Food Chemistry 171 (2015) 426–431

Contents lists available at ScienceDirect

Food Chemistry

journal homepage: www.elsevier.com/locate/foodchem

Analytical Methods

Electrochemical determination of copper ions in spirit drinks using carbon paste electrode modified with biochar

Paulo Roberto Oliveira[a], Alyne C. Lamy-Mendes[a], Edivaltrys Inayve Pissinati Rezende[b], Antonio Sálvio Mangrich[b,c], Luiz Humberto Marcolino Junior[a], Márcio F. Bergamini[a,*]

[a] *Laboratório de Sensores Eletroquímicos (LabSensE), Departamento de Química, Universidade Federal do Paraná (UFPR), CEP 81.531-980 Curitiba, PR, Brazil*
[b] *Laboratório de Química de Húmus e Fertilizantes, Departamento de Química, Universidade Federal do Paraná (UFPR), CEP 81.531-980 Curitiba, PR, Brazil*
[c] *Instituto Nacional de Ciência e Tecnologia de Energia e Ambiente (INCT E&A/CNPq), Brazil*

ARTICLE INFO

Article history:
Received 25 February 2014
Received in revised form 1 September 2014
Accepted 6 September 2014
Available online 16 September 2014

Keywords:
Copper ions
Spirit drinks
Stripping analysis
Biochar

ABSTRACT

This work describes for first time the use of biochar as electrode modifier in combination with differential pulse adsorptive stripping voltammetric (DPAdSV) techniques for preconcentration and determination of copper (II) ions in spirit drinks samples (Cachaça, Vodka, Gin and Tequila). Using the best set of the experimental conditions a linear response for copper ions in the concentration range of 1.5×10^{-6} to 3.1×10^{-5} mol L^{-1} with a Limit of Detection (LOD) of 4.0×10^{-7} mol L^{-1}. The repeatability of the proposed sensor using the same electrode surface was measured as 3.6% and 6.6% using different electrodes. The effect of foreign species on the voltammetric response was also evaluated. Determination of copper ions content in different samples of spirit drinks samples was also realized adopting inductively coupled plasma optical emission spectroscopy (ICP-OES) and the results achieved are in agreement at a 95% of confidence level.

1. Introduction

Production and consumption of alcoholic beverages have been growing and promoting a large influence in several sectors like economic, social and health (Jernigan, Monteiro, Room, & Saxena, 2000; Room, Babor, & Rehm, 2005; Sierksma, Hulshof, Grobbee, & Hendriks, 2003). In general, several elements could be found in distilled beverages such as As, Pb, Zn, Fe and principally Cu (Cassella, Caldas, Francisco, & Pereira Netto, 2011; Nascimento-Filho, Cunha e Silva, Almeida, & Valencia, 2004). Despite of copper is an essential micronutrient required for numerous cellular functions (Double et al., 2013), the ingestion in excess of this metal, is toxic and may cause serious damages to health (Brewer, 2008; Nobrega, Neves, Oliveira, & Fernandes, 2007; Tapiero, Townsend, & Tew, 2003). Cachaça a distilled drink prepared from the fermentation of sugar cane, is one of the most popular alcoholic beverages consumed in Brazil (Pereira et al., 2012; Vicente et al., 2006). Brazilian legislation requires that copper concentration in the Cachaça should not be higher than 5.0 mg L^{-1} (Araujo, Almeida, Martins, Silva, & Moreira, 2003; Nascimento-Filho et al., 2004). The presence of large amounts of copper in Cachaça and other spirit drink scan be attributed to the lixiviation from the distillation apparatus during the production process of these drinks (Navarro et al., 2007). Thus, it is very important the development of analytical methods cheap, fast and reliable for the copper determination in alcoholic beverages.

The recommended method for determination of copper in distilled beverages in Brazil is the atomic absorption spectrometry using the method of standard addition (Zenebon, Pascuet, & Tiglea, 2008, chap. 9). There are other methods that can also determinate copper in beverages such as X-ray fluorescence spectrometry (Galani-Nikolakaki, Kallithrakas-Kontos, & Katsanos, 2002), atomic absorption spectrometry (Bermejo-Barrera, Jurado, Martin, Pablos, & Moreda-Piñeiro, 2007) and ICP-OES (Inductively Coupled Plasma-Optical Emission Spectrometry) (Bingöl, Yentür, Erand, & Öktem, 2010). However, these techniques are relatively expensive and, in most cases, require a complex and rigorous pre treatment of the sample to be analysed (Araujo et al., 2003; Nascimento-Filho et al., 2004). In this way, electroanalytical techniques have been widely evaluated as alternatives strategies to develop simple and precise methods for copper determination. From electroanalytical view, for determination of several metallic species is very common the use of stripping voltammetry (SV) combined with chemically modified electrodes (CME). The use of CME under SV conditions promotes not only an improvement of the detection limits but also a high sensibility allowing to reach greater selectivity for the analyte and sometimes eliminate the

---

* Corresponding author. Tel.: +55 41 3361 3177; fax: +55 41 3361 3186.
E-mail address: bergamini@ufpr.br (M.F. Bergamini).

http://dx.doi.org/10.1016/j.foodchem.2014.09.023
0308-8146/

pretreatment of the sample (Ganjali, Motakef-Kazami, Faridbod, Khoee, & Norouzi, 2010; Janegitz, Marcolino-Junior, Campana-Filho, Faria, & Fatibello-Filho, 2009; Oliveira, Tanaka, Stradiotto, & Bergamini, 2012). The most important aspect is the choice of modifier which confers special characteristic to the electrode surface.

