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Spectrophotometric Determination of Copper(II) in Sugarcane Spirit Using 1-(2-pyridylazo)-2-naphthol and a Homogeneous Ternary Mixture of the Solvents Water, Ethanol and Methyl Isobutyl Ketone

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Determinação Espectrofotométrica de Cobre(II) em Aguardente de Cana-de-Açúcar Usando 1-(2-piridilazo)-2-naftol e a Mistura Ternária Homogênea dos Solventes Água, Etanol e Metilisobutilcetona

Resumo: Uma nova técnica analítica rápida, barata e sensível é descrita para a determinação espectrofotométrica de íons cobre(II) em aguardente de cana-de-açúcar, empregando o agente complexante 1-(2-piridilazo)-2-naftol (PAN). Sistemas ternários homogêneos de solventes, comumente denominados de solução fase única, podem ser utilizados como alternativa para pré-concentração de amostras. Por tal razão, empregou-se uma mistura dos solventes água-etanol-metilisobutilcetona (MIC), na proporção 5,0:5,0:2,5 v/v respectivamente. A máxima formação do complexo bis[1-(2-piridilazo)-2-naftalato]cobre(II) ($Cu(PAN)_2$) ocorreu com 0,01% m/v de PAN em MIC, pH de 4,50 da fração aquosa, 15 minutos de tempo de reação e 20 °C de temperatura. Foi verificado que os íons ferro(III) e níquel(II) interferiram na reação. Ácido malônico a uma concentração de 0,10% m/v foi, portanto utilizado como agente mascarante, na qual reduziu a magnitude dos efeitos de interfrência de 10,4% para aproximadamente 2,6%. Nas condições otimizadas de determinação de cobre(II), a curva analítica obtida pode ser descrita por: $\Delta Abs = 0{,}152\ C_{Cu(II)} + 0{,}011$ ($r^2 = 0{,}9997$). A linearidade foi obtida até uma concentração de 8,00 mg L^{-1} de cobre(II), e limite de detecção e de quantificação (calculados usando o desvio padrão do branco) foram 0,02 mg L^{-1} e 0,13 mg L^{-1} de cobre(II), respectivamente, na fração aquosa da solução fase única. O método foi aplicado para determinar íons cobre(II) em amostras comerciais de aguardente de cana-de-açúcar. Os resultados obtidos pelo método proposto foram estatisticamente iguais com os obtidos pelo método padrão.

Palavras-chave: Cobre; espectrofotometria de absorção molecular; 1-(2-piridilazo)-2-naftol; sistema ternário homogêneo de solventes; aguardente de cana-de-açúcar.

Abstract

A fast, inexpensive and sensitive new analytical technique is described for the spectrophotometric determination of copper(II) ions in sugarcane spirit, employing the complexation agent 1-(2-pyridylazo)-2-naphthol (PAN). Homogeneous ternary solvent systems, commonly known as single-phase solutions, can be used as a way of preconcentrating samples. Here, a solvent mixture consisting of water-ethanol-methyl isobutyl ketone (MIBK) at a ratio of 5.0:5.0:2.5 (v/v) was employed. Maximum formation of the bis[1-(2-pyridylazo)-2-naphthalate]copper(II) ($Cu(PAN)_2$) complex was achieved with 0.01% (m/v) of PAN in MIBK, pH 4.5 in the aqueous fraction, 15 min reaction time, and temperature of 20 °C. It was found that iron(III) and nickel(II) ions interfered in the reaction. Malonic acid at a concentration of 0.10% (m/v) was therefore used as a masking agent, which reduced the magnitude of the interference effect from around 10.4% to approximately 2.6%. Under optimized conditions for determination of copper(II), the analytical curve obtained could be described by: $\Delta Abs = 0.152\ C_{Cu(II)} + 0.011$ ($r^2 = 0.9997$). Linearity was obtained up to a concentration of 8.0 mg L^{-1} of copper(II), and limits of detection and quantification (calculated using the standard deviation of the blank) were 0.02 and 0.13 mg L^{-1} of copper(II), respectively, in the aqueous fraction of the single-phase solution. The method was applied to determine copper(II) ions in commercial brands of sugarcane spirits. The results obtained by the proposed method were statistically similar with those given by the standard method.

Keywords: Copper; molecular absorption spectrophotometry; 1-(2-pyridylazo)-2-naphthol; homogeneous ternary solvent system; sugarcane spirit.

