7.0). [H_2TSPP]=2.0 mg/mL; [MWCNT]=2.0 mg/mL. Deposition time: 30 s; Applied potential: -0.25 V *vs* Ag/AgCl.

3.2. Influence of the amounts of MWCNT and H_2TSPP on the response of the modified electrode

Optimization of sensor preparation required evaluation of the influence of the concentrations of MWCNT and H_2TSPP. The assays were performed in a medium containing 0.1 mol/L phosphate buffer solution (pH 7.0) in the presence of 0.1 mmol/L Cu(II). A constant potential of –0.25 V *vs.* Ag/AgCl was applied to this solution for 30 s with an equilibrium time was 5 s. Firstly, the dependence of the sensor response for Cu(II) on the amount of MWCNT was investigated by preparing dispersions containing different amounts of the nanotubes (0.5, 1.0, 2.0, 3.0, and 4.0 mg/mL) in DMSO, and maintaining a constant H_2TSPP concentration (2.0 mg/mL). The results showed that an increase in the MWCNT concentration significantly increased the response [33], up to a MWCNT concentration of 3.0 mg/mL (Table 1a).

The small response obtained for lower MWCNT concentrations could be attributed to leaching of the H_2TSPP ionophore from the electrode surface because the MWCNT concentration used was insufficient to immobilize the ionophore. A concentration of MWCNT of 3.0 mg/mL was therefore selected for preparation of the H_2TSPP/MWCNT/BPPG electrode.

The response of the H_2TSPP/MWCNT/BPPG electrode was also affected by the amount of H_2TSPP on the surface. This amount was adjusted by using the same volume of suspension with different concentrations of ionophore (1.0, 1.5, 2.0, 2.5, and 3.0 mg/mL), and maintaining the MWCNT concentration at 3.0 mg/mL (Table 1b). The results indicated that a higher analytical signal for Cu(II) was obtained using 2.0 mg/mL of ionophore solution. The use of H_2TSPP concentrations lower than 2.0 mg/mL resulted in low responses, probably due to the small amount of the ionophore on the electrode surface. The use of H_2TSPP concentrations higher than 2.0 mg/mL did not increase the analytical signal, which could have been due to a maximum capacity of the MWCNT for ionophore immobilization. An ionophore concentration of 2.0 mg/mL was therefore used for electrode preparation.

Table 1. Effects of MWCNT concentrations with [H_2TSPP] = 2.0 mg mL^{-1} (a) and H_2TSPP concentration with [MWCNT] = 3.0 mg mL^{-1} (b) for 1.0 µmol l^{-1} Cu(II) in phosphate buffer solution at pH 7.0.

(a) [MWCNT] (mg mL^{-1})	dt/dE (Sec./V)
0.5	5794 (±18)
1.0	6119 (±15)
2.0	7452 (±16)
3.0	9038 (±10)
4.0	8281 (±18)
(b) [H_2TSPP] (mg mL^{-1})	dt/dE (Sec./V)
1.00	3241 (±10)
1.50	4917 (±15)
2.00	9071 (±11)
2.50	8194 (±13)
3.00	8192 (±18)

3.3. Influences of pH, buffer and its concentration

Potentiometric stripping analysis, similar to other electrochemical techniques, requires the use of supporting electrolytes [34]. In the present study, phosphate buffer solution was used as the supporting electrolyte. Firstly, the influence of pH on the response of the electrode was studied in the pH range from 6.0 to 8.0, using 1.0 µmol/L Cu(II) in 0.1 mol/L phosphate buffer solution (Fig. 2a). The pH of the solutions was adjusted with either 0.1 mol/L HCl or 0.2 mol/L NaOH. A constant potential of –0.25 V was applied to the solution for 30 s. The equilibrium time was 5 s, and the chemical stripping step was carried out from -0.25 V. The potentiometric response for Cu(II) increased with increasing pH, up to pH 7.0. The sensor response remained almost constant between pH 7.0 and 8.0. Phosphate buffer solution at pH 7.0 was therefore employed for the stripping measurements.

After choosing the electrolyte pH, Fig. 2b presents the influence of the buffer solution on the analytical signal obtained with the sensor for copper. The sensor response was verified in four different buffer solutions (Tris, PIPES, HEPES and Phosphate) with concentrations of 0.1 mol L^{-1} and indicated that phosphate buffer solution gives the best responses. In this sense, the phosphate buffer solution was chosen for further experiments.