Biochar is a kind of carbonaceous obtained from thermal degradation of organic materials in the absence of air (pyrolysis) (Lehmann & Joseph, 2009, chap. 1–2). Several biomass such as agricultural crop residues, forestry residues, wood waste, and animal manures have been proposed as feedstock for biochar production. This product has a surface highly rich in functional groups, and these organic carbon components of biochar can stabilize heavy metals by (1) electrostatic interactions; (2) ionic exchange; (3) sorptive interaction; and/or (4) specific binding of metal ions by surface ligands (e.g., carboxyl, hydroxyl, phenol) abundant in the volatile matter component of biochar (Uchimiya, Bannon, Wartelle, Lima, & Klasson, 2012). Given the great efficiency of preconcentration of species, the biochar has been largely applied for the remediation of soils and waters contaminated by several species (organic and/or inorganic) (Uchimyia, Lima, Klasson, & Wartelle, 2010). In spite of significant adsorbent proprieties of the biochar its use in electroanalytical procedures is still poorly explored. Suguihiro et al. (2013) proposed recently the use of biochar as electrode modifier for Lead and Cadmium preconcentration applied with successful for waste water analysis.

Based on this, the present paper describes for first time a procedure for selective preconcentration and determination of copper ions in Cachaça and other spirit drink samples by applying anodic stripping analysis using the electrochemical characteristics of a carbon paste electrode modified with biochar. The method is based on the effective preconcentration of copper ions on the electrode surface containing biochar in open circuit conditions followed by the analyte reduction and subsequent anodic sweep under differential pulse voltammetry conditions.

2. Experimental

2.1. Apparatus

Differential pulse adsorptive stripping voltammograms (DPAdSV) were performed in a potentiostat/galvanostat μAUTOLAB Type III (EcoChemie, Utrecht, Netherlands) connected to a microcomputer controlled by software (GPES 4.9, EcoChemie, Utrecht, Netherlands) for data acquisition and experimental control. All the voltammetric measurements were carried out in a 20 mL glass cell at 25 °C, with a three-electrode configuration: modified carbon paste electrode as the working electrode, Ag/AgCl KCl 3 mol L^{-1} as the reference electrode and platinum plate as auxiliary electrode. During the measurements, the solution in the cell was not stirred. The pH measurements were carried out using a pH meter (Metrohm, Utrecht, Netherlands) with a combined pH reference electrode.

Preparation of biochars was realized from castor oil cake using an EDG FT-40 microprocessor-controlled furnace. The elementar composition (C, H and N) was determined using a Perkin Elmer 2400 Series II CHNS/O Elemental Analyzer (Perkin Elmer, Waltham, MA, USA). Information about functional groups present at surface of the biochar was provided by a FTIR Bomem MB100 spectrometer (Bomem Corp., Quebec, Canada) recording the spectrum scope from 4000 to 350 cm^{-1} with a resolution of 4 cm^{-1}.

2.2. Reagents and solutions

All the solutions were prepared with purified water in a Milli-Q system (Millipore (Merck), Darmstadt, Germany). All the chemicals were of analytical grade and were used without further purification. A stock solution containing 1000 mg L^{-1} of copper ions (Merck, Darmstadt, Germany) was used. Ammonium and Acetate buffer solutions 0.1 mol L^{-1} in different pH values were used as preconcentration solution and supporting electrolyte, respectively in all experiments. Different solutions of copper (II) ions were prepared by dilution of stock solution.

2.3. Experimental procedures

2.3.1. Sensor construction

Biochar samples were prepared from castor oil cake, gridding in ball mills to a particle size of 80 meshes, it was placed in porcelain boats in the inner glass tube furnace microprocessor-controlled (EDG, São Carlos, São Paulo, Brazil). The factors used were: heating rate (10 °C min^{-1}), final temperature (300 °C) and warm-up period (60 min).

Carbon paste (1.0 g) electrode was prepared by carefully mixing the graphite powder (45–75% (w/w)) (Sigma–Aldrich, St. Louis, MO, USA), with biochar sample at a varying ratio (0–30% (w/w)) and subsequently added to 0.250 g of mineral oil (25% (w/w)). The components were mixed manually in a mortar and pestle for at least 10 min to obtain an appropriate homogenization. Composite obtained was packed into an adequate support of electrode consisting of a plastic cylindrical tube (o.d. 5 mm, i.d. 3 mm) with a copper rod inside used as an external electric contact. Appropriate packing was achieved by pressing the electrode surface against a filter paper.