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Spectrophotometric Determination of Copper(II) in Sugarcane Spirit Using 1-(2-pyridylazo)-2-naphthol and a Homogeneous Ternary Mixture of the Solvents Water, Ethanol and Methyl Isobutyl Ketone

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1. Introduction

The production of sugarcane spirit is expanding in Brazil, with the aid of government support. It is the second most popular alcoholic drink in the country, after beer, and occupies third place in terms of global consumption of spirits, behind vodka and sochu (a South Korean spirit derived from sorghum). In Brazil, sugarcane spirit is defined in Normative Instruction n° 13 of 29/06/2005, of the Ministry of Agriculture, Livestock and Supply (MAPA), as a drink with an alcohol content of between 38 and 54% v/v at 20.0 °C, obtained from simple alcoholic distillation of sugarcane or by distillation of the fermented sugarcane must.[1-6]

The increased consumption of sugarcane spirit, together with greater exports, requires that the manufacturing process should be based on rigorously controlled practices in order to obtain a standardized product with satisfactory physicochemical and sensory characteristics. Suitable analytical procedures are therefore required to ensure the quality of the product, in terms of both its organic (secondary components) and inorganic (metals and other substances) composition. Amongst the inorganic compounds, copper plays an important role in determining the final quality of the product, and a maximum concentration of 5.00 mg L^{-1} is permitted according to national legislation . In the European Union, the maximum permissible copper concentration is 2.00 mg L^{-1}.[6-8]

Sugarcane spirit is normally produced using copper stills, which enables a better quality product to be obtained, compared to the use of stills manufactured from other materials such as stainless steel. Nevertheless, this practice can result in contamination of the product with copper when improper procedures are used, especially during the cleaning and sterilization steps. Contamination can occur during the distillation process, when the metal of the internal walls of the still is exposed to humid air containing carbon dioxide and becomes slowly oxidized and covered with a green layer of copper(II) dihydroxycarbonate ($[CuCO_3Cu(OH)_2]$). This compound can be dissolved by the acidic alcoholic vapors, hence contaminating the distillate.[9-12]

An excess of copper in the organism causes interference in the catalytic activities of several enzymes, and can result in a variety of neurodegenerative diseases such as Wilson's Disease, Menkes' Disease, and Alzheimer's Disease, as well as aceruloplasminemia, sclerosis, and rheumatoid arthritis. Copper in excess can also be carcinogenic, causing melanoma, a type of malignant cancer characterized by the appearance of black patches on the skin, potentially leading to blindness and death.[13,14]

A relatively simple technique that can be used for the quantitative analysis of metal ions, employing complexation agents, is to use homogeneous mixtures of solvents, together with spectrophotometry employing molecular absorption in the visible region. The homogeneous mixture of solvents consists of a single liquid phase composed of an aqueous phase, an organic liquid immiscible in water, and a third liquid miscible in both of the former liquids. This system was first proposed as a reaction medium for subsequent liquid-liquid extraction, as an alternative preconcentration technique. The metallic ion is introduced into the system by means of the aqueous fraction, and the complexation agent is contained in the organic fraction that is immiscible with water. Addition of the second organic solvent, which is immiscible in the two other solvents, results in all the phases becoming miscible, enabling the complexation reaction between the metal ion and the complexation agent to proceed. This type of ternary system offers a useful alternative methodology for a variety of analytical measurements.[15,16]

The objective of the present work was to develop an alternative procedure for the determination of copper(II) ions in sugarcane spirit, employing the reaction with the complexation agent 1-(2-pyridylazo)-2-naphthol conducted in a homogeneous ternary mixture of the solvents water, ethanol, and MIBK, with spectrophotometric detection in the visible region.

2. Materials and Methods

2.1. Phase diagram obtainment

To obtain the phase diagram, the technique used was phase titration using the solvents water, ethanol, and MIBK [17,18]. Pairs of the miscible solvents were titrated with the third solvent until the point of opalescence was reached, characterized by the appearance of an emulsion in the titration medium. Different combinations of volumes of the miscible solvents were used in the procedure, and the volumes of water, ethanol, and MIBK used in the titration were converted to mass percentages. A binodal curve was obtained for the system, with the phase diagram split into two regions, one monophasic (single-phase solutions) and the other biphasic (binary mixtures).

2.2. Molecular absorption measurements

The molecular absorption spectrum of the PAN ligand in the visible region (350-700 nm) was recorded using a solution consisting of 5.0 mL of deionized water, 5.0 mL of ethanol, and 2.5 mL of a solution of 0.01% (m/v) PAN in MIBK. The spectrophotometer (Model SP-850, Metertech, Nangang, Taiwan) was fitted with a 1 cm optical path length quartz cuvette and was operated at an ambient temperature of 20 ± 2 °C. The molecular absorption spectrum of the coordination compound formed by reaction between the PAN ligand and the copper(II) ions (at a concentration of 5.00 mg L^{-1} in water), as well as that of the mixture of solvents (solvent blank), were obtained under the same conditions described previously. All the experiments employed measurements at the maximum absorbance wavelength of the $Cu(PAN)_2$ complex (556 nm).

2.3. Optimization of reaction conditions

2.3.1. pH

The influence of the pH of the aqueous fraction of the ternary system, in terms of the formation of the coordination compound, was evaluated using a pH range of 2.0-6.0, in increments of one pH unit. The adjustment of pH employed dilute solutions of nitric acid (0.01 mol L^{-1}) or ammonium hydroxide (0.01 mol L^{-1}).