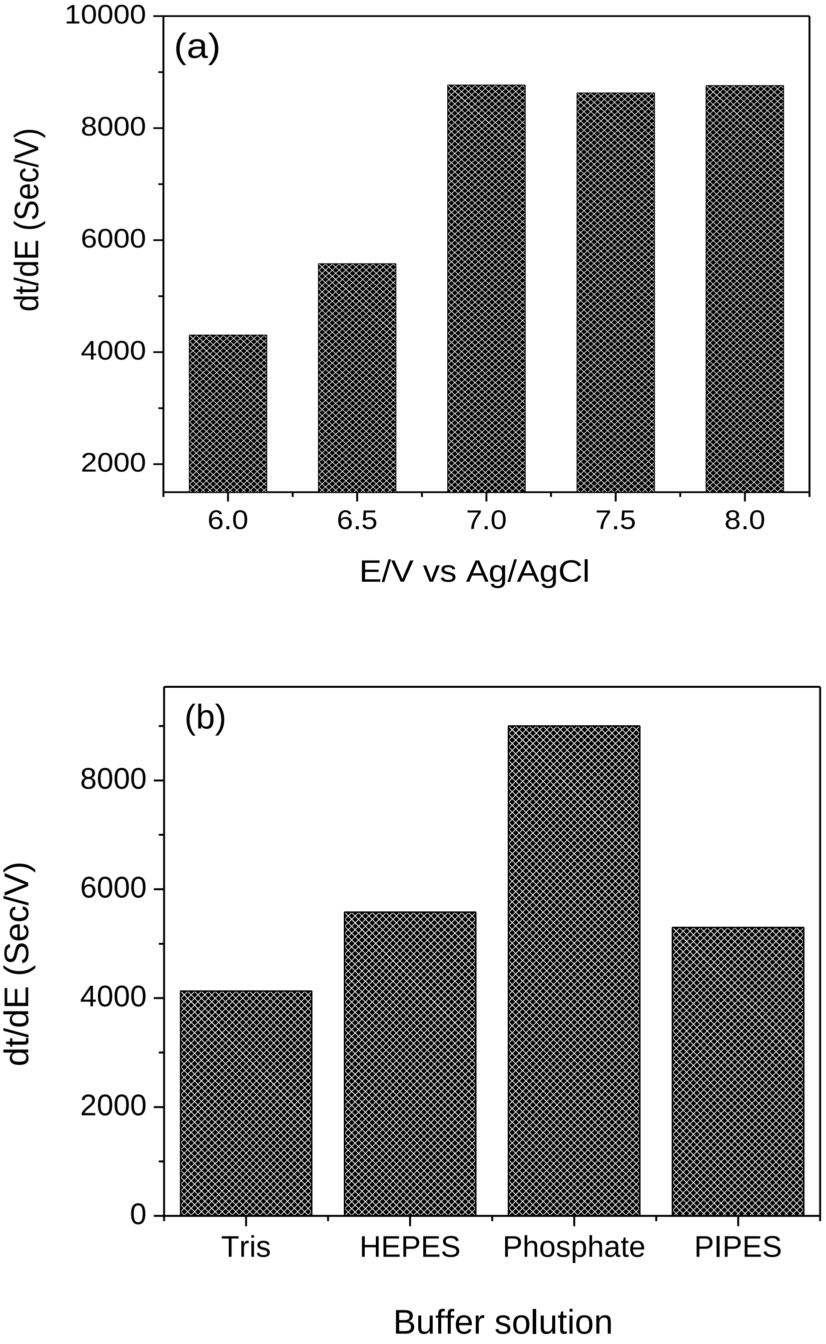

Figure 2. Influence of pH (a) and buffer solution (b) on the analytical signal for Cu(II). The experiment was performed in a medium containing 0.1 mol/L phosphate buffer solution in the presence of 1.0 μmol/L Cu(II). [MWCNT] = 3.0 mg/mL; [H_2TSPP] = 2.0 mg/mL.

After choosing the electrolyte, the influence of phosphate buffer solution concentration was investigated in the range from 0.0025 to 0.2 mol/L. The potentiometric signal increased as the buffer solution concentration was increased up to 0.1 mol/L. At concentrations lower than 0.1 mol/L, the analytical signal decreased rapidly, because the ionic strength was insufficient to conduct the electric current during the deposition step. The analytical signal was not significantly altered for buffer concentrations higher than 0.1 mol/L. A phosphate buffer concentration of 0.1 mol/L was therefore established as the best value for use in the subsequent experiments.