2.3.2. Voltammetric procedures

Best analytical performance was found adopting a procedure with four steps: (1) copper ions had been directly preconcentrated at electrode surface in open circuit potential under controlled stirring in ammonium buffer solution at pH = 9.0; (2) After that, electrode was removed from the preconcentration cell, briefly rinsed with deionized water and placed in the electrochemical cell containing 10 mL of 0.1 mol L^{-1} acetate buffer solution (pH 5.0); the reduction of the adsorbed ions was realized at controlled potential conditions; (3) Measurements of DPAdSV were registered and (4) Finally, the electrode surface was cleaned by putting it in 0.1 mol L^{-1} H_2SO_4 solution.

2.3.3. Interfering studies

For interfering studies a well-known amount of copper ions were spiked to an aliquot of 100.0 mL of simulated sample in order to reach maximum amount allowed by Brazilian Department of Agriculture (5 mg L^{-1}). By a similar way, samples were prepared with potential interfering species using concentration according to Brazilian legislation (Ministry of Agriculture. Normative Instruction 13, June 29, 2005): Iron (2.0 mg L^{-1}), Zinc (3.0 mg L^{-1}), Arsenium (100 μg L^{-1}), Lead (200 μg L^{-1}). The pH was adjusted at 9.0 and preconcentration step was realized directly by immersion of the CPME in the solution. Effect of the interfering ions was verified by comparing the anodic current of copper ions in presence and absence of the foreign species.

2.3.4. Sample preparation and copper determination

Determination of copper ions was realized by analysis of several spirit drink samples (commercial Cachaça, homemade Cachaça, Vodka, Gin and Tequila) adopting both stripping voltammetric method and inductively coupled plasma optical emission spectroscopy (ICP-OES) using triplicate of each sample available. Samples have purchased from local stores and the trademarks were chosen because are relatively common in Brazil. For comparison reasons, all samples examined had been produced recently, stored in the dark and analysed shortly after opened. Aliquots of original samples were evaporated until certain of the initial volume and after that was added buffer solution in order to reach the volume final of the 10 mL. Final ratio dilution used for preconcentration step were (original sample:preconcentration solution): Cachaça industrialized (1:1), Cachaça homemade (1:10), Vodka (10:1), Gin (4:1) and Tequila (3:1). Preconcentration of copper ions using the CPME was realized directly in these solutions under magnetic stirring by 10 min.

The differential pulse voltammograms were recorded in the potential range from −0.3 to 0.3 V, using −0.3 V (vs. Ag/AgCl), 10 mV s^{-1}, 75 mV and 10 ms for reduction potential, scan rate, potential pulse amplitude and pulse duration time, respectively. The content of copper ions in these samples was determined by the standard addition method and compared with the ICP-OES results.

3. Results and discussion

3.1. Voltammetric performance of the carbon paste modified electrode for preconcentration of copper (II) ions

Initially voltammetric experiments were realized in order to verify the performance of biochar in the copper ions preconcentration. Fig. 1 shows DPAdS voltammograms obtained using CPE (without modification) after preconcentration step (Fig. 1A), CPME content 25% (w/w) of biochar before (Fig. 1B) and after preconcentration step (Fig. 1C).

No peaks were observed in the potential range of −0.3 V to 0.3 V (vs. Ag/AgCl, KCl 3 mol L^{-1}) in acetate buffer solution for the unmodified carbon paste electrode (curve A) after preconcentration step. This result has demonstrated that CPE is not able to promote an effective interaction between copper ions and electrode surface. Similar results were obtained for CPME (curve B) before the preconcentration step suggesting a not significative amount of electroactive groups at electrode surface. However, when the CPME was submitted to preconcentration step previously the voltammetric measurement, a significative oxidation peak appears at −0.02 V (curve C), attributed to copper oxidation ($Cu^0 \rightarrow Cu^{2+} + 2e^-$). That behaviour can be explained by presence of biochar at electrode surface providing a strong interaction with copper ions and playing an important role for the improvement in the copper ions detection. Consecutive measurements were performed and they had demonstrated good stability of voltammetric signal.