2.3.2. Time and temperature

The influence of temperature and reaction time on formation of the complex was investigated in a chemometric study employing a factorial design (star-type with a central point) with two levels and two factors, performed using Statistica v.8.0 software [19,20]. Temperatures of 20.0 and 30.0 °C were used, with times of 10.0 and 20.0 min. The solvent ratio was maintained constant at 5.0:5.0:2.5 (v/v) (water/ethanol/MIBK), the pH of the aqueous fraction was 4.50, the copper(II) concentration was 5.00 mg L^{-1}, and the concentration of PAN in MIBK was 0.01% (m/v).

2.3.3. Concentration of complexation agent

The influence of the concentration of the PAN complexation agent in the MIBK fraction was evaluated in the range from 0.002 to 0.02% (m/v), with increments of 0.002%. The conditions of the ternary system, pH of the aqueous fraction, concentration of copper(II) ions, temperature, and reaction time were maintained fixed at the optimized values.

2.3.4. Influence of the solvents on sensitivity

An experimental design was performed with 10 mixtures in the monophasic region of the water-ethanol-MIBK phase diagram (Figure 1), as recommended for this type of study [20]. For preparation of the homogeneous mixtures, the solvent ratio was maintained constant at 5.0:5.0:2.5 (v/v) (water/ethanol/MIBK), the pH of the aqueous fraction was 4.50, the copper(II) concentration was 5.0 mg L^{-1}, and the concentration of PAN in MIBK was 0.01% (m/v).

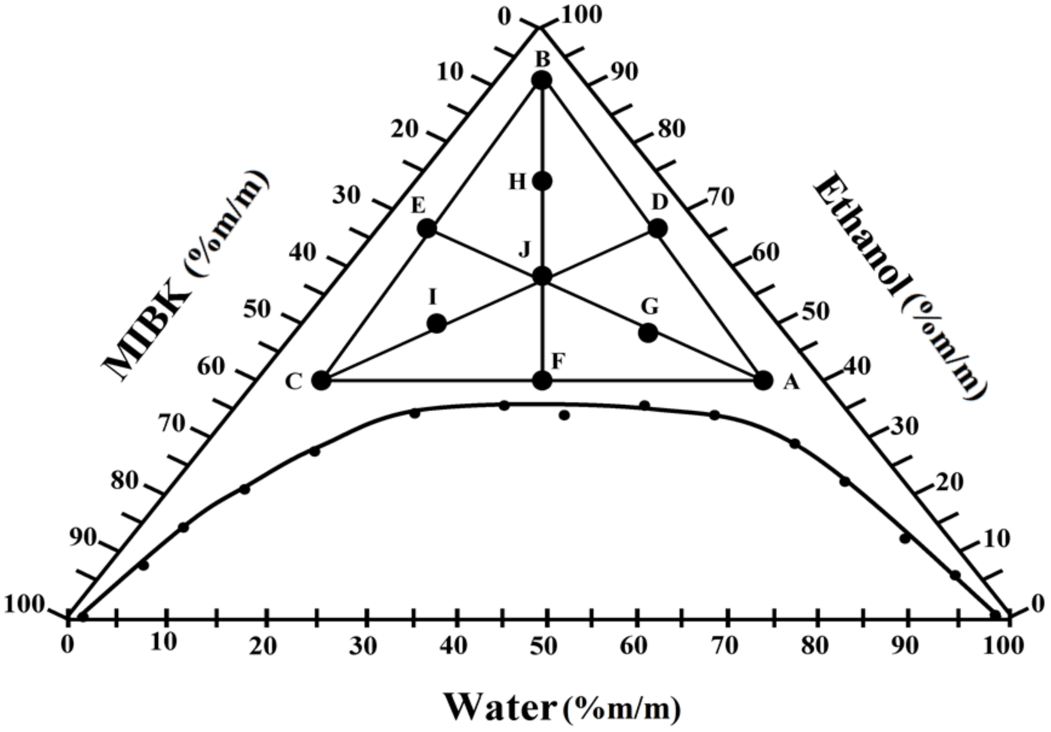


Figure 1. Water-ethanol-MIC phase diagram (% m/m) at 20 ºC, indicating the selected solvent compositions for the study of influence of solvents in sensitivity

3. Validation of the method

3.1. Analytical calibration curve

The calibration curve was constructed using 15 points, using concentrations of copper(II) ions in the aqueous phase ranging from 1.0 to 15.0 mg L^{-1}, with increments of 1.00 mg L^{-1} and maintaining the complexation agent concentration at 0.01% (m/v), the pH at 4.50, the reaction time at 15 min, and the temperature at 20 ± 2 °C. All the points of the curve were measured in triplicate. The relative standard error of the curve was determined using copper(II) ion concentrations of 1.00 and 7.00 mg L^{-1}. These measurements were made in quintuplicate.