3.4. Effect of the deposition potential and deposition time

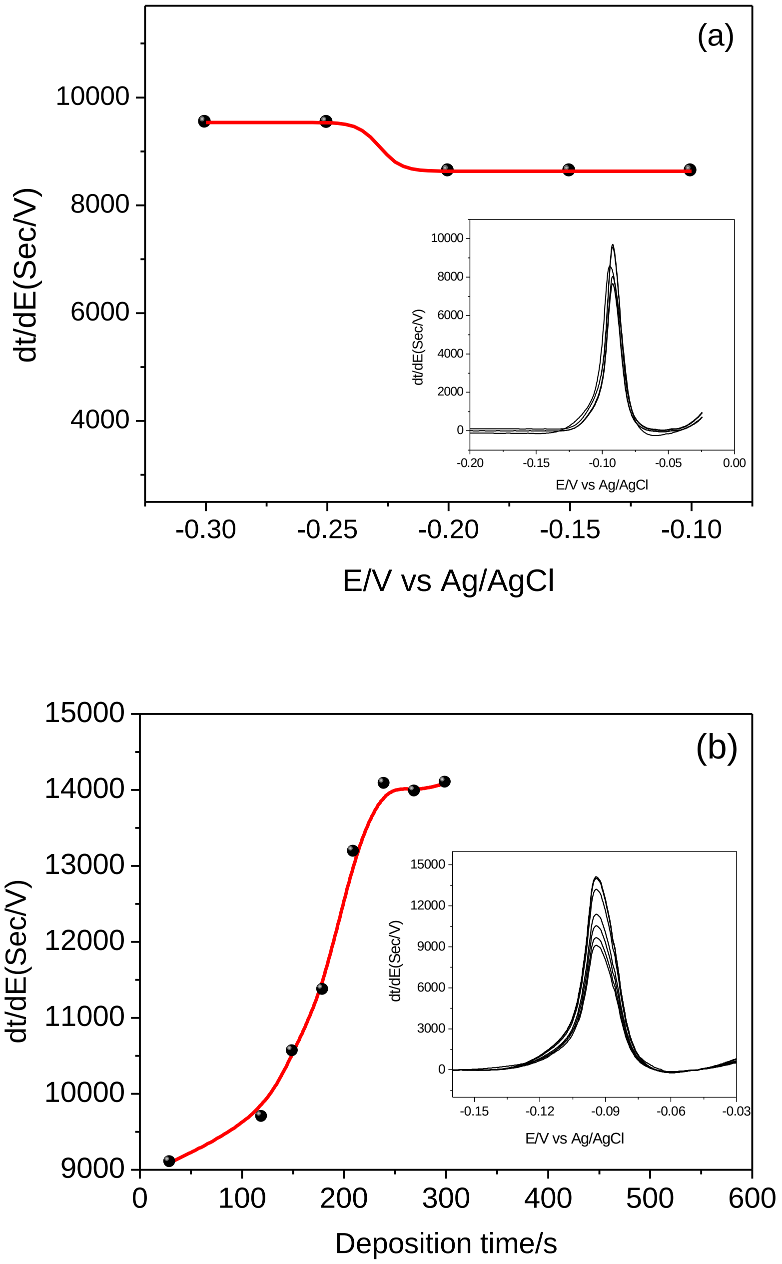

Figure 3. Influence of deposition potential on the potentiometric response for Cu(II) (a), and influence of electrodeposition time on the potentiometric response for Cu(II) (b). The experiment was performed in a medium containing 0.1 mol/L phosphate buffer (pH 7.0) in the presence of 1.0 μmol/L Cu(II). [MWCNT] = 3.0 mg/mL; [H_2TSPP] = 2.0 mg/mL.

It is well known that in stripping analysis an adequate deposition potential is essential to achieve good sensitivity and selectivity. The influence of this parameter on the potentiometric response is shown in Fig. 3(a). The potential was varied from –0.30 to –0.10 V, and it was observed that when a deposition potential more negative than –0.25 V was employed, there was a significant decrease in the response to Cu(II) ions. The dt/dE signal was maximum and constant from –0.25 V to –0.30 V, so a deposition potential of –0.25 V was therefore selected.

