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Copper(II) Trace Determination in Aqueous/Ethanolic Medium Using an Ionic Imprinted Hybrid

Paulo Cesar Mendes Villis[1,*], *Wolia Costa Gomes*[1], *Fabricio Brito Silva*[1], *Diego Rosa dos Santos*[1], *Gustavo Silveira*[2], *Andréia de Morais*[2], *Rodrigo Vieira Blasques*[3], *Gilvanda Silva Nunes*[3], *Fábio Luiz Pissetti*[2], *Yoshitaka Gushikem*[4] *and Alzira Maria Serpa Lucho*[2]

[1] Laboratory of Materials and Electrochemistry– LME, University of CEUMA - UNICEUMA, 65.065-470, São Luís, MA, Brazil
[2] Institute of Chemistry, Federal University of Alfenas – UNIFAL-MG, 37130-000, Alfenas, MG, Brazil
[3] Nucleus of Pesticide Residue Analysis- NARP, Federal University of Maranhão – UFMA, 65.080-040, São Luís, MA, Brazil
[4] Institute of Chemistry, State University of Campinas - UNICAMP, Inorganic Chemistry, Campinas, SP, Brazil
[*]E-mail: paulo.villis@ceuma.br

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In this work, an ionic imprinted hybrid material organically modified with 3-(2-imidazolin-1-yl)propyltriethoxysilane with copper(II) as template was prepared and structurally characterized, using elemental analysis, X-ray powder diffraction (XRD), thermogravimetric analysis, infrared spectroscopy and solid state ^{13}C and ^{29}Si nuclear magnetic resonance (NMR). Experiments with cyclic voltammetry and differential pulse anodic stripping voltammetry (DPASV) showed that the electrode prepared was stable over 100 cycles, with high reproducibility. Copper(II) ions could be quantified in water/Brazilian sugar cane spirit (cachaça). Calibration curve for detection was obtained from 5.98 – 201.42 $\mu g\ L^{-1}$ of copper(II) concentration, with a correlation coefficient of $R^2 = 0.995$; $n = 12$. The detection limit obtained was (LOD) as 0.74 $\mu g\ L^{-1}$ and the limit of quantification (LOQ) was of 2.48 $\mu g\ L^{-1}$ in water/cachaça. The interference studies in presence of Na(I), Fe(II), Pb(II), Ni(II), and Zn(II) do not significantly affected the peak currents, with high recovery of copper(II) in the range 91.20 % to 109.11 % in ethanolic medium and 89.54 % to 116.78% in aqueous medium. The DPASV technique was used to determine copper(II) in commercial samples in aqueous/ethanolic medium such as tap water, cachaça and ethanol fuel and the results were compared with the values found by flame atomic absorption spectrometry (FAAS).

Keywords: hybrid material; imidazole; copper(II); tap water; cachaça; ethanol fuel

1. INTRODUCTION

Silica allows for the immobilization of different organic functional groups on its surface, which has led to the development of several materials with different characteristics from those observed in the chemical precursors, such as stability and rigidity [1,2]. These organic-inorganic hybrid materials combine the mechanical, thermal, and chemical stability and rigidity of silica with the chemical properties of organofunctional groups [3–5].

Organic-inorganic hybrid materials are promising candidates for a broad range of applications, such as biomedical applications [6,7], catalysis [7,8], environmental monitoring [9], chemical sensors [10–14], chromatography [15,16], smart biochip devices [17], intelligent materials [18] and in adsorption processes [19–22].

Organic-inorganic hybrid materials containing azo groups, thiols, and oxygen functionalities have been quite useful for pre-concentration of metal ions. Organofunctionalized silica with 2-benzothiazolethiol was used in the preparation of modified electrodes for the determination of Pb(II), Cu(II), Hg(II) [23], and Cd(II) [23,24] in water samples and copper(II) in ethanol fuel [23] by anodic stripping voltammetry. Dithioacetal derivatives with different *para*-substituents were synthesized and chemically immobilized on the surface of silica gel and used as new selective solid phase extractors for Hg(II) from aqueous natural samples [25]. Oliveira et al. [26] modified silica gel firstly with aminepropyltrimethoxisilane and subsequently with thioglycolic acid for removing Cu ion from aqueous/ethanolic solutions. Ghiaci, Rezaei and Arshadi [27] developed a carbon paste electrode modified with a Schiff base ligand covalently linked onto the SiO_2-Al_2O_3 mixed-oxide for anodic stripping voltammetric determination of copper(II). The quantitative analysis of Cu(II) and Ni(II) with 2-aminothiazole organofunctionalized silica was carried out by the Stradiotto group [28,29], using a solid paraffin-based carbon paste electrode modified in ethanol fuel by *DPASV*, resulting in a detection limit of about 10^{-9} mol L^{-1}. These studies confirmed the statement [26], that the modified silica containing basic center groups has a behavior adsorbing copper ions and can be used for extracting and quantifying metallic cations in aqueous and non-aqueous solutions.

The synthesis of organic-inorganic hybrid materials as a template using the analyte of interest has increased because of the higher sensitivity and selectivity provided by this method [30]. The synthesis of the material consists essentially of a polymerization reaction in which the formation of a three-dimensional structure from the monomer is guided by the template of interest. After the synthesis, the template is removed and the formed three-dimensional structure is able to recognize the specific analyte template in a mixture of similar chemical compounds [31]. Prasad and Jauhari [32] have reported for the first time, the development of a modified pencil graphite electrode using imprinted polymer network for the simultaneous analysis of a binary mixture of Cd(II) and Cu(II) ions in real samples.

Recently, the growing importance of biofuels, for instances, of the bioethanol sector in the world energy matrix [33–35], corroborates the idea of the development of new analytical methods for quantifying metals in fuels. Atomic absorption spectrometry has been historically well-established [36,37], but there is also great potential for voltammetry techniques [23,28,29,38,39], because of some advantageous features such as high sensitivity, instrumental simplicity, moderate cost and portability

[40]. The presence of some metal ions in ethanol fuel can induce corrosion, undesirable metal deposition in parts of the engine in contact with the liquid and poor fuel performance, due the oxidative decomposition reactions [41,42]. These problems demonstrate that a careful quality control is required for this type of product.

This work describes, the first report of the synthesis of a silica functionalized with 3-(2-imidazoline-1-yl)propyltriethoxysilane (imidazole group), with copper(II) ions used as a template for preparation of a carbon paste electrode. This electrode was used to determine these ions in aqueous/ethanolic medium by *DPASV* in commercial samples such as tap water, cachaça and ethanol fuel. Cachaça is one of the most popular alcoholic beverages consumed in the nation and one product made in Brazil only [43,44]. The choice of Cu(II) is justified by its importance in biological systems, environmental and process monitoring and control in natural waters and wastewater, drinking water and ethanol fuel [45–50].

2. MATERIAL AND METHODS

2.1 Reagents and solutions

The working aqueous/ethanolic solutions were prepared with distilled-deionized water (18.0 MΩ at 298 K). A 0.50 mol L^{-1} potassium chloride (Merck) electrolyte solution was used for most experiments.

A standard 1000 mg L^{-1} solution (Sigma-Aldrich, 1000 mg/L Cu in nitric acid) was used for the preparation of the working copper solutions (1.0 mmol L^{-1} for electrochemical studies; 0.5, 1.0, 1.5 μgL^{-1} and 0.5, 1.0, 2.0 μgL^{-1} for aqueous medium and ethanolic medium, respectively). Stock solutions of sodium(I), iron(II), lead(II), nickel(II) and zinc(II) ions were prepared by dilution of analytical purity grade chloride and fluoride salts. Nitric acid from Merck was used to prepare the supporting electrolyte solution. Methanol (MeOH) 99.8 % (Vetec), Ethanol absolute (EtOH) PA > 99.5 % (Sigma-Aldrich), HCl > 37 %, $CH_3COONa.3H_2O$ (Merck), silica gel 60 (Sigma-Aldrich, particle size 0.2 - 0.5 mm; 35 – 70 mesh), 3-(2-imidazolin-1-yl)propyltriethoxysilane (Acros Organics), graphite (powder, <150 μm, 99.99 % Aldrich), mineral oil (Nujol, Aldrich) and $CuCl_2$ (99% Sigma-Aldrich) were used as received. Buffer solutions (pH 3.0 to 8.0) were prepared by mixing appropriate volumes from 1.0 mol L^{-1} hydrochloric acid solution and 1.0 mol L^{-1} sodium acetate trihydrate solution.

Other buffer solutions were prepared from Na_2HPO_4 and KH_2PO_4 (*Sörensen's* phosphate, 0.50 mol L^{-1} KCl, pH 5.28). The pH values of the resulting solutions were verified by a pH meter.

Tap water samples were collected from the research laboratory. Brazilian sugar cane spirit (known as cachaça) samples were purchased at the local market in the South of the State of Minas Gerais. The commercial ethanol fuel samples were acquired from different local gas stations in Alfenas, MG and São Luís, MA.

2.2 Instrumentation

The elemental analyses were carried out in triplicate on a Perkin–Elmer Model 2400 CHNS/O Analyzer.

X-ray powder diffraction (XRD) was carried out on a PANalytical X'Pert Pro X-ray diffractometer with Cu Kα radiation (λ=1.54178 Å).

The thermogravimetric analyses of the samples were carried out with a mass of approximately 10.0 mg with a heating rate of 10 K min^{-1} in a temperature range of 298 to 1373 K under a nitrogen atmosphere. The measurements were made on a TA Instruments thermoanalyzer Model SDT Q600.

Infrared spectra were measured using a Shimadzu IR Prestige-21 FTIR spectrometer at room temperature (298 K) in the range of 4000 to 400 cm^{-1}, with a resolution of 2 cm^{-1} and 20 cumulative scans. Powder samples were prepared by dispersing the samples in KBr and compressing them to form disks.

^{29}Si and ^{13}C high power proton decoupling (HPDEC) – magic angle spinning (MAS) NMR spectra were obtained at 298 K on a Bruker AC 300P spectrometer operating at 59.6 MHz for ^{29}Si and 75.5 MHz for ^{13}C. Tetramethylsilane (TMS), $Si(CH_3)_4$, was used as an external reference for the chemical shifts.