3.2. Study of interferences

A chemometric study employing a 2^4 star-type factorial design was used to evaluate the behavior of the analytical signal for the determination of copper(II) ions in the presence of iron(III), nickel(II), and malonic acid. The concentrations in the aqueous fraction of the single-phase solution used were 0 and 5.00 mg L^{-1} of copper(II), 0 and 0.10 mg L^{-1} of nickel(II), 0 and 0.30 mg L^{-1} of iron(III), and 0 and 0.10% (m/v) of malonic acid. The upper levels selected for nickel(II) and iron(III) were based on the permissible limit values for these ions in sugarcane spirit, according to the norms established by National Health Surveillance Agency (ANVISA) (0.10 mg L^{-1} for nickel(II) and 0.30 mg L^{-1} for iron(III)) [21]. The effects of these interferents were evaluated using a cause-effects graph [20](Figure 5).

3.3. Optimization of the concentration of the malonic acid masking agent

The influence of the malonic acid concentration in reducing the interference effects was assessed using concentrations in the aqueous fraction in the range 0.02-0.10% (m/v), with increments of 0.02%. The interference factor was calculated considering the amounts of the interfering ions, relative to copper(II). The pH of the aqueous fraction was maintained constant at 4.50, the concentration of copper(II) was 5.00 mg L^{-1}, the reaction time was 15 min, and the temperature was 20 ± 2 °C.

3.4. Precision and accuracy of the method

Three samples of sugarcane spirit were simulated, employing an aqueous solution of 40.0% (v/v) ethanol in water. The alcohol content was measured using a hydrometer, and the samples were contaminated with 1.00, 3.00, 5.00, and 7.00 mg L^{-1} of copper(II).

4. Application of the methodology in the determination of copper in samples of sugarcane spirit

Analyses were made of seven brands of sugarcane spirit commonly available in local supermarkets. The alcohol content of each sample was determined using a hydrometer. The copper(II) content was determined by the method proposed in this work, as well as by the standard Association of Official Analytical Chemists (AOAC) methodology [22]. An aliquot of 10.0 mL of sugarcane spirit was pipetted into a beaker (considering the spirit to be a mixture of water and ethanol, and obeying the proportions of the selected point in the diagram: 5.0:5.0:2.5 (v/v) of water-ethanol-MIBK). Additions were then made of the malonic acid masking agent and the PAN complexation agent, under the conditions established previously, and the reaction was allowed to proceed as described above.

All the experiments and analyses were performed in triplicate, and the copper(II) concentrations were determined using the analytical curve.

5. Results and Discussion

5.1. Phase diagram

The results obtained in the titrations using the pairs of solvents were used to construct the ternary phase diagram of the solvents. The values were converted into mass percentages of the solvents used to construct the diagram, employing their respective densities and volumes. This enabled construction of the binodal phase diagram curve (Figure 2).

In the phase diagram, there are two points, located at the base of the triangle, that were not determined by the titrations of the pairs of solvents (Figure 2). The first is the solubility of water in MIC (1.9 g/100.0 g of MIBK at 20 °C) and the second is the solubility of MIBK in water (1.7 g/100.0 g of water at 20 °C), which converted into percentages gives the points obtained from the diagram (1.9 and 98.3% (m/m), respectively). The initial condition was empirically selected as a point in the monophasic region of the phase diagram for which small variations in the quantities of water or MIBK did not affect the equilibrium of the single solution phase, which lay within the demarcated region for the alcohol content of sugarcane spirit (indicated by the dashed lines in Figure 2). The point corresponds to a water-ethanol-MIBK mass ratio of 45.7:36.1:18.2 (% m/m), equivalent to a volume ratio of 5.0:5.0:2.5 (v/v).