For the best understanding of copper and biochar interaction, qualitative analysis of the FTIR biochar spectra were done and revealed presence of several functional groups at biochar surface. Based on these results, is possible to attribute that interaction between biochar surface and copper ions occurs mainly via hydroxyl and carboxylic acid groups. For all evaluated biochar samples, the FTIR spectra were very similar, all featuring a broad band at 3680–3300 cm^{-1}, associated with the O–H stretching from alcohol, carboxylic acids and water. Absorption in 1625 cm^{-1} attributed to the structural vibrations of C=C aromatics, asymmetric stretching of C=O (COO^-) and bending of O–H groups. Shoulder at 1720 cm^{-1} is associated to C=O stretching of ketone, esther and carboxylic acid (Chen, Zhou, & Zhu, 2008; Keiluweit, Nico, Johnson, & Kleber, 2010). Biochar FTIR spectra data displayed a significative number of sorption peaks indicating the complex nature of samples. The peaks attributed to C–O stretch of carboxylate ions, hydroxyl bending vibration, CO stretching vibration of the alcoholic groups and aromatic compounds were observed at 1375, 1317, 1049 and 780 cm^{-1} respectively. Furthermore, elemental analysis of biochar samples has revealed that with the increase in the pyrolytic temperature there is an increased in the C content in contrast with decreasing in the hydrogen, oxygen and nitrogen content. This decrease indicates an increasing in the hydrophobicity and the reduction of polar groups at surface which could diminish the efficiency of the modifier for interaction with copper ions. Results showed that samples with elevated content of nitrogen atoms can exert a more significant effect on preconcentration suggesting that both sorption and complexation process are the mechanisms by which the copper ions are retained at electrode surface.

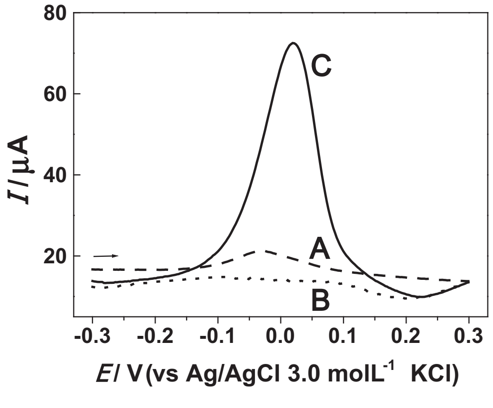

Fig. 1. Differential pulse stripping voltammetric responses obtained in acetate buffer pH 5.0 for the following: (A) CPE unmodified after preconcentration step; (B) CPME modified with 25% (w/w) Biochar before preconcentration step; (C) CPME modified after preconcentration step. Deposition potential: −0.3 V; deposition time: 90 s; scan rate: 10 mV s^{-1}; pulse amplitude: 100 mV; pulse width: 150 ms. The preconcentration step was realized for 300 s in ammonium buffer pH 9.0 content of 1.0×10^{-5} mol L^{-1} of Cu^{2+}.

In order to avoid memory effect, the CPME was submitted to a cleaning step in H_2SO_4 solution. In this stage, copper ions adsorbed had substituted by H^+ at the electrode surface and after that, no more anodic peak referent to copper oxidation was observed. Aiming to compare the effect of the modifier surface area on the voltammetric response a study using CPME with activated charcoal had realized. In spite of charcoal has superficial area significantly bigger (480 cm^2 g^{-1}) than biochar used (1.8 cm^2 g^{-1}) the voltammetric signals obtained using CPME with charcoal were 20 times lower than those observed using modifier proposed. Summing up, these results have supported that an effective interaction between biochar and copper ions is not based on the superficial area.

3.2. Effect of the experimental parameters on the voltammetric response

Firstly, the influence of CPME composition on the voltammetric response was investigated using carbon pastes prepared with 0–40% (w/w) of biochar content under DPAdS voltammetry conditions after preconcentration in presence of 1.0×10^{-5} mol L^{-1} Cu(II). Voltammetric signal has increased for CPME electrodes prepared using biochar content between 5 and 25% (w/w). Electrodes constructed using composition of 30% have shown a slight decrease of the anodic current peak with more pronounced effect for carbon paste content with more than 35%. This behaviour could be attributed to decrease in the conductive area at the electrode surface. Thus, a carbon-paste composition of 25% (w/w) biochar, 50% (w/w) graphite powder and 25% (w/w) mineral oil was used in further studies.

The influence of the pH on the voltammetric response was studied for measurement solution in the pH range between 3.0 and 8.0. The best voltammetric profile was verified for solution of acetate buffer pH 5.0 which was chosen for other investigations. The influence of the pH on the adsorption step was studied using preconcentration solution adjusted in the pH range between 3.0 and 10.0 by using of acetate (pH < 7.0) and ammonium (pH > 7.0) buffer solution (Fig. 2). Voltammetric performance of CPEM revealed that for acidic solutions of pH < 4, copper ions are not retained at