2.3 Electrochemical measurements, apparatus, and procedures

The electrochemical behavior of the hybrid material was characterized by cyclic voltammetry. The carbon paste working electrode containing the hybrid material was named SiO_2/SiIm.

The Autolab PGSTAT 302N potentiostat-galvanostat apparatus associated with the GPES electrochemical analysis system, in conjunction with a three-electrode system, was used for the voltammetric measurements. An electrochemical cell with 0.50 mol L^{-1} KCl solution as the supporting electrolyte using a saturated calomel electrode (CSE) reference electrode, a platinum wire counter electrode, and the carbon paste as the working electrode. The voltammograms of copper(II) ions were obtained by cyclic voltammetry (scan rate: 20 mV s^{-1}) between − 1.00 and − 1.40 V or DPASV (scan rate: 20 mV s^{-1}; pulse amplitude: 50 mV; pre-concentration times: 600 and 720 s; and, equilibration time: 5 s) between − 0.8 and + 0.8 V.

The measurement of pH was performed with a Metrohm (model 827) pH meter equipped with a combined glass electrode with Negative Temperature Coefficient semiconductor (NTC) and platinum resistance thermometer (Pt1000) temperature sensor. The Ag/AgCl reference electrode was filled with 3.0 mol L^{-1} NaCl.

FAAS experiments were carried out using a spectrometer (Shimadzu, model AA-7000) equipped with a cathode lamp, air-acetylene flame, and with a wavelength of 324.8 nm.

The standard addition method was applied in triplicate for the quantification of copper(II) by FAAS. The voltammograms of copper(II) ions were obtained by DPASV (scan rate: 20 mV s^{-1}; pulse amplitude: 50 mV; pre-concentration times: 600 and 720 s; and, equilibration time: 5 s) between − 0.4 and + 0.6 V (see Table S2 of the supplementary material).

2.4 Synthesis of Copper(II) - imprinted imidazole silica

The method for functionalization of silica gel is illustrated in Scheme 1. In the preparation, the reaction between the silylating agent 3-(2-imidazolin-1-yl)propyltriethoxysilane and the silanol groups on the silica surface is carried out in a molar ratio of 1:4.5 in an ethanolic medium, according to the imprinted ionic procedures described in literature [15].

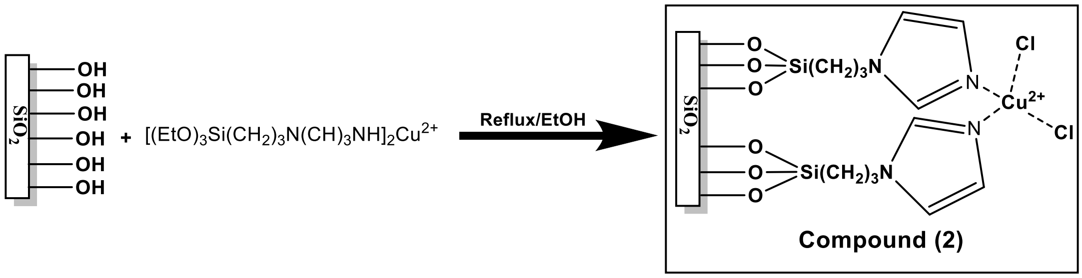
Silica gel 60 (0.2–0.5 mm) was activated using 5.0 g, refluxed for 8 hours in HCl 6.0 mol L^{-1}. Then, the silica was vacuum (–630 mm Hg) filtered and maintained in an oven for 20 hours at 353.15 K.

5.0 g of this silica was immersed in 20.0 mL of ethanol. The mixture was refluxed under nitrogen atmosphere for 2 hours and forming as SiO_2OH. A solution containing 5.20 mL of $(CH_3O)_3Si(CH_2)_3N(CH)_3N$ (19.04 mmol) in 10.0 mL of ethanol was prepared, then, under constant stirring, 0.32 g (2.38 mmol) of $CuCl_2$ was added dissolved in 20.0 mL ethanol at 298 K. The resulting product of this reaction was designated as compound (1), represented by Equation (1):

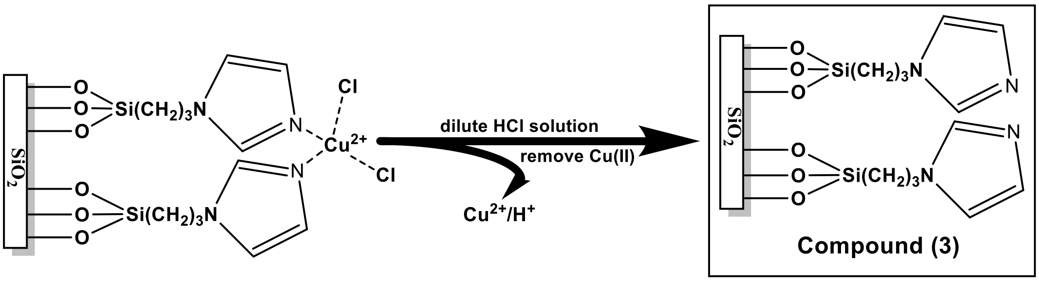
$$2\,(EtO)_3Si(CH_2)_3N(CH)_3N \;+\; CuCl_2 \xrightarrow{EtOH} \boxed{\begin{array}{c}[(EtO)_3Si(CH_2)_3N(CH)_3N]_2Cu\\ \textbf{Compound (1)}\end{array}} \;+\; 2\,Cl^- \qquad \text{(Eq. 1)}$$

Compound (1) was stirred with SiO_2OH for 20 minutes at a temperature of 353.15 K. Then, 250 μL of water was added, and the mixture was heated at the reflux temperature of the solvent for approximately 6 hours. The solid obtained was separated from the solution by filtration, washed with ethanol and water, and then dried in an oven at 353.15 K for 24 hours. The formation of a blue solid product was observed compound (2) in Scheme 1.

This blue solid product was washed in 0.50 mol L^{-1} HCl to remove the copper followed by neutralization with a solution of 10 % $CH_3COONa.3H_2O$ and then washing with ethanol/water (1:1; v/v) in a *Soxhlet* extractor for 4 hours. Finally, the yellow solid product was pulverized in a porcelain mortar, washed with water, then ethanol, then 0.1 mol L^{-1} HNO_3 and again with water, dried under vacuum (– 630 mm Hg, 353.15 K, 6 hours) and stored. The product is hereinafter referred to as SiO_2/SiIm. The formation of a yellow solid product was observed compound (3) in Scheme 1 and shown a proposed model for the template.



Compound (2)



Scheme 1. Synthesis route of the hybrid material

3. RESULTS AND DISCUSSION

3.1 Characterization of the material

Elemental analysis results indicate that the porous silica chemically modified with the imidazole moiety contains 5.95 % nitrogen and 16.06 % carbon. Based on these values, the hybrid material SiO_2/SiIm contains 5.39 m mol g^{-1} and 13.37 m mol g^{-1} of nitrogen and carbon, respectively. These results confirm the presence of organic groups in the functionalized silica.

X-ray powder diffraction studies confirmed the amorphous nature of the hybrid material SiO_2/SiIm. The diffractogram (not shown) indicate a vitreous halo between 20° and 30° (2θ), typical of non-crystalline silica matrices.

Thermogravimetric curves are usually used to determine thermal stability and to confirm the amount of immobilized compounds [26]. The result for SiO_2/SiIm (see Figure S1 of the supplementary material) indicate the existence of three different weight losses. The first loss, visible in the temperature range 41.26 – 80.64 °C (was comprised between 3.58 and 16.26 %), was associated with evaporation of solvent, specifically ethanol and/or water. The second stage, produced between 80.64 and 310.99 °C (25.22 %) can be associated with the loss of the organic groups attached to the silica surface [51]. Finally, the third stage produced between 407.92 and 439.48 °C, ascribed to the dehydration of silanol groups present in SiO_2 networks, with weight losses between 3.06 and 0.01 %.

In general, the observed weight loss in the range 41.26 - 150 °C is explained by evaporation of adsorbed or attached water on the surface, whereas the higher temperature range is related to the degradation of imidazole groups. Thermogravimetric events reflecting the removal of 3-*n*-propylimidazole groups partially overlap in the range of 300 – 650 °C. Thus, a more detailed analysis of these profiles is difficult.

The IR spectrum and assignments of the characteristic absorption bands of the functional groups are shown in detail in Fig. S2 on the supplementary material. The IR spectrum of the hybrid material includes typical bands associated with the inorganic backbone, such as a large band between 3400 and 3200 cm^{-1}, assigned to the O-H stretching frequency of the silanol groups bonded to the inorganic structure, as well as to the adsorbed water molecules [26,52,53]. The vibrational band at 469 cm^{-1} in the spectrum arises from δ(O-Si-O). Two vibrational bands, characteristic of ν_{as}(Si-O-Si) and ν_{as}(Si-C) of the silanol groups, appear in the regions of 1100 and 994 cm^{-1}. The expected peak ν_s and ν_{as}(N-H) stretching frequencies should be superposed by the broad silanol-water stretching frequencies that appeared in the 3275 – 3170 cm^{-1} region. Peaks in the region between 2946 and 2881 cm^{-1} are related to the C-H stretches of tetrahedral carbon, and the two peaks at 1409 and 1668 cm^{-1} are related to the ν_s(C-N) and ν_s(C=N) of the imidazole molecule.

The hybrid material was characterized by solid-state ^{13}C and ^{29}Si NMR. The solid state ^{13}C NMR spectra of SiO_2/SiIm is shown in Fig. S3 on the supplementary material, along with the idealized structure of the functional group attached to the chain, with numerated carbon atoms. The spectrum shows two signals at 165.9 and 80.3 ppm, which can be associated with the C^4 and C^5 of the imidazole group attached to the chain. The chemical shifts at 9.7, 22.9, and 48.1 ppm are attributed to carbon C^1, C^2 and C^3 of the methylene groups [54–57].