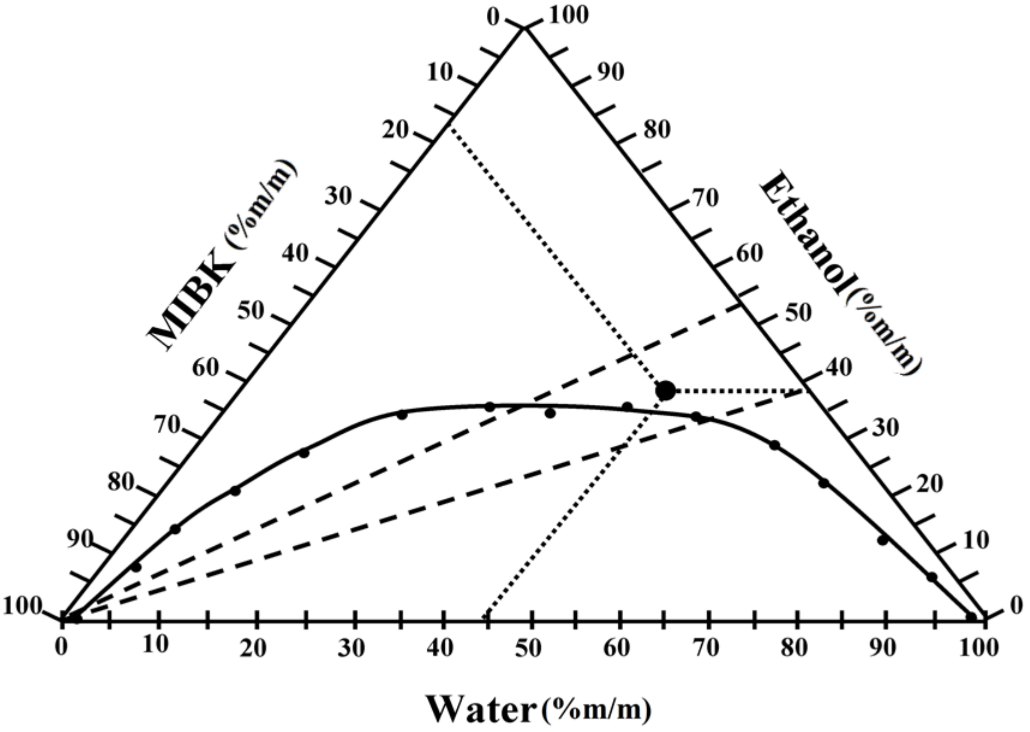


Figure 2. Phase diagram for the water–ethanol–MIC system (%m/m) at 20 ºC

5.2. Absorption spectrum

The PAN form stable complexes with metal ions (copper ions for example) and for presenting a absorptivity coefficient value, relatively high, was chosen as complexing agent for carrying out the studies.

The maximum absorbance of the $Cu(PAN)_2$ coordination compound formed was at 556 nm, at which the absorbance of the ligand was close to its minimum value, resulting in the greatest absorbance difference (ΔAbs). A wavelength of 556 nm was therefore selected for use in the subsequent analyses.

5.3. Optimization of reaction conditions

5.3.1. pH

The significant formation of the coordination compound occurred at pH of around 4.50. On the other hand, at pH greater than 6.00, there was destabilization of the complex, probably due to the formation of copper(II) hydroxide ($Cu(OH)_2$) in the single-phase solution. A pH of 4.50 was therefore adopted as the ideal value for the hydrogen ion concentration in the aqueous fraction of the single-phase solution.

5.3.2. Time and temperature

The aim of the chemometric study of the variables time and temperature was to obtain the greatest difference in absorbance (ΔAbs) in order to maximize sensitivity for determination of the copper(II) ions. Table 1 presents the conditions used and the results obtained, in terms of the absorbance of the $Cu(PAN)_2$ complex, under the experimental conditions described previously. The scaling equations for temperature and reaction time are also shown in Table 1 (Equations 1 and 2, respectively).

Table 1. Factorial design (2^2, star-type with central point) used for optimization of the variables time and temperature

Variable			Levels		
			(-)		(+)
Temperature	(°C), T		20		30
Time (min),	t		10		20
Order of execution	Scaled variables		Absorbance		
	T	t	$Cu(PAN)_2$	PAN	ΔAbs
2	+1	-1	0.689	0.009	0.680
9	0	0	0.693	0.023	0.670
3	-1	+1	0.676	0.003	0.673
10	0	0	0.691	0.024	0.667
6	-1,41	0	0.689	0.010	0.679
7	0	+1,41	0.677	0.017	0.660
8	0	-1,41	0.671	0.016	0.655
1	-1	-1	0.703	0.021	0.682
11	0	0	0.692	0.024	0.668
4	1	1	0.674	0.006	0.668
5	+1,41	0	0.665	0.017	0.648

The values of ΔAbs and the scaled variables (Table 1) were used to obtain the mathematical model describing the ternary solvent system (Equation 1), illustrated graphically in Figure 3.

$$\Delta Abs = 0.668 - 0.006T - 0.002t + 0.001T^2 - 0.002t^2 - 0.001Tt \qquad \text{(Eq. 1)}$$

The term in the mathematical model describing the interaction between the variables (-0.001Tt) shows that the effects of temperature (T) and time (t) were almost independent. The surface response plot (Figure 3) shows that there was greater complex formation (maximum absorbance difference, (ΔAbs) at lower temperatures and intermediate reaction times. Increased sensitivity for the determination of copper(II) ions was achieved at a temperature of 20 °C and reaction time of 15 min.