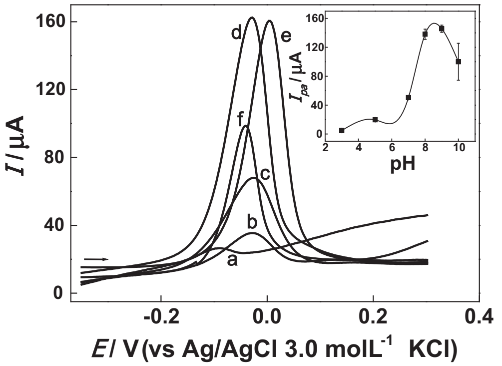

Fig. 2. DPAdSV obtained for CPEM modified with 25% (w/w) Biochar after preconcentration in aqueous solution adjusted in different pH values ((a) pH = 3.0; (b) pH = 5.0; (c) pH = 7.0; (d) pH = 8.0; (e) pH = 9.0; (f) pH = 10.0) containing 1.0×10^{-5} mol L^{-1} of Cu^{2+}. In detail: effect of pH of the preconcentration solution on the anodic peak current of Cu^{2+} using a CPEM.

electrode probably due competition between H^+ and Cu^{2+} ions for the adsorptive sites present on the surface. A pronounced increase of the anodic peak current was verified for pH > 6.0 reaching a maximum value for pH values between 8.0 and 9.0 in ammonium buffer solution. Above this pH value, the signal decreased and only a small wave has observed at a pH higher than 10.0. These results can be attributed to hydrolysis reaction of copper ions. From these results, an ammonium buffer solution at pH = 9.0 has been adopted for preconcentration step.

In order to investigate the effect of immersion period (preconcentration time) CPME was loaded in an ammonium buffer solution (pH 9.0) containing copper ions at different concentrations (1.0×10^{-5} mol L^{-1} and 1.0×10^{-6} mol L^{-1}) by preconcentration times varying between 0 (without) to 60 min. After wards preconcentration step, the electrode was transferred to the electrolyte and DPAdS voltammograms were recorded. Results obtained from preconcentration studies showed a dependence of anodic peak current on preconcentration time (0–60 min). For both evaluated concentrations, the anodic peak current increases linearly up to 15 min and 30 min for concentration of 1.0×10^{-5} mol L^{-1} and 1.0×10^{-6} mol L^{-1}, respectively. Above these values the current signals reached a plateau at longer accumulation time indicating a stationary condition dependent of the surface equilibrium of copper ions. The same behaviour was related in previous works (Janegitz et al., 2009; Oliveira et al., 2012; Suguihiro et al., 2013) indicating a well-defined correlation between accumulation time and analyte concentration for stripping methods, that allows the modulation of analytical performance as a function of preconcentration time. In this way, the proposed sensor could be applied for determination of low level of analyte adopting an accumulation time of 30 min. Despite of accumulation time value seems relatively long, an excellent repeatability and reproducibility was found using CPME and so the preconcentration step could be realized using several electrodes at same time accumulations. By other side, a short time could be use if the copper ions level is more elevated. For further studies a preconcentration time of 10 min was chosen.

Instrumental parameters such as reduction potential (applied before potential scanning step), scan rate, potential pulse amplitude and pulse duration could promote serious influence on the voltammetric behaviour of the CPEM. For the best performance of the proposed sensor, that parameters were investigated. Magnitude of the anodic peak current (sensibility) and width of peak ($W_{1/2}$, selectivity) had chosen as reference for evaluation of these parameters. The best voltammetric response was obtained using −0.3 V (vs. Ag/AgCl), 10 mV s^{-1}, 75 mV and 10 ms for reduction potential, scan rate, potential pulse amplitude and pulse duration time, respectively.

3.3. Analytical curve and interference studies

After to study the effect of experimental parameters on the voltammetric signal, analytical calibration curves (triplicates) were obtained adopting the best set of experimental conditions. A Linear Dynamic Range (LDR) between copper ions concentration and anodic current peak was found for values varying from 1.5×10^{-6} to 3.1×10^{-5}mol L^{-1}. Limit of Detection (LOD) of 4.0×10^{-7} mol L^{-1} (three times the signal blank/slope) and Limit of Quantification (LOQ) of 1.3×10^{-6} mol L^{-1} (ten times the signal blank/slope) were found. For concentration values above 3.1×10^{-5} mol L^{-1} a deviation from linearity occurred probably due to saturation of the electrode surface. Relative standard deviation of 3.6% was observed for repeatability studies performing five successive measurements of 1.0×10^{-5} mol L^{-1} copper ions at the same CPME without renewing of the electrode surface between successive runs. When five different electrodes surfaces were used adopting the same voltammetric procedure, a RSD of 6.6% was verified. Analytical performance of the sensor was evaluated five times in the same day by preparation of a calibration curve for each electrode used. Considering figures of merits (LDR, LD and LQ) provided by the proposed methodology a standard deviation lower than 5.8% was verified. This value is very close those obtained using different electrode

Table 1
General characteristics of the electrochemical methods used for copper ions determination in spirit drinks samples.