The solid state ^{29}Si NMR spectrum of SiO_2/SiIm is shown in Fig. S4 on the supplementary material. The spectrum shows a region with two peaks around – 99.2 and – 109.1 ppm, corresponding to Q^3 single silanol, $(\equiv SiO)_3SiOH$, and Q^4 siloxane, $(\equiv SiO)_4Si$. The presence of two peaks related to the dislocation of T^2 and T^3 at – 57.2 and – 66.2 ppm confirms that the silane was attached to the silica [52,56–58]. These results show the incorporation of imidazole without degradation.

3.2 Electrochemical studies

3.2.1 Cyclic voltammetry (CV)

Initial investigations were made on the cyclic voltammetric behavior of SiO_2/SiIm by CV in 0.50 mol L^{-1} KCl solution over the range –1.00 V to –1.40 V (not shown) versus the saturated calomel electrode (SCE). A comparison between the hybrid material and the precursor for the preparation of this (silica gel) was obtained. The results indicates that a significant potential variation occurred, in comparison with carbon paste electrodes containing silica gel, displacing the peak potential to more negatives values from – 0.058 V to – 0.220 V, nearly 162.0 mV.

The cyclic voltammograms obtained at 298 K are shown in Fig. 1. These Fig. 1b shows a cathodic peak potential at – 0.55 V and no anodic peak potential. The observed cathodic peak can correspond to the reduction potential of amino groups. In the literature, potentials larger than 0.8 V versus the normal hydrogen electrode (NHE) indicate electrooxidation of amino groups [59]. However, two redox couples are observed in the presence of 1.0 mmol L^{-1} copper(II) ions (Fig. 1c), with peaks at (**i**) – 0.22, (**ii**) 0.16, (**iii**) 0.04, and (**iv**) – 0.55 V .

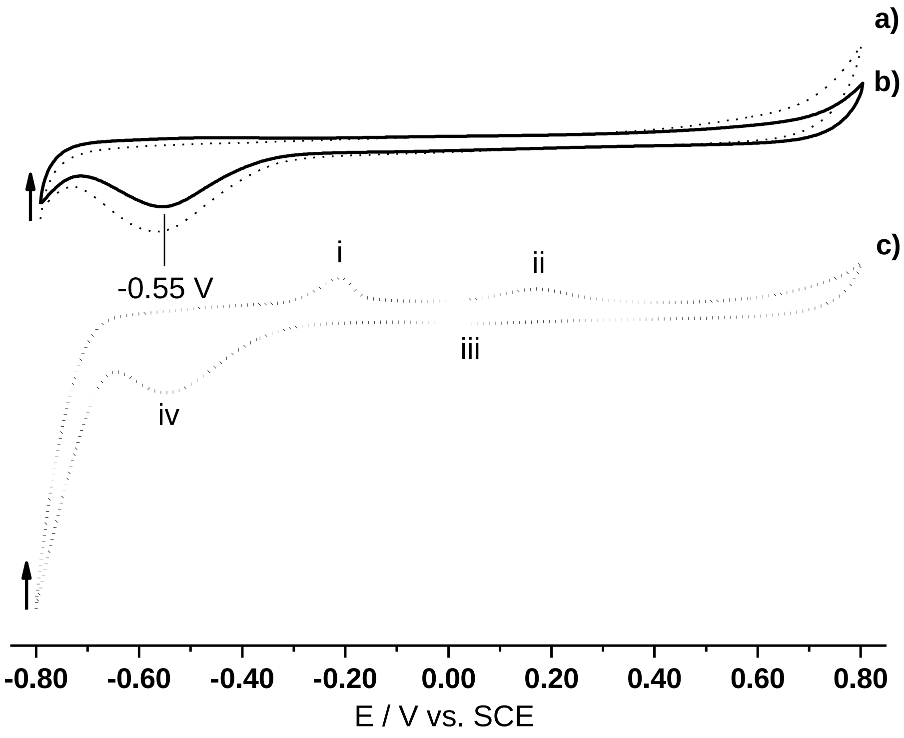


Figure 1. Cyclic voltammograms of SiO_2/SiIm obtained in 0.50 mol L^{-1} KCl at a potential scan rate of 20 mV s^{-1}. a) 1° scan, b) after 100° scan, and, c) in the presence of 1.0 mmol L^{-1} copper(II) ions

Peaks (**i**) and (**ii**) relate to the oxidation process of $Cu(0) \rightarrow Cu(II)$ and peaks (**iii**) and (**iv**) relate to the reduction process of $Cu(II) \rightarrow Cu(0)$ [23,39,46,60,61]. These peaks, (**i**), (**ii**), (**iii**) and (**iv**), can be assigned to the difference between of the coordination form of copper ions with the donor atoms (amine nitrogens) [62]. The stability of the SiO_2/SiIm was tested as a function of the number of cycles. The results show no significant change after 100 cycles and the best potential values, between – 0.80 and 0.80 V, reaching their stabilities only after 30 cycles (Fig. 1b).

The stripping voltammograms in the same electrode after a week were also recorded, and the maximum deviation obtained was 2.0 %. The results indicate that the SiO_2/SiIm electrode presents reproducibility and stability.

3.2.2 Differential pulse anodic stripping voltammetry (DPASV)

3.2.1 Optimization of the electroanalytical parameters and experimental conditions

The voltammetric behavior of SiO_2/SiIm was evaluated by DPASV in terms of the influence of stripping parameters such as electrode composition, the effect of pH, supporting electrolyte, accumulation potential (E_{red}), pre-concentration time (t_{pc}) and scan rate.

The influence of the composition of the working electrode on the voltammetric response of the SiO_2/SiIm was evaluated by DPASV of 1.0 mmol L^{-1} copper(II) in *Sörensen* buffer solution (0.50 mol L^{-1} KCl) and 0.01 mol L^{-1} nitric acid solution using the optimized conditions (see Table S1 and S2 of the supplementary material), with a t_{pc} of 600 s for the aqueous medium and 720 s for the ethanolic medium.

The presence of ethanol in the supporting electrolyte was studied at different ethanolic compositions (20 %, 40 %, 50 % and 60 % (v/v) water-ethanol solution). An interesting fact was observed in voltammograms performed in solutions containing different water-ethanol ratios. The presence of ethanol in the electrolyte promoted the shift of the current peak to more negative potentials, whereas the copper current peak moved to more positive potentials, compared to the corresponding signals obtained in aqueous medium [38]. The enhancement of the signals in the lower water-ethanol ratio solution was expected, since the higher ethanol proportion in the solution decreases the electrochemical signals of the copper ions. In compositions containing above 60 % ethanol (v/v), a decrease of the anodic current peak occurs, in which case a swelling of the carbon paste working electrode is observed.

The pH dependence of anodic peak potentials (E_p) and the influence of pH at the pre-concentration stage for SiO_2/SiIm electrodes were examined by cyclic voltammetry in the pH range 3.0 - 8.0, in a solution containing 1.0 mmol L^{-1} copper(II) added to 0.1 mol L^{-1} phosphate buffer solution. A maximum in the E_p peak was observed at values of pH near 5.0. Higher values of pH cause a decrease in the peak current, probably owing to partial or total hydrolysis of the metallic copper(II) ions, decreasing the copper(II) concentration, and, hence, the formation of complexed species between copper(II) and OH^- anions [45,63]. At values of pH lower than 4.0, quick degradation and swelling of the carbon paste occurred, in which there exists a competition between H^+ ions and copper(II) ions, causing a decrease in the amount of pre-concentrated copper(II) ions at the electrode surface. Therefore, a *Sörensen* buffer solution (0.50 mol L^{-1} KCl; pH 5.28) was selected for subsequent measurements in aqueous medium, and 0.01 mol L^{-1} nitric acid solution (60:40; water/ethanol) was selected for subsequent measurements in ethanolic medium.

Compared to other electrolytes (H_2SO_4, HCl, and perchloric acids), the nitric acid provided the best voltammetric signals for copper using a platinum electrode as the working electrode. Further voltammograms in ethanolic solutions were performed using 0.01 mol L^{-1} nitric acid solution (60:40; water/ethanol) as the electrolyte.

The effect of applied potential was studied for a 1.0 mmol L^{-1} copper(II) solution over the range − 0.4 V to − 0.6 V vs. SCE using a pre-concentration time of 60 to 1800 s. Under these conditions, it was observed that reduction potential values less negative than − 0.4 V *vs*. SCE produced an anodic stripping voltammetric peak with low intensity and, consequently, inappropriate for copper(II) determination. Accordingly, further investigations were made using an applied potential of − 0.55 V vs. SCE.

The effect of the reduction time on peak current values was also examined. Significant increases in the peak current values were observed until the reduction time reached 720 seconds. At higher reduction times, the peak current values were almost constant and did not improve further with increasing reduction time. Thus, in all subsequent experiments, a reduction time of 720 seconds was employed.

In Table S2 on the supplementary material, the optimized parameters for the working conditions for the determination of copper(II) ions in anodic stripping voltammetric measurements are presented.

3.2.2 Analytical curves, precision, detection limits

The obtained optimal conditions and parameters were used for the measurement of calibration curves. Analytical curves were constructed with t_{pc} = 600 s and 720 s, using DPASV with $E_{red} = -0.55$ V, with subsequent stripping step from − 0.4 to +0.6 V. No current peaks were observed in the potential range from − 0.4 to +0.6 V (vs. SCE) at the SiO_2/SiIm in the absence of copper(II). Fig. 2 and 3 present the differential pulse anodic stripping voltammograms obtained under the optimized DPASV conditions described in Table S1 and S2 on the supplementary material.

An analytical curve for copper(II) is presented in the inset in Fig. 2, defined from the peak current values for concentration in the range 38.10 – 604.18 $\mu g\ L^{-1}$ (according to Equation 2), and obeying the linear relationship:

$$j_p/\mu A\ cm^{-2} = 2.85 \times 10^{-6}\ (\pm 1.40 \times 10^{-7}) + 1.19631\ (\pm 2.05 \times 10^{-2})\ [copper(II)]\ (\mu g\ L^{-1}) \qquad (Eq.2)$$

with a linear correlation coefficient equal to 0.997 (n = 10). The LOD and LOQ, calculated from the standard deviation (σ) of a set of five measurements of the blank, and evaluated by the following equations: LOD = 3σ / analytical curve slope and LOQ = 10σ / analytical curve slope, are found to be 18.83 $\mu g\ L^{-1}$ and 62.78 $\mu g\ L^{-1}$, respectively. These values indicate that SiO_2/SiIm can be used for the determination of copper in samples of aqueous media [64].