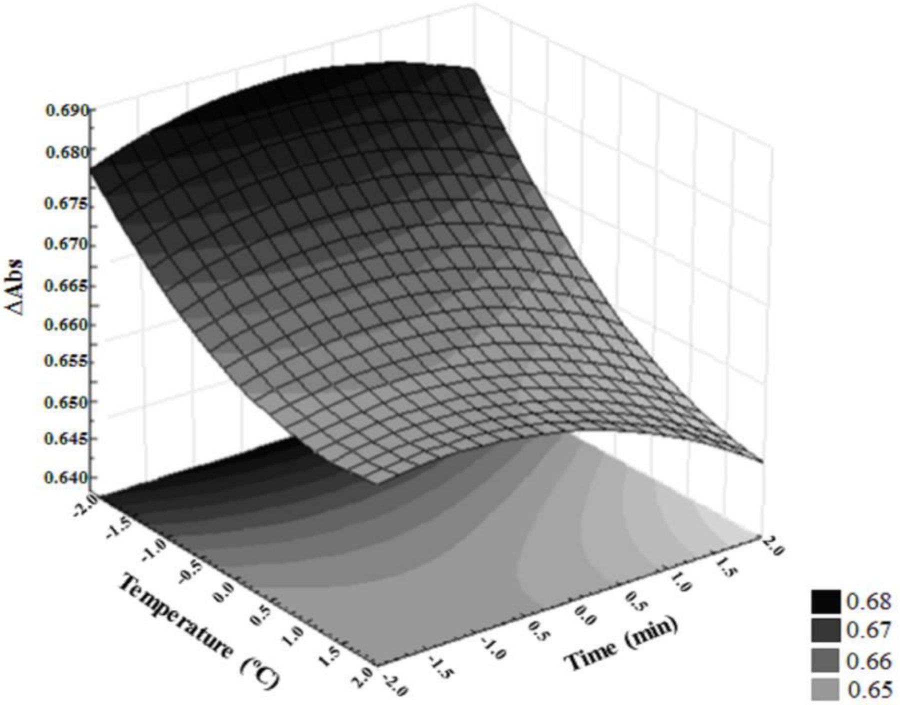


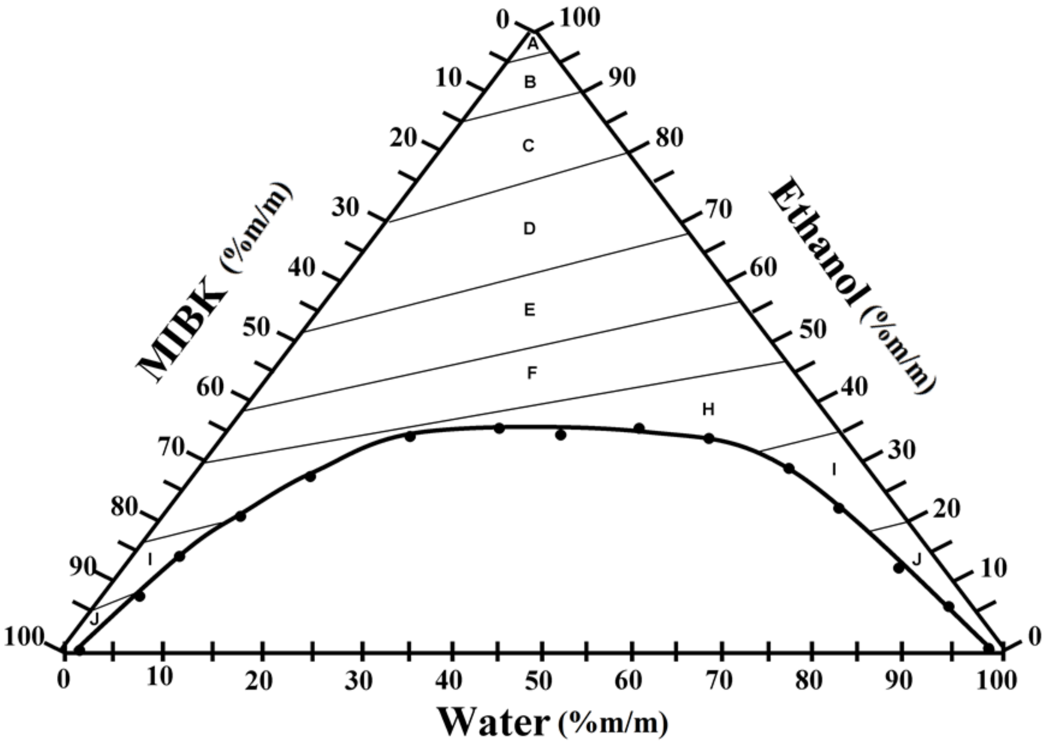
Figure 3. Response surface graph for the influence of the variables time and temperature on formation of the complex

5.3.3. Concentration of complexation agent

An increase in the concentration of the ligand up to around 0.01% (m/v) caused a positive shift in the value of the analytical signal. After this reagent concentration, the gain in the analytical signal was relatively insignificant, relative to the increase in the concentration of PAN. A concentration of 0.01% (m/v) PAN in MIBK was therefore selected based on satisfactory absolute absorbance values and a good increase in sensitivity.

5.3.4. Influence of the solvents on sensitivity

The influence of the solvents was evaluated using a surface contour diagram of the phases (Figure 4). It can be seen that the absorbance increased closer to the internal binodal curve dividing the diagram into two regions. Nevertheless, the absolute value of this increase was not significant, so a change in the composition of the water-ethanol-MIC solvent mixture was not justified. Furthermore, the solvent composition initially selected (5.0:5.0:2.5 (v/v)) possessed the same alcohol content as sugarcane spirit, enabling the direct determination of copper(II) ions in this matrix.



Absorbance values for the regions: A<B<C<D<E<F<G<H<I<J.

Figure 4. Lines of contour of surface for the water-ethanol-MIBK system (%m/m) at 20 ºC

6. Validation of the method

6.1. Analytical calibration curve

The analytical curve (Figure 5) presented linearity up to 8.0 mg L^{-1}, and could be described by the equation: $\Delta Abs = 0.152\ C_{Cu(II)} + 0.011$ ($r^2 = 0.9997$). The detection and quantification limits were 0.02 and 0.13 mg L^{-1}, respectively, calculated using the standard deviation of the reagent blank.