Sample	Electrode	Technique[b]	LOD[c]	Refs.
Whisky	Hanging mercury drop electrode	SWASV	5 µg L^{-1}	Barbeira and Stradiotto (1998)
Beer	Mercury film and glassy carbon electrodes	SWASV	nr	Agra-Gutiérrez, Hardcastle, Ball, and Compton (1999)
Cachaça	Paraffin-based carbon electrode modified with 2-aminothiazole-silica-gel	DPASV	110 µg L^{-1}	Costa, Takeuchi, and Santos (2011)
Grappa	Platinum microelectrode	LSASV	9.5 µg L^{-1}	Baldo and Daniele (2006)
Cachaça, Tequila, Vodka and Gin	*Carbon paste electrode modified with biochar*	*DPAdSV*	*25.4 µg L^{-1}*	[a]
Wines and spirits	Dental amalgam electrode	DPASV	nr	Mikkelsen and Schrøder (2002)
Cachaça	Carbon paste electrode modified with ascorbic acid and carbon nanotubes	SWASV	23.9 µg L^{-1}	Tavares et al. (2012)

nr – not reported.

[a] Procedure proposed.

[b] SWASV – Square Wave Anodic Stripping Voltammetric; DPASV – Differential Pulse Anodic Stripping Voltammetric; LSASV – Linear Sweep Anodic Stripping Voltammetric; DPAdSV – Differential Pulse Adsorptive Stripping Voltammetric.

[c] LOD – Limit of Detection.

surfaces. Similar experiments were conducted in different days and the analytical performance was compared. A RSD of 7.0% was verified indicating a good concordance between the results if other possible variations were taken in consideration. Based on these results is possible to conclude that an excellent performance of the CPME and paste homogenization was found in this work. Table 1 shows analytical characteristics of several methodologies employed for copper ions determination in spirit drinks in order to compare the performance of proposed method.

The effect of several concomitant species on voltammetric signal was studied using Iron (2.0 mg L^{-1}), Zinc (3.0 mg L^{-1}), Arsenium (100 μg L^{-1}), Lead (200 μg L^{-1}) separately and combined in multicomponent sample. The results obtained are shown in Fig. 3. The choice of foreign compounds and its concentration used was based on Brazilian legislation for Cachaça samples. No significant influence was verified for species evaluated demonstrating good selectivity for the proposed device when applied in this kind of samples.

The proposed procedure was evaluated for copper ions determination in different commercial samples (Vodka, Cachaça, Gin and Tequila) in order to demonstrate the applicability of the sensor to the real samples. Standard addition method was adopted for analyte quantification being a representative curve shown in Fig. 4. Values obtained using proposed procedure were compared to those found by the comparative method (ICP-OES). The results were summarized in Table 2 indicating a good relationship for a confidence level of 95%. These values indicate that the copper ions determination in real samples is possible without significative matrix effects.

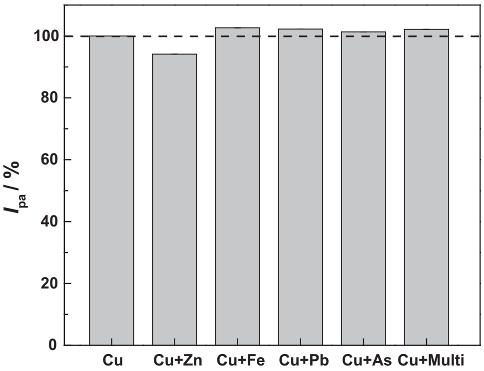

Fig. 3. Percentual interference of the voltammetric responses verified for CPEM with Biochar in presence of only Copper ions, Copper ions combined with each foreign ions as Iron (2.0 mg L^{-1}), Zinc (3.0 mg L^{-1}), Arsenium (100 μg L^{-1}), Lead (200 μg L^{-1}) and Copper (5.0 mg L^{-1}) ions in solution content all species evaluated.

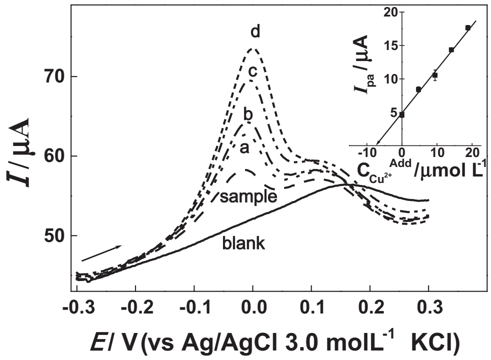

Fig. 4. Differential pulse voltammetric response and standard addition curve (inset curve) obtained for determination of Copper ions in the commercial *Cachaça* sample.

Table 2
Mean values obtained for the determination of Copper ions in spirit drinks by using Stripping Voltammetric (SV) method proposed and the comparative method (ICP-OES).