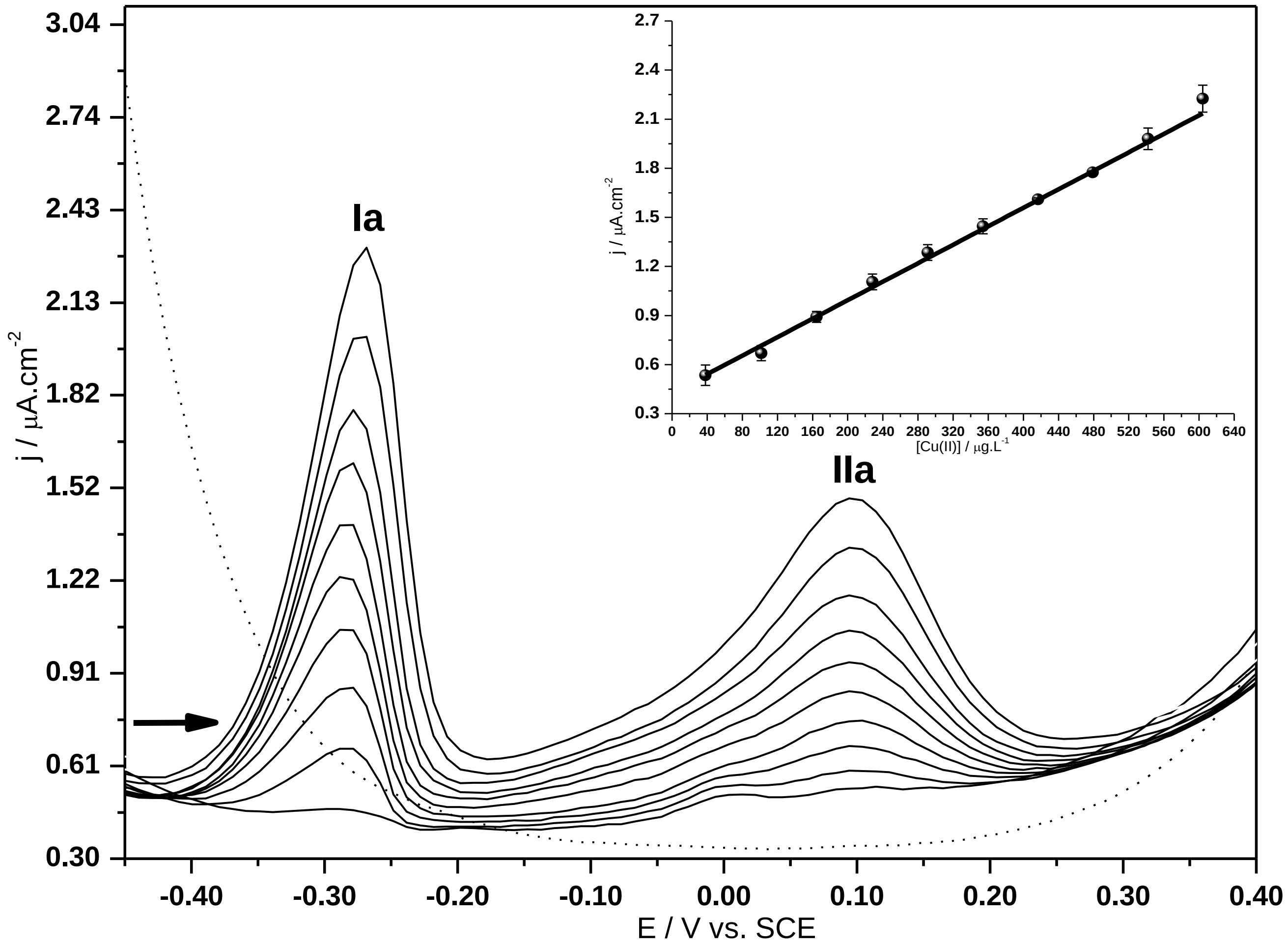


Figure 2. Differential pulse anodic stripping voltammograms of SiO_2/SiIm obtained in *Sörensen* buffer solution (0.50 mol L^{-1} KCl) and pH 5.28 in the presence of different concentrations of copper(II) ions. Conditions: ν = 20 mV s^{-1}, t_{pc} = 600 s, E_{red} = – 0.55 V. Inset shows the plot of the electrocatalytic peak current as a function of copper(II) concentration with standard deviation in triplicate. The arrow indicates the direction of the initial scan

Another analytical curve for copper(II) is presented in the inset in Fig. 3. The anodic peak current at the SiO_2/SiIm increases linearly with the concentration of copper(II) in the range from 5.98 to 201.42 μg L^{-1}, with LOD = 0.74 μg L^{-1} and LOQ = 2.48 μg L^{-1}. The linear regression equation (see detail in Fig. 3) is j_p/μA cm^{-2} = -1.60 × 10^{-7} (± 2.54 × 10^{-8}) + 2.09148 (±4.32 × 10^{-2}) [copper(II)] (μg L^{-1}), with a linear correlation coefficient equal to 0.995 (n = 12). The values indicate that SiO_2/SiIm can be used for the determination of copper in samples of ethanolic media [64].

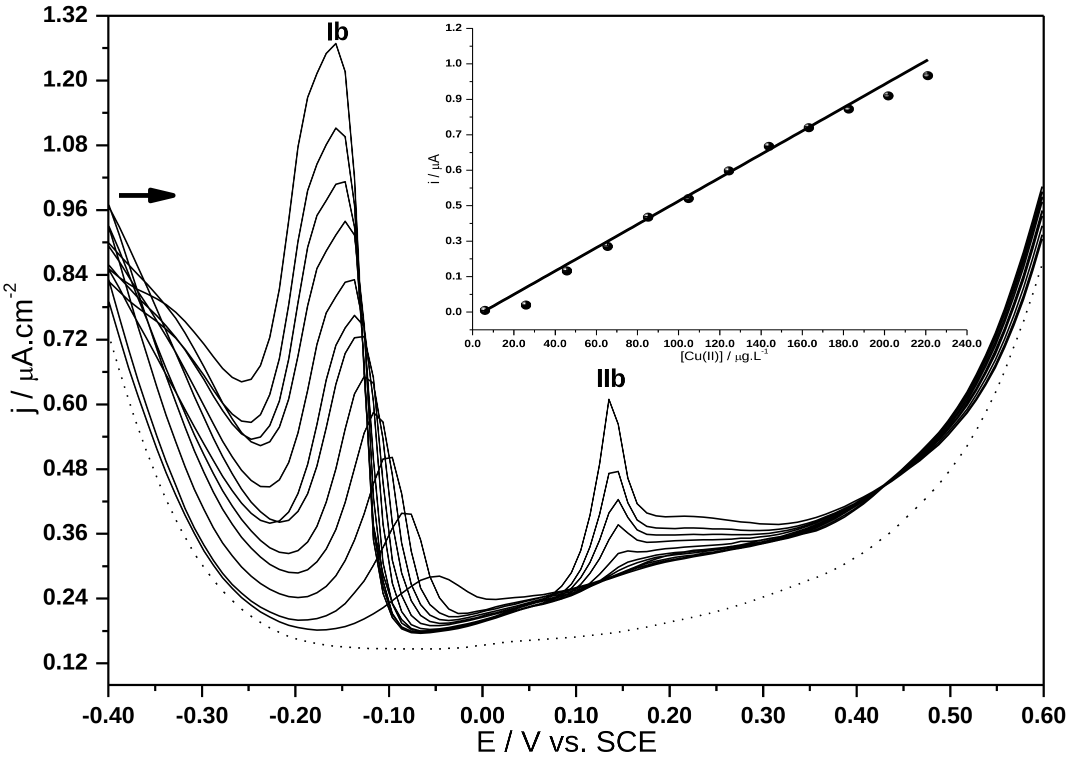


Figure 3. Differential pulse anodic stripping voltammograms of SiO_2/SiIm obtained in 0.01 mol L^{-1} nitric acid solution (60:40 water-ethanol) in the presence of different concentrations of copper(II) ions. Conditions: ν = 20 mV s^{-1}, t_{pc} = 720 s and E_{red} = – 0.55 V. Inset shows the plot of the electrocatalytic peak current as a function of copper(II) concentration with standard deviation in triplicate. The arrow indicates the direction of the initial scan

In Fig. 2 and 3, at concentrations lower than 38.18 and 5.98 µg L^{-1}, respectively, an anodic peak at – 0.288 V (**Ia**) and another one at – 0.147 V (**Ib**), respectively, can be observed. Above these concentrations, the appearance of a second peak is observed at 0.094V (**IIa**) and 0.145 V (**IIb**), respectively, which is related to the oxidation of accumulated copper. At concentrations above 604.18 µg L^{-1} and 201.42 µg L^{-1}, respectively, linearity deviation occurs, probably arising from saturation of the active sites at the working electrode surface. Under the optimized conditions (see Table S1 and S2 of the supplementary material), the SiO_2/SiIm was used to identify 40 µmol L^{-1} of copper eight (for aqueous medium) and twelve (for ethanolic medium) times by DPASV. The relative standard deviation (RSD, in percent) of the oxidation peak current was 2.73 % and 1.29 % for copper(II) ions in aqueous/ethanolic medium. The results revealed good stability and reproducibility of SiO_2/SiIm.

3.2.3 Proposed mechanism

Fig. S5 (see Figure S5 of the supplementary material) presents the proposed mechanism of the SiO_2/SiIm electrode in the determination of copper ions [61]. The proposed mechanism for the ratios is based on the chelation of metallic copper(II) ions with imidazole (1:2 molar ratio) at the electrode surface. A dependence of the anodic current peaks with pH was observed, arising from competition between H^+ protons and copper(II) ions by the basic imidazole groups. Next, the metallic ions complexed at the electrode surface are reduced to metallic copper at a potential of – 0.55 V *vs.* SCE during a reduction time of 600 or 720 s [Cu(II)/Cu(0)]. Finally, using differential pulse anodic stripping voltammetry in the potential range of – 0.8 to 0.8 V, with a scan rate of 20 mV s^{-1}, the oxidation of copper(0) adsorbed in the electrode surface to copper(II) occurs, resulting in an analytical signal proportional to the concentration of Cu(0) oxidized to copper(II) (anodic oxidation peak at – 0.288 and – 0.147 V, respectively), which is directly proportional to the copper(II) concentration in the solution [23,65].