6.2. Standard error of the analytical calibration curve

The relative standard error of the calibration curve was determined using copper(II) ion concentrations of 1.00 and 7.00 mg L^{-1} (within the linear range of the curve) in the aqueous fraction of the single-phase solution. The values obtained were 1.1 and 1.9% for the 1.00 and 7.00 mg L^{-1} levels, respectively.

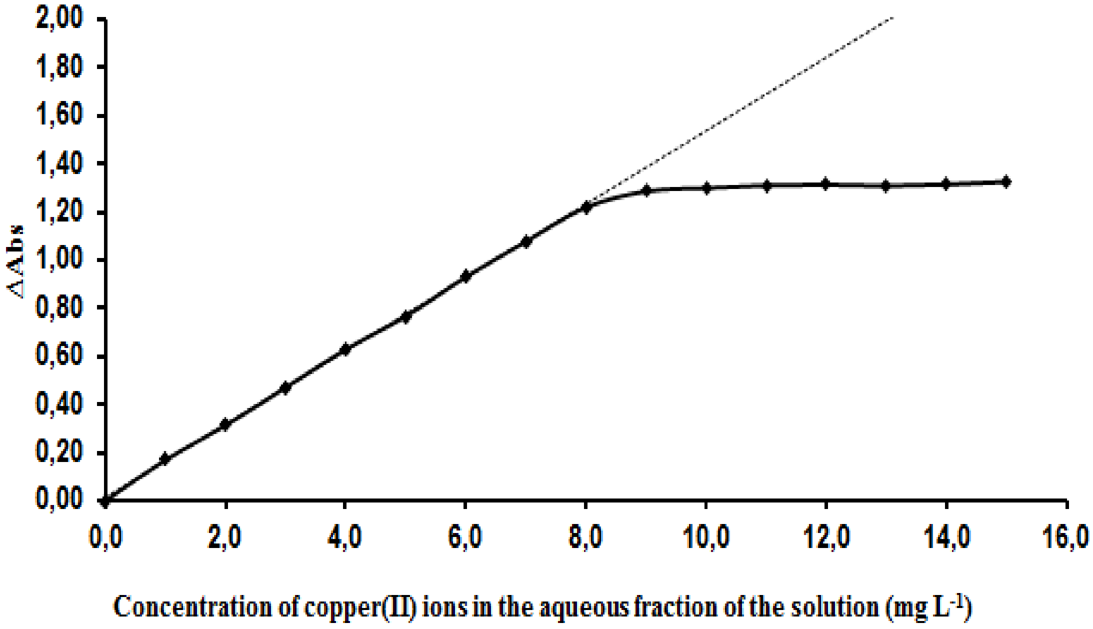


Figure 5. Analytical calibration curve for copper(II) ions in the aqueous fraction of the single-phase solution

6.3. Study of interferences

The main interferents identified, which reacted with PAN under the conditions used and absorbed in the region where they competed with the absorbance of the coordination compound formed between copper(II) and PAN, were the ions iron(III) and nickel(II) (Figure 6).[23] Malonic acid has been used in order to minimize or eliminate such interferences.[24] A 2^4 star-type factorial design was therefore used to evaluate the behavior of the analytical signal for the determination of copper(II) ions in the presence of iron(III), nickel(II), and malonic acid. Calculation was made of the main effects and interactions, which were plotted in the form of a cause-effects graph (Figure 5).[20]

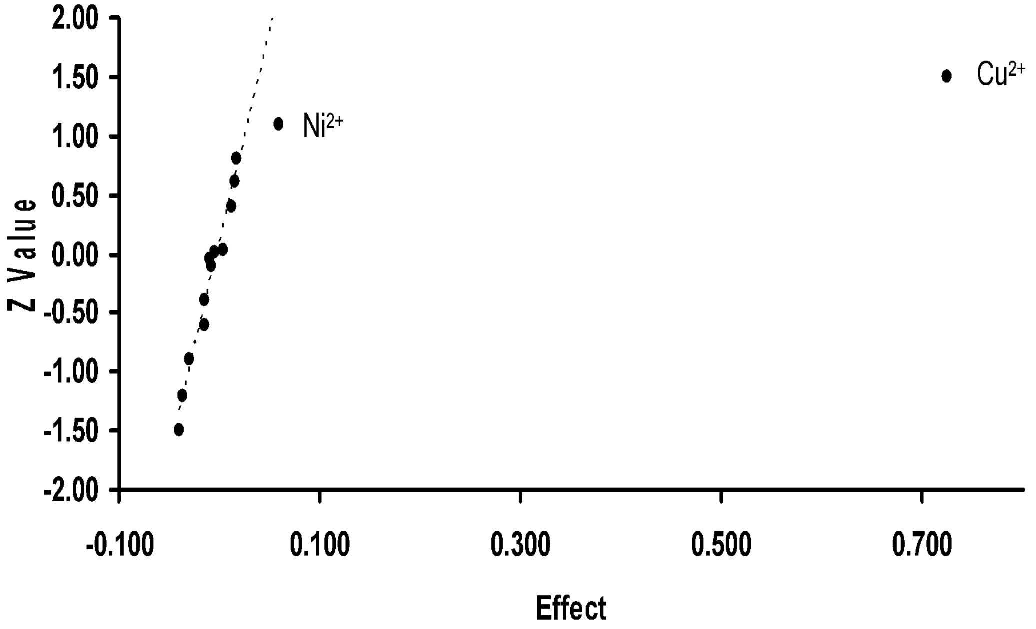


Figure 6. Cause-effects graph for copper(II), nickel(II), iron(III), and malonic acid