The deposition time must be carefully controlled since this parameter can significantly affect the sensitivity of the determination. Figure 3(b) shows a plot of potentiometric response against deposition time, for times varying from 30 to 300 s.

The best result was obtained for a deposition time of 240 s, while use of times longer than 240 s resulted in a constant analytical signal, presumably due to saturation of the electrode surface. An optimum deposition time of 240 s was therefore selected. This value is either similar to [13] or smaller than [32, 41] values that have been reported previously in the literature.

3.5. Analytical characterization

After optimizing the experimental conditions, an analytical curve for the sensor was prepared from stripping potentiograms obtained for different concentrations of Cu(II) in 0.1 mol/L phosphate buffer at pH 7.0. The proposed sensor showed a linear response in the concentration range from 5 to 1600 nmol/L (Fig. 4), described by the following equation:

dt/dE (Sec/V) = 159.560 (±65.814) + 11.442 (±0.087) [Cu(II)] (nmol/L) (1)

The correlation coefficient obtained was 0.9998 (for n = 10). A detection limit (DL) of 1.0 nmol/L Cu(II) was determined according to the IUPAC recommendations [34].

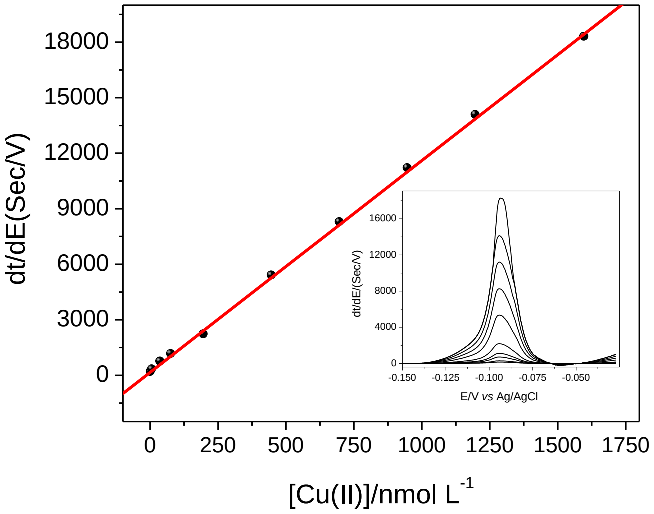

Figure 4. Calibration plot for Cu(II) determination in phosphate buffer solution at pH 7.0 for the concentration range between 5 nmol/L and 1.6 μmol/L. Data points (from left to right) for Cu(II) concentrations of 5, 10, 40, 80, 200, 450, 700, 950, 1200 and 1600 nmol/L (Inset: potenciograms of the calibration curve). Deposition time = 240 s; deposition potential = -0.25 V *vs.* Ag/AgCl.

Table 2 provides the analytical parameters reported for several Cu(II) sensors using different modifiers, from which it can be seen that the H_2TSPP/MWCNT/BPPG electrode is a feasible alternative compared to other techniques.

Table 2. Comparison of the figures of merit for the H_2TSPP/MWCNT/BPPG electrode developed in the present work, and for other electrodes described in the literature.

Modifier	Electrode	Method	Detection Limit (µmol/L)	Linear Ranger (µmol/L)	Accumulation time (s)	Ref.
CTS-ECH[a]	MCNP[b]	LSASV[c]	0.01	0.08-16	300	20
PCHA[d]	MCP[e]	DPASV[f]	0.00005	0.01 to 1	600	21
Calix[4]arene	MCP	DPASV	1.1	0.05-0.16	600	22
2-Aminothiazole	MCP	DPASV	0.031	0.08- 2.5	1200	23
Alirazin red S - $K_2S_2O_8$	CP[g]	SV[h]	0.0002	0.0008-0.03	180	24
Mercury film	MCP	DPASV	0.001	0.001-10	120	25
SBL-MO[i]	MCP	ASV[j]	0.00018	0.00034-0.33	600	26
Mercury film	GCE	PSA[k]	-	0.08-15.75	300	27
DHB-DA[l]	CPE[m]	Amperometry	0.04	0.05-0.1	-	36
DPNSG[n]	MCP	POT[o]	0.08	0.1- 10000	-	37
PYTT/GNPs[p]	CPE	Amperometry	0.001	0.004-70000	-	38
DPTA[q]	CPE	POT	-	9.8-100000	-	39
CTS[r]	CPE	ASV	0.055	0.05- 14	180	40
L^1 and L^2	CPE	POT	6.31 and 15.85	10-10.000	-	41
H_2TSPP/MWCNT[s]	BPPG[t]	PSA	0.001	0.005-1.60	240	The present work