3.2.4 In aqueous/ethanolic medium

The voltammetric sensor was applied to the determination of copper ions in aqueous/ethanolic media, as shown in Fig. 4 and 5. To evaluate the applicability of this electrode for determination of copper(II) in real samples, aqueous/ethanolic medium of tap water and ethanol fuel was examined by voltammetric determination of copper(II) by using the standard addition method. The results for these analyses with DPASV, using SiO_2/SiIm electrode are presented in Table S3 on the supplementary material.

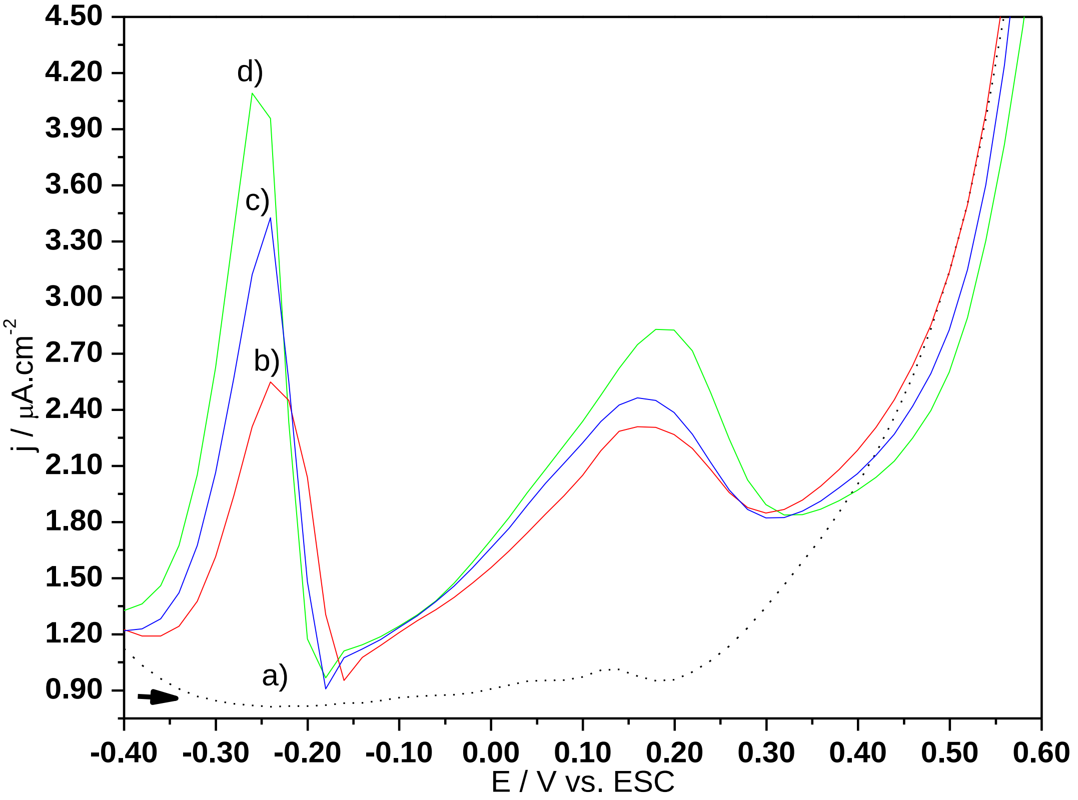


Figure 4. Differential pulse anodic stripping voltammograms of SiO_2/SiIm obtained in *Sörensen* buffer solution (0.50 mol L^{-1} KCl) and pH 5.28 in the presence of different aqueous samples: a) 0.0 mL, b) 10.0 mL, c) 20.0 mL, and d) 30.0 mL aqueous samples. Conditions: $\nu = 20$ mV s^{-1}, $t_{pc} =$ 600 s, $E_{red} = -0.55$ V

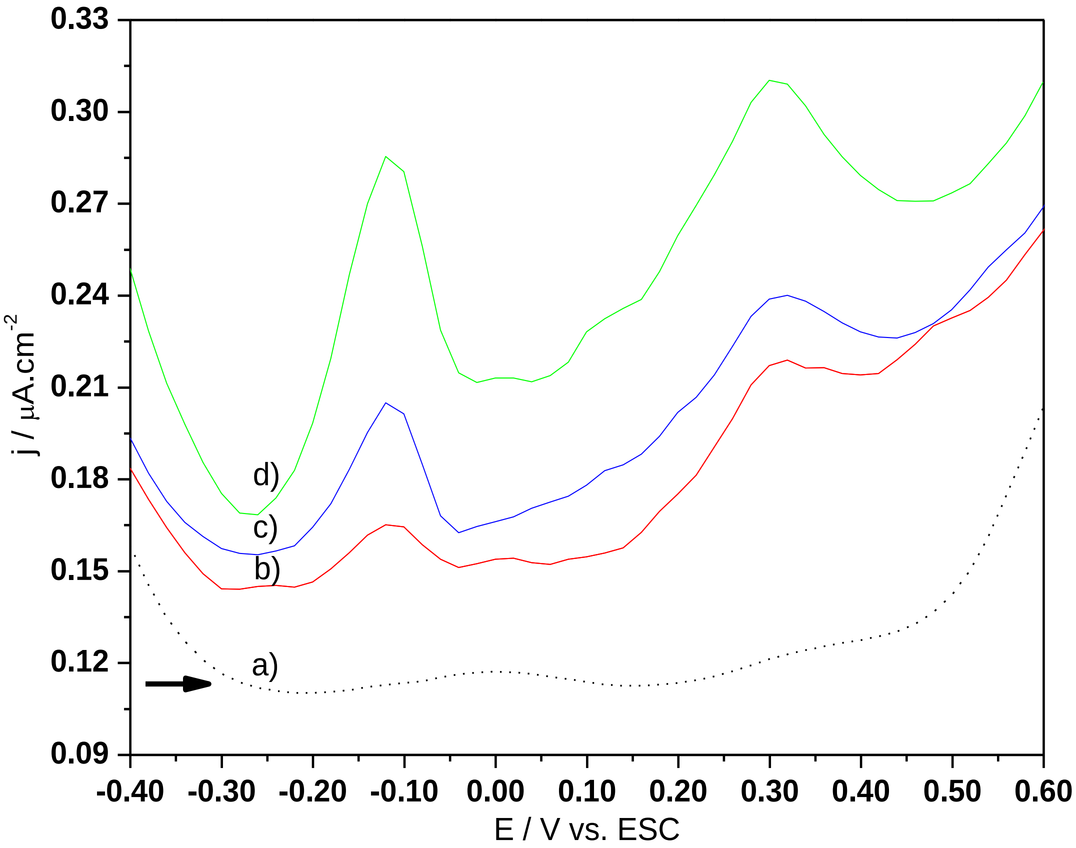


Figure 5. Differential pulse anodic stripping voltammograms of SiO_2/SiIm obtained in 0.01 mol L^{-1} nitric acid solution (60:40 water-ethanol) in the presence of different ethanolic samples: a) 0.0 mL, b) 10.0 mL, c) 20.0 mL, and d) 30.0 mL ethanolic samples. Conditions: ν = 20 mV s^{-1}, t_{pc} = 720 s and E_{red} = – 0.55 V

The data shown in Table 1 indicate that the LOD of the SiO_2/SiIm for copper(II) ion is undoubtedly major to that of all other working electrodes composed of functionalized silica, including in ethanolic media, presenting lower LOD values than those reported in the literature [10,64].

The results obtained in this work were compared with other studies in the literature, observed by the methods of DPASV in aqueous/ethanolic media as described in Table 1.

Table 1. Comparison between the present work and other studies in the literature

Sample	**Modifier**	**Technique**	**Concentration range ($\mu g\ L^{-1}$)^a**	**Detection limit ($\mu g\ L^{-1}$)^a**	**Accumulation time (s)**	**Refs.**
Tap water	Calix[4]arene	DPASV	3.18 – 101.66	1.1	600	[66]
Tap water	OPPy/Nitroso-R	DPASV	1.2 – 243.9	0.7	480	[60]
Tap water	NH_2-MCM-41	ASV^b	0.005 – 1	0.9		[67]
Cachaça	SBA – 15 with 2-benzothiazolethiol	DPASV	50.83 – 635.40	12.71	180	[68]

Cachaça	Mercury electrode	ASV[b]	1 – 100	90	300	[69]
Cachaça		FAAS	100.0 – 4000.0	15		[48]
Fuel ethanol	Sílica gel with 2-aminothiazole	DPASV	4.77 – 158.85	1.97	1200	[28]
Fuel ethanol	Graphite-polyurethane	DPASV	6.35 – 69.89	2.48	1200	[23]
Fuel ethanol	Silica gel modified with 2-aminothiazole groups	FAAS		1.7		[70]
Tap water	Silica gel with imidazole	DPASV	38.10 – 604.18	18.83	600	This work
Cachaça		DPASV	5.98 – 201.42	0.74	720	
Fuel ethanol		DPASV	5.98 – 201.42	0.74	720	

[a] Adapted values in µg L^{-1}

[b] Anodic stripping voltammetry (ASV)

3.2.4 Interference studies

The influence of other metal ions, which can compete for complexation at binding sites of SiO_2/SiIm, were tested using the same procedure as that optimized for copper determination (see Table S1 and S2 of the supplementary material). The interference of Na(I), K(I), Fe(II), Pb(II), Ni(II), and Zn(II) with the current stripping peak was investigated because they are the main interferences in samples of tap water, cachaça, and ethanol fuel [48,49].

The interference studies were performed by using interfering metal ion/copper(II) mass ratios equal to 0.5, 1.0, 1.5 and 0.5, 1.0, 2.0 for aqueous and ethanolic media, respectively. The interference of Na(I), Fe(II), Pb(II), Ni(II) and Zn(II) with the current stripping peak was investigated by adding increasing amounts of these metals to a solution containing 381.24 and 101.66 µgL^{-1} Cu(II). The influence of interfering ions on the Cu(II) voltammetric response is shown in Table 2.