Sample	Trade mark	Value found/mol L^{-1} (μg L^{-1})		*E*%
		SV	ICP-OES	
Vodka	Natasha	2.00×10^{-7} (12.70)	1.98×10^{-7} (12.57)	+1.0
Tequila	Sauza	3.07×10^{-7} (19.49)	2.86×10^{-7} (18.16)	+7.3
Gin	Seagers	2.98×10^{-7} (18.92)	3.03×10^{-7} (19.24)	−1.6
Cachaça	Pirassununga	8.20×10^{-6} (520.7)	8.94×10^{-6} (567.7)	−8.3
Cachaça	Guaiuvira	5.06×10^{-5} (3,213)	5.01×10^{-5} (3,181)	+1.0
Cachaça	Coluninha	6.75×10^{-6} (428.6)	6.92×10^{-6} (439.4)	−2.4

4. Conclusion

For the first time, a study exploring a CPME with biochar for the copper ions determination in the spirit drinks samples by using the differential pulse voltammetry technique was reported. In comparison with other methods reported, the proposed CPME has many advantages such as easy methodology, possibility of application in real samples with quick or without pretreatment, high stability, good selectivity and long lifetime. Moreover, in comparison with the atomic spectroscopy procedures, the proposed method exhibited good results in terms of selectivity, sensibility and the instrumental cost. The practical usefulness of the proposed method was demonstrated by the determination of the content of copper ions in different samples of spirits drinks and validation of the results by comparative methodology using ICP-OES.

Acknowledgements

We gratefully acknowledge Brazilian financial support from Fundação Araucaria, CAPES and CNPq.

References

Agra-Gutiérrez, C., Hardcastle, J. L., Ball, J. C., & Compton, R. G. (1999). Anodic stripping voltammetry of Copper at in sonated glassy carbon-based electrodes: Application to the determination of Copper in beer. *Analyst, 124*, 1053–1057.

Araujo, M. C. U., Almeida, L. F., Martins, V. L., Silva, E. C., & Moreira, P. N. T. (2003). Implementation of an automatic standard addition method in a flow-batch system: Application to Copper determination in a alcoholic beverage by atomic absorption spectrometry. *Analytica Chimica Acta, 486*, 143–148.

Baldo, M. A., & Daniele, S. (2006). Voltammetric monitoring and speciation of Copper ions in italian "Grappa" with platinum microelectrodes. *Electroanalysis, 18*, 633–639.

Barbeira, P. J. S., & Stradiotto, N. R. (1998). Anodic stripping voltammetric determination of Zn, Pb and Cu traces in whisky samples. *Journal of Analytical Chemistry, 361*, 507–509.

Bermejo-Barrera, P., Jurado, J. M., Martin, M. J., Pablos, F., & Moreda-Piñeiro, A. (2007). Direct determination of copper, lead and cadmium in aniseed spirits by electrothermal atomic absorption spectrometry. *Food Chemistry, 101*, 1296–1304.

Bingöl, M., Yentür, G., Erand, B., & Öktem, A. B. (2010). Determination of some heavy metal levels in soft drinks from turkey using ICP-OES method. *Czech Journal of Food Sciences, 28*, 213–216.

Brewer, G. J. (2008). The risks of free copper in the body and the development of useful anti copper drugs. *Current Opinion in Clinical Nutrition & Metabolic Care, 11*, 727–732.

Cassella, R. J., Caldas, L. F. S., Francisco, B. B. A., & Pereira Netto, A. D. (2011). Multivariate optimization of a spectrophotometric method for Copper determination in Brazilian sugar-cane spirits using the Doehlert design. *Microchemical Journal, 99*, 118–124.

Chen, B. L., Zhou, D. Q., & Zhu, L. Z. (2008). Transitional adsorption and partition of nonpolar and polar aromatic contaminants by biochars of pine needles with different pyrolytic temperatures. *Environmental Science and Technology, 42*, 5137–5143.

Costa, D. A., Takeuchi, R. M., & Santos, A. L. (2011). Direct quantification of Cu^{2+} in Cachaça using a solid paraffin-based carbon paste electrode chemically modified with 2-aminothiazole-silica-gel. *International Journal of Electrochemical Science, 6*, 6410–6423.

Double, K. L., Davies, K. M., Hare, D. J., Cottam, V., Chen, N., Hilgers, L., et al. (2013). Localization of copper and copper transporters in the human brain. *Metallomics, 5*, 43–51.

Galani-Nikolakaki, S., Kallithrakas-Kontos, N., & Katsanos, A. A. (2002). Trace element analysis of Cretan wines and wine products. *Science of The Total Environment, 285*, 155–163.

Ganjali, M. R., Motakef-Kazami, N., Faridbod, F., Khoee, S., & Norouzi, P. (2010). Determination of Pb^{2+} ions by a modified carbon paste electrode based on multi-walled carbon nanotubes (MWCNTs) and nanosilica. *Journal of Hazardous Materials, 173*, 415–419.

Janegitz, B. C., Marcolino-Junior, L. H., Campana-Filho, S. P., Faria, R. C., & Fatibello-Filho, O. (2009). Anodic stripping voltammetric determination of copper(II) using a functionalized carbon nanotubes paste electrode modified with crosslinked chitosan. *Sensors and Actuators B: Chemical, 142*, 260–266.