[a]CTS-ECH: chitosan crosslinked with epichloridrin; [b]MCNPD: modified carbon nanotube paste; [c]LSASV: linear scan anodic stripping voltammetry; [d]PCHA: N-phenylcinnamohydroxamic acid;. [e]MCP: modified carbon paste; [f]DPASV: differential pulse anodic stripping voltammetry; [g]CP: Carbon paste; [h]SV: Stripping voltametric; [i]SBL-MO: *Schiff base ligand-Metallic Oxide;* [j]*ASV: Anodic Stripping Voltammetry;* [k]*PSA: Potentiometric Stripping Analysis;* [l]DHB-DA: bis(2, 4-dihydroxybenzyliden)-1,6-diaminohexane; [m]CPE: Carbon paste electrode; [n]DPNSG: nanoporous silica gel with dipyridyl group; [o]POT: Potentiometry; [p]PYTT/GNPs: [5-(pyridin-2-ylmethyleneamino)-1,3,4-thiadiazole-2-thiol/gold nanoparticles; [q]DPTA: Dimethyl 4, 4′ (o-phenylene) 2 bis(3-thioallophanate); [r]CTS: chitosan microspheres; [s]H_2TSPP/MWCNT: 4-[10,15,20-tris(4-sulfophenyl)-21,22-dihydroporphyrin-5-yl] benzenesulfonic acid /multiwalled carbon nanotubes; [t]BPPG: basal plane pyrolytic graphite; L^1 and L^2: thiohydrazone and thiosemicarbazone.

3.6. Sensor application using gasoline samples

It is important to mention that in Brazil gasoline contains about 20 to 25% v/v of anhydrous ethanol, while hydrated ethanol is also used alone as an automotive fuel. The blending of gasoline and ethanol can increase the concentrations of certain metals such as Cu, Fe, Ni, and Zn, due to the procedures used for production, storage, and transportation. According to the Brazilian national petroleum agency (ANP) [35], the concentration limits for Cu are different for anhydrous and hydrated ethanol. In anhydrous fuel ethanol, the maximum permissible Cu concentration is 0.07 mg/kg (1.1 µmol/L).

The proposed sensor was applied in the determination of Cu(II) in four commercial gasoline samples containing different ethanol percentages (Table 3). The samples were collected in glass bottles, kept at 4 °C during transport to the laboratory, and immediately prepared for analysis. All measurements were made in triplicate. The concentrations of Cu(II), calculated using the standard additions method, were compared with the values obtained with the Graphite Furnace Atomic Absorption Spectrometry (GF-AAS) method, using the paired t-test. The results were statistically equal, at a confidence level of 95%.

Table 3. Determination of Cu(II) in four gasoline samples (n=3) by the proposed procedure and by the comparative GF-AAS method.

Samples	Proposed method (µmol/L)	GFAAS method (µmol/L)
Gasoline A + 15 % AEAF	0.13 (+ 0.01)	0.12 (+ 0.02)
Gasoline B + 15 % AEAF	0.16 (+ 0.05)	0.15 (+ 0.05)
Gasoline C + 25 % AEAF	0.35 (+ 0.03)	0.34 (+ 0.04)
Gasoline D + 25 % AEAF	0.30 (+ 0.02)	0.28 (+ 0.08)

AEAF: Anhydrous Ethyl Alcohol Fuel, Brazil

3.7. Recovery tests for the proposed method

Table 4. Recovery values of Cu(II) obtained for four gasoline samples (n = 3).