Table 2. Effect of interfering metal ions on the anodic stripping peak current observed in 101.66 and 381.24 µg L^{-1} Cu(II) solutions under the optimized DPASV conditions

Interfering ion	**Medium**	**Concentration (µg L^{-1})**	**Recovery of Cu(II) (%)***
Na(I)	Aqueous	190.62	100.28
		381.24	99.01
		571.22	89.54
Fe(II)		190.62	92.41
		381.24	100.01
		571.22	102.32

Pb(II)		190.62	102.71
		381.24	107.59
		571.22	105.43
Ni(II)		190.62	103.44
		381.24	106.78
		571.22	104.28
Zn(II)		190.62	98.86
		381.24	111.66
		571.22	116.78
Na(I)	Ethanolic	50.83	95.64
		101.66	101.03
		571.22	106.48
Fe(II)		50.83	94.45
		101.66	101.32
		203.33	104.65
Pb(II)		50.83	91.20
		101.66	105.55
		203.33	103.42
Ni(II)		50.83	93.53
		101.66	102.64
		203.33	102.71
Zn(II)		50.83	95.78
		101.66	106.60
		203.33	109.11

* % Recovery = Recovery/Concentration x 100

It was observed that the presence of interfering metal ions in aqueous medium at concentrations smaller or lager a 381.24 μg L^{-1} than Cu(II) concentration has an effect (positive or negative) on the Cu(II) voltammetric response. All the interferants increased the copper signal, except for Fe(II) and Zn(II) at lower concentrations, which provoked a decrease in the copper signal.

The presence of Na(I), Ni(II) and Zn(II) in ethanolic medium at concentrations lower or higher than that of Cu(II) has only a small effect on the Cu(II) voltammetric response, causing a decrease or increase of less than 1.32 – 9.11 % in the voltammetric peak currents. Zn(II) at a higher concentration caused an increase in the Cu(II) signal greater than 10.0 % (116.78).

3.2.5 Commercial samples analysis

3.2.5.1 Analysis of copper in tap water, cachaça (Brazilian sugar-cane spirits) and ethanol fuel

The voltammetric sensor was applied to the determination of copper ions in tap water (IQ-Unifal-MG), cachaça and ethanol fuel from the South of the State of Minas Gerais and the results were compared with the proposed standard analytical method, FAAS, using a Student's t-test.

Table 3. Comparison between the Cu(II) concentrations determined in tap water, cachaça and ethanol fuel samples by DPASV method and by FAAS

Sample	Medium	[Cu(II)] (μg L^{-1})[c,e]		Relative error[d] (%)
		DPASV	FAAS	
Tap water	Aqueous[a]	76.24	77.38	1.47
		53.74	54.63	1.62
		48.25	47.66	–1.23
Cachaça	Ethanolic[b]	3550	3534	– 0.45
		2527	2483	–1.77
		2769	2800	1.10
Ethanol fuel		17.81	17.77	– 0.22
		28.90	28.85	– 0.17
		60.61	61.42	1.31

[a] t_{pc} = 600 s
[b] t_{pc} = 720 s
[c] n = 3
[d] FAAS vs. DPASV(FAAS – DPASV/FAAS) x 100%
[e] $t_{critical}$ = 2.1199 (P = 0.05 with 16 degrees of freedom, t statistic = 0.0105)

An accurate volume of the sample (20.0 mL) was directly subjected to voltammetric measurements using the voltammetric sensor with DPASV method (Fig. 4), without any sample pretreatment, and with only dissolution in the supporting electrolyte solution. It was necessary to use longer pre-concentration times (600 and 720 s) to obtain a good signal for copper in this sample, under the optimized conditions (see Table S1 and S2 of the supplementary material). The results are summarized in Table 3. As can be seen, there is satisfactory agreement between the DPASV method and FAAS. The obtained results are very similar, showing that the electrode could be efficiently used for determination of copper in commercial samples.

The obtained t-values were always smaller than the critical value, indicating that there is no statistical difference at the 95 % confidence level between the results obtained with both methods.

4. CONCLUSIONS

The hybrid material was characterized by several spectroscopic techniques, which confirm the formation of a hybrid material organofunctionalized with imidazole group. The techniques of infrared absorbance spectroscopy and elemental analysis indicate functionalized silica formation. The presence of organic groups in the hybrid material was also confirmed by *solid state* ^{13}*C and* ^{29}*Si NMR.*

The SiO_2/SiIm can be used in the preparation of electrochemical sensors for differential pulse anodic stripping voltammetry of copper(II) in aqueous/ethanolic media. A literature survey shows that this study is the first report to apply this hybrid material organically modified with 3-(2-imidazolin-1-ylpropyltriethoxysilane for electroanalytical purposes. Optimized working conditions were described. Compared with other modified materials in the literature, the values shown in Table 1 are similar and even lower than those previously reported using DPASV. This technique showed selectivity in ethanolic medium. In addition, the SiO_2/SiIm exhibited some advantages such as simple preparation, surface renewal, good stability, reproducibility and finally, was able to determine trace amounts of copper(II) in commercial samples such as tap water, cachaça and ethanol fuel, with significant results and acceptable. In DPASV, the best results and a linear response to copper(II) was observed in the 5.98 – 201.42 $\mu g\,L^{-1}$ ($R^2 = 0.995$; n = 12) concentration range, using a pre-concentration time of 720 s at – 0.55 V vs. SCE and a scan rate of 20 $mV\,s^{-1}$, with a LOD of 0.74 $\mu g\,L^{-1}$ and LOQ of 2.48 $\mu g\,L^{-1}$ in ethanolic medium.

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SUPPLEMENTARY MATERIAL:

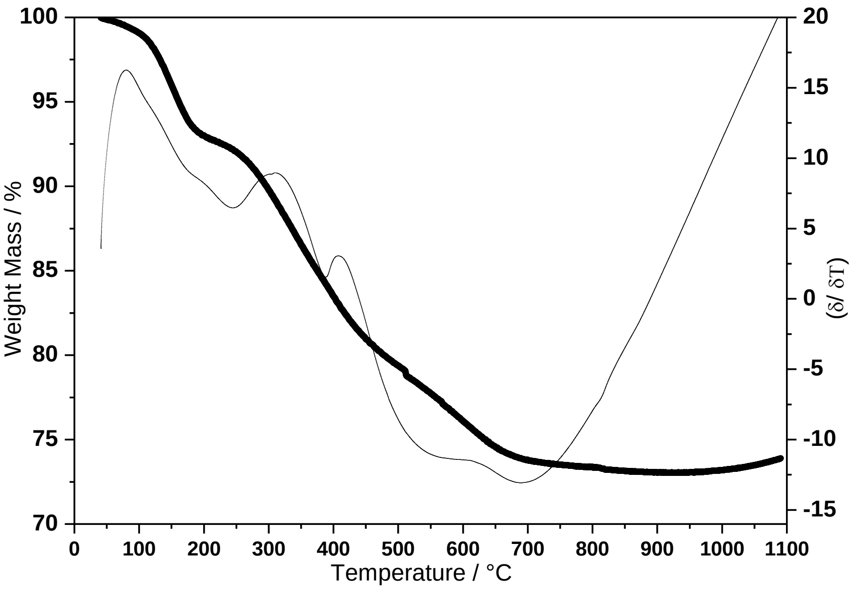

Figure S1. Thermogravimetric curves of the hybrid material SiO_2/SiIm

Table S1. Optimum parameters in aqueous and ethanolic medium for the determination of copper using SiO_2/SiIm

Solution	**Parameter**	**Optimized values**
Aqueous	Electrode composition	32.7 % (w/w) SiO_2/SiIm, 42.3 % graphite and 25% mineral oil
	Supporting electrolyte and pH	*Sörensen* buffer solution (0.50 mol L^{-1} KCl) and 5.28
Ethanolic	Electrode composition	32.7 % (w/w) SiO_2/SiIm, 42.3 % graphite and 25% mineral oil
	Supporting electrolyte	0.01 mol L^{-1} nitric acid solution (60:40 water-ethanol ratio)

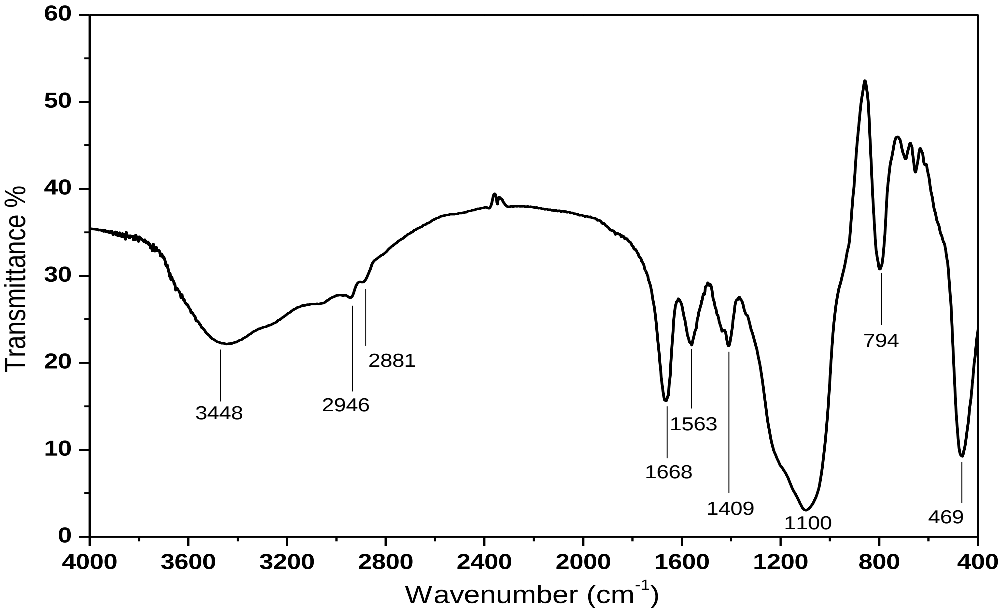

Figure S2. Infrared spectrum of SiO_2/SiIm, with bands relating to vibrations of both inorganic and organic structural units