Jernigan, D. H., Monteiro, M., Room, R., & Saxena, S. (2000). Towards a global alcohol policy: Alcohol, public health and the role of WHO. *Bulletin of the World Health Organization, 78*, 491–499.

Keiluweit, M., Nico, P. S., Johnson, M. G., & Kleber, M. (2010). Dynamic molecular structure of plant biomass derived black carbon (biochar). *Environmental Science and Technology, 44*, 1247–1253.

Lehmann, J., & Joseph, S. (2009). *Biochar for environmental management: Science and technology*. London: Earthscan.

Mikkelsen, O., & Schrøder, K. H. (2002). Voltammetry using a dental amalgam electrode for heavy metal monitoring of wines and spirits. *Analytica Chimica Acta, 458*, 249–256.

Ministry of Agriculture. Normative Instruction 13, June 29, 2005 http://extranet.agricultura.gov.br/sislegis-consulta/consultarLegislacao.do?operacao=visualizar&id=12386, http://extranet.agricultura.gov.br/sislegis-consulta/servlet/VisualizarAnexo?id=14175. Accessed November 2013.

Nascimento-Filho, V. F., Cunha e Silva, R. M., Almeida, E., & Valencia, E. P. E. (2004). Determination of Fe, Cu and Zn in sugar-cane spirits commercialized in Southeastern Brazil by TXRF. *Journal of Radioanalytical and Nuclear Chemistry, 260*, 3–7.

Navarro, M., Velasco, C., Jodral, A., Terrés, C., Olalla, M., Lopez, H., et al. (2007). Copper, zinc, calcium and magnesium content of alcoholic beverages and by-products from Spain: Nutritional supply. *Food Additives & Contaminants, 24*, 685–694.

Nobrega, J. A., Neves, E. A., Oliveira, A., & Fernandes, A. P. (2007). Simple and efficient elimination of copper (II) in sugar-cane spirits. *Food Chemistry, 101*, 33–36.

Oliveira, P. R., Tanaka, A. A., Stradiotto, N. R., & Bergamini, M. F. (2012). Anodic stripping voltammetric determination of lead (II) and cadmium (II) by using a carbon nanotubes paste electrode modified with ion exchange synthetic resin. *Current Analytical Chemistry, 8*, 520–527.

Pereira, R. F. R., Vidal, C. B., Lima, A. C. A., Melo, D. Q., Dantas, A. N. S., Lopes, G. S., et al. (2012). Characterization of Alembic and industrial sugar cane spirits from Cape Verde and Ceará, Brazil. *International Journal of Analytical Chemistry, 2012*, 1–6.

Room, R., Babor, T., & Rehm, J. (2005). Alcohol and public health. *Lancet, 365*, 519–530.

Sierksma, A., Hulshof, K. F. A. M., Grobbee, D. E., & Hendriks, H. F. J. (2003). Alcohol: Alcohol consumption. *Encyclopedia of Food Sciences and Nutrition* (2nd ed. pp. 119–126). Baltimore, MD.

Suguihiro, T. M., Oliveira, P. R., Rezende, E. I. P., Mangrich, A. S., Marcolino-Junior, L. H., & Bergamini, M. F. (2013). An electroanalytical approach for evaluation of biochar adsorption characteristics and its application for lead and cadmium determination. *Bioresource Technology, 143*, 40–45.

Tapiero, H., Townsend, D. M., & Tew, K. D. (2003). Trace elements in human physiology and pathology. Copper. *Biomedicine and Pharmacotherapy, 57*, 386–398.

Tavares, E. F. L., Okumura, L. L., Cardoso, M. G., Oliveira, M. F., Magriotis, Z. M., & Saczk, A. A. (2012). An alternative method for the simultaneous determination of copper and lead for quality control of sugar cane spirit using a nanotube-based sensor. *Journal of the Brazilian Chemical Society, 23*, 1614–1622.

Uchimiya, M., Bannon, D. I., Wartelle, L. H., Lima, I. M., & Klasson, K. T. (2012). Lead retention by broiler litter biochars in small arms range soil: Impact of pyrolysis temperature. *Journal of Agriculture and Food Chemistry, 60*, 5035–5044.

Uchimyia, M., Lima, I. M., Klasson, K. T., & Wartelle, L. H. (2010). Contaminant immobilization and release by biochar soil amendment: Roles of natural organic matter. *Chemosphere, 80*, 935–940.

Vicente, M. A., Fietto, L. G., Castro, I. M., Santos, A. N. G., Coutrim, M. X., & Brandao, R. L. (2006). Isolation of *Saccharomyces cerevisiae* strains producing higher levels of flavoring compounds for production of "cachaça" the Brazilian sugarcane spirit. *International Journal of Food Microbiology, 108*, 51–59.

Zenebon, O., Pascuet, N. S., & Tiglea, P. (2008). *In Métodos físico-químicos para análise de alimentos* (4th ed. São Paulo: Instituto Adolfo Lutz (pp. 444–445).