In this graph, the points that departed substantially from the straight line were considered to indicate important effects that significantly influenced the analysis of copper(II) ions in sugarcane spirit. It can be seen that only nickel(II) and copper(II) exerted any effects on the system, and that although nickel(II) was an interferent, the intensity of the effect was low. On the other hand, since copper(II) was the analyte of interest, it was expected that it would present this effect. The interference effect of the nickel(II) ions was able to be minimized or eliminated using the masking agent, because these ions showed no effect in the presence of malonic acid (Figure 6). The results showed that iron(III) ions did not exert any interfering effects, under the analytical conditions used, even in the absence of the masking agent.

6.4. Optimization of the concentration of the malonic acid masking agent

Having shown that addition of the malonic acid masking agent could reduce the interference effects of the nickel(II) ions, the concentration of malonic acid was optimized by altering its concentration in the aqueous fraction, while maintaining all other conditions constant, and observing the degree of interference in the reaction. The higher concentration of the masking agent acted to decrease the interference effect, up to a concentration of around 0.10% (m/v) of malonic acid in water. After this concentration, there were no further significant changes in the value of the analytical signal. The results showed that the interference effect could be reduced from 10.4 to 2.6%, which was within established tolerable limits.

6.5. Precision and accuracy of the method

Due to the absence of certificated sugarcane spirit standards, the precision and accuracy of the method were evaluated by preparing simulated samples of sugarcane spirit. The results obtained, in terms of recovery, standard deviation, and analytical error, are shown in Table 2.

Table 2. Recoveries, standard deviations, and relative errors obtained for measurement of copper(II) ions in simulated samples of sugarcane spirit

Simulation	[Cu^{2+}] added (mg L^{-1})	[Cu^{2+}] recovered (mg L^{-1})	Relative error (%)
1	1.00	0.994 ± 0.008	- 0.60
2	3.00	2.980 ± 0.010	- 2.00
3	5.00	5.018 ± 0.006	1.80
4	7.00	6.988 ± 0.013	- 1.20

For all the concentrations of copper(II) ions evaluated, the relative errors were within the range considered acceptable (≤5.0%). The recovery values showed that the method provided good accuracy, and low standard deviations were indicative of satisfactory precision.

7. Application of the methodology in the determination of copper(II) ions in sugarcane spirit

The proposed method was applied using seven commercial brands of sugarcane spirit purchased in supermarkets and specialized shops. The official method was also employed for comparative purposes (Table 3).

Comparison of the two methodologies showed that there were only very small differences in the measured concentrations of copper(II) ions in the samples analyzed. The differences were within acceptable levels of reliability, showing that the proposed methodology provided good accuracy and precision for the analysis of sugarcane spirit. None of the samples analyzed contained copper(II) concentrations exceeding the limit established by Brazilian legislation, indicating that the procedures used to clean and maintain the stills employed in the production processes were satisfactory.

Table 3. Concentrations of copper(II) ions in commercial samples of sugarcane spirit

Sample	Alcohol content (% v/v)	[Cu^{2+}] (mg L^{-1}) (standard method)	[Cu^{2+}] (mg L^{-1}) (proposed method)	Relative error (%)
1	40.0	0.72 ± 0.026	0.74 ± 0.009	2.77
2	42.0	1.56 ± 0.040	1.51 ± 0.005	- 3.21
3	46.0	1.07 ± 0.060	1.09 ± 0.006	1.87
4	39.0	0.93 ± 0.093	0.92 ± 0.002	- 1.08
5	44.0	0.84 ± 0.067	0.86 ± 0.015	2.84
6	38.0	1.45 ± 0.038	1.48 ± 0.007	2.07
7	40.0	3.30 ± 0.031	3.34 ± 0.010	1.21

8. Conclusions

The proposed methodology employing a homogeneous ternary solvent system (water-ethanol-MIBK at a ratio of 5.0:5.0:2.5 (v/v), with PAN as a complexation agent, provided a fast, efficient and low-cost technique for the determination of copper(II) ions in sugarcane spirit. The accuracy achieved was within acceptable levels.

Concentrations of copper(II) ions in commercial samples of sugarcane spirit were within the limit established by Brazilian legislation. However, one of the samples contained copper(II) at level exceeding the limit value established by the European Union, and would therefore be unsuitable for export.

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