Table S2. Optimized parameters for determination of copper using SiO_2/SiIm in DPASV

Parameter	**Evaluated range**	**Optimized value**
Scan rate	1 – 50 mV s^{-1}	20 mV s^{-1}
Pulse amplitude	50 – 100 mV	50 mV
Accumulation potential	– 0.40 to – 0.60 V vs. SCE	– 0.55 V vs. SCE
Pre-concentration time	60 - 1800 s	600 and 720 s
Equilibration time	0 - 10 s	5 s
Initial potential	– 1.0 to – 0.6 V vs. SCE	– 0.4 V
Final potential	0.4 to 1.4 V vs. SCE	+ 0.6 V

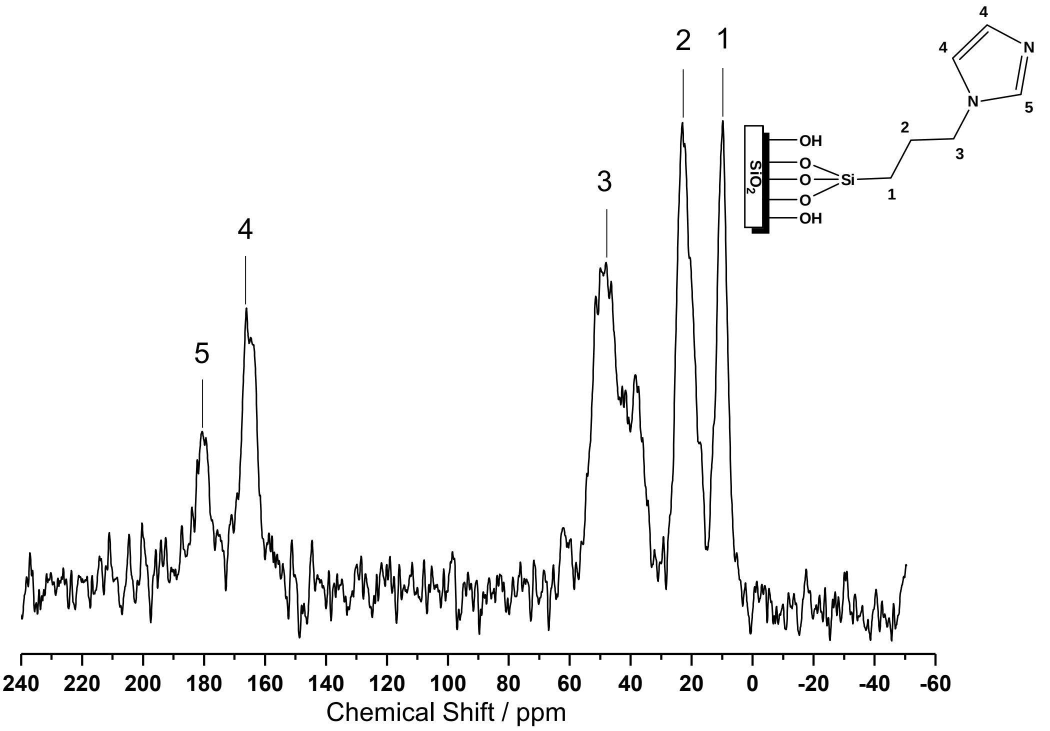

Figure S3. ^{13}C NMR spectrum of the hybrid material SiO_2/SiIm, showing the numbered carbon atoms in the attached structure

Table S3. Results of the determination of Cu(II) ions in aqueous/ethanolic samples of SiO_2/SiIm

Medium	**Sample Volume (mL)**	**Peak Current (μA)**	**[Cu(II)] / μg L^{-1}**
Aqueous samples	10.0	0.981	198.24
	20.0	1.311	312.61
	30.0	1.577	407.01
Ethanolic samples	10.0	0.166	38.93
	20.0	0.204	47.44
	30.0	0.284	62.79

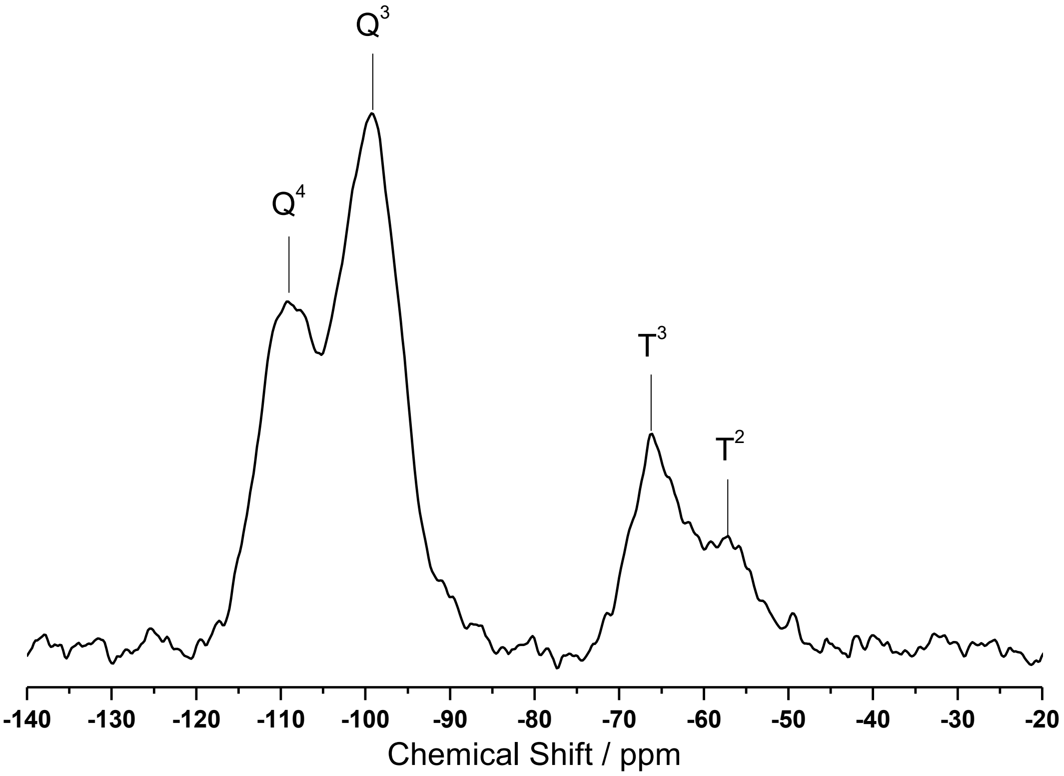

Figure S4. ^{29}Si NMR spectrum of the hybrid material SiO_2/SiIm

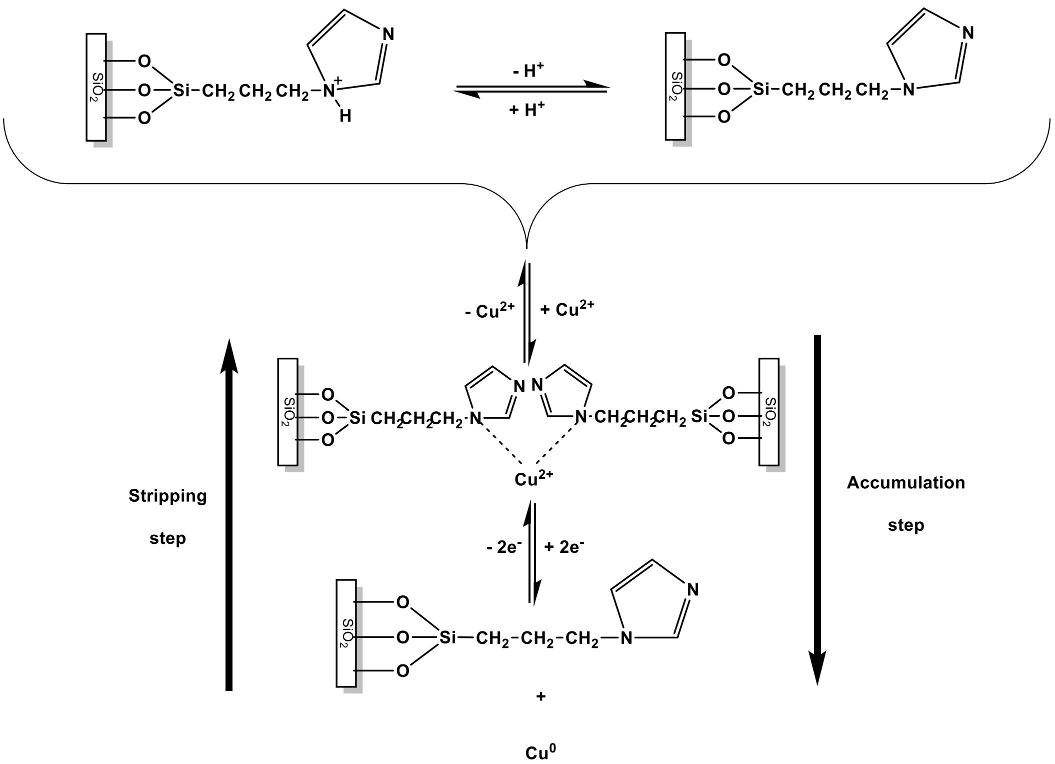

Figure S5. Proposed mechanism of the accumulation and anodic stripping steps at the surface of SiO_2/SiIm