Samples	Added (µmol/L)	Expected (µmol/L)	Found (µmol/L)	Percent. recovery (%)
Gasoline A + 15 % AEAF	2.00	2.13	2.10 (± 0.03)	98.5 (± 0.1)
	20.00	20.13	20.13 (± 0.01)	100 (± 0.1)
Gasoline B + 15 % AEAF	2.00	2.16	2.14 (± 0.02)	99.1 (± 0.1)
	20.00	20.16	20.10 (± 0.01)	99.7 (± 0.2)
Gasoline C + 25 % AEAF	2.00	2.35	2.30 (± 0.02)	97.8 (± 0.2)
	20.00	20.35	20.34 (± 0.01)	99.6 (± 0.1)
Gasoline D + 25 % AEAF	2.00	2.30	2.29 (± 0.01)	99.6 (± 0.2)
	20.00	20.30	20.18 (± 0.03)	99.4 (± 0.1)

AEAF: Anhydrous Ethyl Alcohol Fuel, Brazil

As an additional check on the accuracy of the developed method, and for evaluation of matrix interferences, analytical recovery experiments were performed by adding known amounts of Cu(II) to four samples of gasoline. The percentage recovery values were calculated by comparing the concentrations obtained for the samples with the added concentrations (Table 4). It can be clearly observed that there was no influence of the matrices of the samples evaluated, demonstrating that the modified electrode offers a sensitive and stable alternative for the determination of Cu(II) in gasoline samples.

3.8. Interference studies

Potential interferences were evaluated considering other metal ions that are commonly found in fuels. The selectivity of the H_2TSPP/MWCNT/BPPG electrode was determined by performing PSA measurements in 1.0 µmol/L Cu(II) solution spiked with 10-fold excesses of Ni(II), Zn(II), Al(III), Co(II), Mg(II), Pb(II), Cd(II), Sn (IV), Bi (III), and Sb (IV). As can be verified, this study reveal that the developed sensor can tolerate a high concentration of interfering ions and, therefore, can be stated as selective over the commonly present interfering ions and therefore did not affect the determination of Cu(II) using the H_2TSPP/MWCNT/BPPG electrode (Table 5).

Table 5. Effect of foreign ions on the copper determination (1.0 µmol L^{-1}).

Ion added	Mole ratio 1:0.5	Mole ratio 1:1	Mole ratio 1:2
Ni(II)	99 (± 2)	98 (± 2)	102 (± 1)
Zn(II)	98 (± 2)	99 (± 1)	101 (± 1)
Al(III)	98 (± 1)	99 (± 1)	100 (± 2)
Co(II)	99 (± 2)	99 (± 2)	101 (± 1)
Mg(II)	98 (± 3)	100 (± 2)	100 (± 3)
Pb(II)	99 (± 2)	98 (± 4)	102 (± 2)
Cd(II)	99 (± 1)	99 (± 2)	100 (± 3)
Sn (IV)	100 (± 2)	100 (± 1)	101 (± 2)
Bi (III)	99 (± 3)	100 (± 2)	101 (± 2)
Sb (IV)	98(± 2)	99 (± 2)	99 (± 3)

Mole ratio=[Cu(II)]:[interfering ion]. Values ±S.D. for four measurements. Relative response (%) obtained with the sensor.

3.9. Stability of the proposed sensor

The stability of the H_2TSPP/MWCNT/BPPG electrode was determined by performing successive potentiometric measurements using 1.0 µmol L^{-1} Cu(II) in 0.1 mol L^{-1} phosphate buffer solution (pH 7.0). No change was observed in the potentiometric profile of the modified electrode, even after 100 measurements. When the electrode was stored at room temperature, no significant change in the response was observed for at least one month.

The modified electrode showed good analytical repeatability, with a relative standard deviation (RSD) of 3% for ten determinations of 1.0 μmol/L Cu(II). Additionally, a series of ten modified electrodes prepared in the same manner were tested using phosphate buffer (pH 7.0) containing 1.0 μmol/L Cu(II), resulting in a relative standard deviation of less than 5.0%. The good stability and repeatability of the H_2TSPP/MWCNT/BPPG electrode was probably due to the ability of MWCNT to fix the H_2TSPP molecules on the electrode surface in a stable and reproducible way.

4. CONCLUSIONS

This work showed that a BPPG electrode modified with H_2TSPP adsorbed onto MWCNT is a feasible alternative for the analysis of Cu(II) in fuel samples by PSA. Benefits of the method include simplicity, speed of electrode preparation, and low cost compared to other techniques. The modified electrode offers good sensitivity, specificity, linear range, and precision. Unlike the majority of PSA methods, in which a mercury film is first placed onto the working electrode prior to the analytical measurement, this treatment is not required for the proposed electrode. These advantages make the new electrode an attractive alternative for determination of Cu(II) in gasoline samples.

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