References

1. B. Lee, H.-J. Im, H. Luo, E.W. Hagaman, S. Dai, *Langmuir*, 21 (2005) 5372.
2. J.E. Lofgreen, G.A. Ozin, *Chem. Soc. Rev.*, 43 (2014) 911.
3. H.A. Magosso, R.C.S. Luz, Y. Gushikem, *Electroanalysis*, 22 (2010) 216.
4. J.D. Mackenzie, E.P. Bescher, *J. Sol-Gel Sci. Technol.*, 13 (1998) 371.
5. M.M. Collinson, *Mikrochim. Acta*, 129 (1998) 149.
6. H. Maleki, L. Duraes, C.A. Garcia-Gonzalez, P. Del Gaudio, A. Portugal, M. Mahmoudi, *Adv. Colloid Interface Sci.*, 236 (2016) 1.
7. R.K. Sharma, S. Dutta, S. Sharma, *Dalt. Trans*, 44 (2015) 1303.
8. M. Zhao, S. Ou, C.-D. Wu, *Acc. Chem. Res.*, 47 (2014) 1199.
9. A. Kaushik, R. Kumar, S.K. Arya, M. Nair, B.D. Malhotra, S. Bhansali, *Chem. Rev.*, 115 (2015) 4571.
10. K. Kalcher, I. Svancara, M. Buzuk, K. Vytras, A. Walcarius, *Monatshefte Für Chemie - Chem. Mon.*, 140 (2009) 861.
11. G. Silveira, A.D. Morais, P.C.M. Villis, C.M. Maroneze, Y. Gushikem, A.M.S. Lucho, F.L. Pissetti, *J. Colloid Interface Sci.*, 369 (2012).
12. S. Wang, Y. Kang, L. Wang, H. Zhang, Y. Wang, Y. Wang, *Sensors Actuators B Chem.*, 182 (2013) 467.
13. A. Walcarius, *Chem. Soc. Rev.*, 42 (2013) 4098.
14. P.C.M. Villis, J.C. Sampaio, W.C. Gomes, R. de C.M. de Miranda, G.S. Nunes, F.L. Pissetti, Y. Gushikem, A.M.S. Lucho, *J. Appl. Electrochem.*, 48 (2018) 867.
15. H.B. He, C. Dong, B. Li, J.. P. Dong, T.Y. Bo, T.L. Wang, Q.W. Yu, Y.Q. Feng, *J. Chromatogr. A*, 1361 (2014) 23.
16. X. Yang, R. Wang, W. Wang, H. Yan, M. Qiu, Y. Song, *J. Chromatogr. B Anal. Technol. Biomed. Life Sci.*, 945–946 (2014) 127.
17. S. Prakash, T. Chakrabarty, A.K. Singh, V.K. Shahi, *Biosens. Bioelectron.*, 41 (2013) 43.
18. E. Bagheri, L. Ansari, K. Abnous, S.M. Taghdisi, F. Charbgoo, M. Ramezani, M. Alibolandi, *J. Control. Release*, 277 (2018) 57.
19. D. Perez-Quintanilla, A. Sanchez, I. Sierra, *J. Colloid Interface Sci.*, 472 (2016) 126.
20. A.M. Lucho, A. V Panteleimonov, Y. V Kholin, Y. Gushikem, *J. Colloid Interface Sci.*, 310 (2007) 47.
21. I. Cesarino, E.T.G. Cavalheiro, C.M.A. Brett, *Electroanalysis*, 22 (2010) 61.
22. B. Samiey, C.-H. Cheng, J. Wu, *Mater.*, 7 (2014) 673.
23. I. Cesarino, G. Marino, E.T.G. Cavalheiro, *Fuel*, 89 (2010) 1883.
24. G. Marino, M.F. Bergamini, M.F.S. Teixeira, E.T.G. Cavalheiro, *Talanta*, 59 (2003) 1021.
25. M.E. Mahmoud, G.A. Gohar, *Talanta*, 51 (2000) 77.
26. R.S.A. Machado, M.G. da Fonseca, L.N.H. Arakaki, J.G.P. Espinola, S.F. Oliveira, *Talanta*, 63 (2004) 317.
27. M. Ghiaci, B. Rezaei, M. Arshadi, *Sensors Actuators B Chem.*, 139 (2009) 494.
28. R.M. Takeuchi, A.L. Santos, P.M. Padilha, N.R. Stradiotto, *Talanta*, 71 (2007) 771.
29. R.M. Takeuchi, A.L. Santos, P.M. Padilha, N.R. Stradiotto, *Anal. Chim. Acta*, 584 (2007) 295.
30. G. Wu, G. Song, D. Wu, Y. Shen, Z. Wang, C. He, *Microchim. Acta*, 171 (2010) 203.
31. L.D. Marestoni, M.D.P.T. Sotomayor, M.G. Segatelli, L.R. Sartori, C.R.T. Tarley, *Quim. Nova*, 36 (2013) 1194.
32. B.B. Prasad, D. Jauhari, A. Verma, *Talanta*, 120 (2014) 398.
33. J.J. Cheng, G.R. Timilsina, *Renew. Energy*, 36 (2011) 3541.
34. H. V Amorim, M.L. Lopes, J.V.D. Oliveira, M.S. Buckeridge, G.H. Goldman, *Appl. Microbiol. Biotechnol.*, 91 (2011) 1267.
35. S.L.M. Salles-Filho, P.F.D. de Castro, A. Bin, C. Edquist, A.F.P. Ferro, S. Corder, *Energy*

Policy, 108 (2017) 70.
36. T. Saint'Pierre, R.Q. Aucelio, A.J. Curtius, *Microchem. J.*, 75 (2003) 59.
37. E.L. da Silva, A.O. Martins, A. Valentini, V.T. de Favere, E. Carasek, *Talanta*, 64 (2004) 181.
38. R.A.A. Munoz, L. Angnes, *Microchem. J.*, 77 (2004) 157.
39. R.M. Takeuchi, A.L. Santos, M.J. Medeiros, N.R. Stradiotto, *Microchim. Acta*, 164 (2009) 101.
40. A. Shrivastava, J. Sharma, V. Soni, *Bull. Fac. Pharmacy, Cairo Univ.*, 51 (2013) 113.
41. I.A. Silva, R.C. Campos, A.J. Curtius, S.M. Sella, *J. Anal. At. Spectrom.*, 8 (1993) 749.
42. N.L. Dias, R.M. Costa, G.L. Okajima, *Sep. Sci. Technol.*, 43 (2008) 624.
43. BRASIL. Regulamento Da Lei 8.918, de 14 de Julho de 1994, Decreto 6871 C.F.R. § 51 (2009).
44. C.B. Portugal, A.P. de Silva, A.M. Bortoletto, A.R. Alcarde, *Food Res. Int.*, 91 (2017) 18.
45. M. Etienne, J. Bessiere, A. Walcarius, *Sensors Actuators B Chem.*, 76 (2001) 531.
46. C. Mariame, M. El Rhazi, I. Adraoui, *J. Anal. Chem.*, 64 (2009) 632.
47. S. Chaperon, S. Sauve, *Soil Biol. Biochem.*, 39 (2007) 2329.
48. E.R. Pereira, K. Miranda, A.G.G. Dionisio, *Microchem. J.*, 96 (2010) 99.
49. T.D. Saint'Pierre, V.L.A. Frescura, A.J. Curtius, *Talanta*, 68 (2006) 957.
50. Y.-L. Xie, S.-Q. Zhao, H.-L. Ye, J. Yuan, P. Song, S.-Q. Hu, *J. Electroanal. Chem.*, 757 (2015) 235.
51. N. Velikova, Y. Vueva, Y. Ivanova, I. Salvado, M. Fernandes, P. Vassileva, R. Georgieva, A. Detcheva, *J. Non. Cryst. Solids*, 378 (2013) 89.
52. K.M. Parida, D. Rath, S.S. Dash, *J. Mol. Catal. A Chem.*, 318 (2010) 85.
53. M.C. Burleigh, M.A. Markowitz, M.S. Spector, B.P. Gaber, *J. Phys. Chem. B*, 105 (2001) 9935.
54. J.J. Yang, I.M. El-Nahhal, I.-S. Chuang, G.E. Maciel, *J. Non. Cryst. Solids*, 209 (1997) 19.
55. I.M. El-Nahhal, N.M. El-Ashgar, *J. Organomet. Chem.*, 692 (2007) 2861.
56. F. Fakhfakh, L. Baraket, J.M. Fraile, J.A. Mayoral, A. Ghorbel, *J. Sol-Gel Sci. Technol.*, 52 (2009) 388.
57. S. Hamoudi, A. El-Nemr, K. Belkacemi, *J. Colloid Interface Sci.*, 343 (2010) 615.
58. R.K. Dey, F.J.V.E. Oliveira, C. Airoldi, *Colloids Surfaces A-Physicochemical Eng. Asp.*, 324 (2008) 41.
59. Y.J. Choi, U. Huh, T.J.M. Luo, *J. Sol-Gel Sci. Technol.*, 51 (2009) 124.
60. A. Mohadesi, A. Salmanipour, S.Z. Mohammadi, A. Pourhatami, M.A. Taher, *J. Braz. Chem. Soc.*, 19 (2008) 956.
61. E.R. de Sousa, E.P. Marques, E.N. Fernandes, J.J. Zhang, A.L.B. Marques, *J. Braz. Chem. Soc.*, 17 (2006) 177.
62. E.A. Ambundo, M.-V. Deydier, A.J. Grall, N. Aguera-Vega, L.T. Dressel, T.H. Cooper, M.J. Heeg, L.A. Ochrymowycz, D.B. Rorabacher, *Inorg. Chem.*, 38 (1999) 4233.
63. E. Birlik, A. Ersoz, A. Denizli, R. Say, *Anal. Chim. Acta*, 565 (2006) 145.
64. I. Svancara, A. Walcarius, K. Kalcher, K. Vytras, *Cent. Eur. J. Chem.*, 7 (2009) 598.
65. I. Cesarino, G. Marino, J.D. Matos, E.T.G. Cavalheiro, *Talanta*, 75 (2008) 15.
66. E.C. Canpolat, E. Sar, N.Y. Coskun, H. Cankurtaran, *Electroanalysis*, 19 (2007) 1109.
67. X. Dai, F. Qiu, X. Zhou, Y. Long, W. Li, Y. Tu, *Anal. Chim. Acta*, 848 (2014) 25.
68. I. Cesarino, G. Marino, R. Matos J do, E.T. Cavalheiro, *Talanta*, 75 (2008) 15.
69. P.J.S. Barbeira, L.H. Mazo, N.R. Stradiotto, *Analyst*, 120 (1995) 1647.
70. P.S. Roldan, I.L. Alcantara, G.R. Castro, J.C. Rocha, C.C. Padilha, P.M. Padilha, *Anal. Bioanal. Chem.*, 375 (2003) 574.