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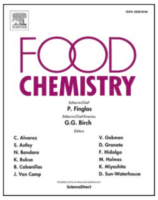

Multivariate optimization of a dispersive liquid-liquid microextraction method for determination of copper and manganese in coconut water by FAAS

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ABSTRACT

In this study, multivariate methodologies were applied in the optimization of a dispersive liquid–liquid microextraction (DLLME) method, aiming at the determination of Cu and Mn in coconut water samples by flame atomic absorption spectrometry. Some extractors (chloroform and CCl_4), dispersants (ethanol, methanol and acetonitrile) and complexing agents (5-Br-PADAP and Dithzone) were previously tested in the extraction. A mixture design was used to optimize the component proportions formed by chloroform (10%), acetonitrile (76%), and 0.020% 5-Br-PADAP solution (14%). Doehlert design optimized the variables pH, NaCl, and buffer amounts for the extraction of both metals. The following analytical characteristics, respectively for Cu and Mn, were accessed: limit of quantification (4.83 and 3.32 μg L^{-1}), enrichment factors (11 and 8 fold), and precision (6.6 and 6.0% RSD, n = 10). Addition/recovery tests of the analytes allowed to find values in the range of 96.5–120% for Cu and 99–107% for Mn.

1. Introduction

Coconut water is an isotonic drink appreciated worldwide due to its pleasant taste and nutritional and medicinal properties (Lakshmanan et al., 2020). It is widely consumed cold in Brazil, mainly in coastal regions with tropical climate, for offering a refreshing sensation, hydrating the body and replenishing the mineral salts lost in sweat. Coconut water is obtained from the fruit of the coconut tree (*Cocos Nucifera* L.), which is formed inside it as a strategy for storing nutrient reserve substances and as a survival mechanism for the plant. This food is a source of carbohydrates, lipids, proteins, vitamins, and minerals such as Ca, Fe, Mg, Na, P, K, among others (Richter et al., 2005, Rosa, Rodrigues, & Ferreira, 2005, Alchoubassi et al., 2021, Cunha et al., 2020). The concentrations of these nutrients can vary widely depending on soil, maturation period of the fruit, frequency of irrigation and climatic conditions. The increasing demand for this product has aroused interest in the development of fast, efficient, sensitive and reliable analytical methods for the determination of its sensory characteristics, physical properties and chemical composition (Kumar et al., 2021, de Sousa et al., 2005, Paixão et al., 2019).

In the development of these new analytical methods, multivariate optimization tools have been widely applied with success (Bezerra et al., 2008, Callao, 2014, Ferreira et al., 2019). The main advantages of this approach are the offer of a faster and more efficient optimization, taking into account the influence and significance of the variables and the evaluation of the interactions between them (Ferreira, 2015, Bruns, Scarminio & Barros Neto, 2006, Brown, Tauler & Walczak, 2009). Mixture design and Doehlert design (Ferreira et al., 2007) were applied to develop the method presented in this article.

Mixture design has been applied to find the best proportions between the components that are part of a mixture. In this type of design, the variables must satisfy the dependency condition $x_1 + x_2 + \ldots + x_k = 1$, where k is the number of components of the mixture to be optimized. It is frequently necessary to establish restrictions on component levels, due to the impossibility of carrying out the experiments in some areas of the design (Bezerra et al., 2020). Doehlert design has been applied to optimize process variables. In this case, the combination between the levels of the variables occurs without meeting the required conditions as in

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mixtures. This design has the advantage of being efficient and allowing variables to be studied at different levels, which is not the case with other designs such as Central Composite and Box-Benhken (Bezerra et al., 2008, Brown, Tauler & Walczak, 2009).

Trace metal determinations sometimes demand a pre-concentration step to make this task possible. Dispersive liquid–liquid microextraction (DLLME) (Dadfarnia and Haji Shabani, 2010, Mousavi, Tamiji & Khoshayand, 2018) is a separation technique based on a ternary solvent system. DLLME differs from the traditional liquid–liquid extraction in dealing with small volumes of solvents and samples. It is performed by injecting an extraction mixture and dispersive solvents in the aqueous sample, causing the formation of droplets of the acceptor phase dispersed within the donor phase. As a consequence, the interfacial area between the phases has a great increase. It leads to a fast and efficient transfer of the analyte present in the sample (donor phase) to the extraction solvent (acceptor phase), since partition equilibrium is immediately achieved. The mixture must be centrifuged, carrying the droplets to settle to the tube bottom. The extraction solvent, already with the analyte, is separated and taken for instrumental determination. The main advantages of DLLME are (i) low cost, (ii) simplicity and operational speed, (iii) the need for a small sample volume, (iv) low solvent consumption, (v) high recoveries, and (vi) the high enrichment factors obtained. Its main disadvantages are: (i) the need to use three solvents, (ii) the separation of the phases must be carried out by centrifugation, and (iii) the need to use a high-density extraction solvent ends up limiting the options to be used (Almeida et al., 2021, Lemos et al., 2019, Santos et al., 2017).

DLLME has already been used in the food field to determine: Cd traces in honey samples by FAAS (Sixto, Mollo & Knochen, 2019), Mn (II) and Mn (VII) in tea samples by FAAS (Wen & Zhu, 2014), total arsenic in edible oil by ETAAS (López-García et al., 2015), Cd, Pb, Ni, Cu and Co in seafood by ICP OES (Lemos & dos Santos Vieira, 2014), Tl in water and spinach by ETAAS (Javedani-Asleh, Eftekhari & Chamsaz, 2016), Cu in flour, rice and water by FAAS (Karadaş & Kara, 2017), Cd and Pb in soft drinks by GFAAS (Mandlate et al., 2017), Sn and Sb in fruit juice and soft drinks by ICP OES (Biata et al., 2017), Al and Cr (VI) in mushrooms, tea leaves, tomato and pepper by FAAS (Altunay, Yildirim & Gürkan, 2018), Fe in banana, carrot and water samples by ultraviolet–visible spectrophotometry (Borzoei et al., 2018), Cd, Cu and Pb in milk samples by FAAS (Sorouraddin, Farajzadeh & Dastoori, 2020), Ni in chocolate by FAAS (Barreto et al., 2019), among others.

In this paper, a method for determining Cu and Mn trace concentrations in coconut water samples by flame atomic absorption spectrophotometry was developed. DLLME was used as a preconcentration technique, and the variables involved in its performance were optimized by multivariate optimization methodologies (mixture design and Doehlert design). Additionally, the method was validated and its analytical characteristics were assessed, showing it is adequate for carrying out this task.

2. Experimental

2.1. Instrumentation

The determinations of Cu and Mn in the extracts obtained after DLLME were performed by a flame atomic absorption spectrometer (Perkin Elmer, Norwalk, CT, USA). Hollow cathode lamps for Cu and Mn were used in the absorption measures. Spectral resolutions (0.7 and 0.7 nm) and wavelengths (324.8 and 279.5 nm) were used according to the manufacturer's recommendation, respectively, for Cu and Mn. The flame consisted of a mixture of acetylene gas (flow rate 2.0 L min^{-1}) and atmospheric air (flow rate 13.5 L min^{-1}). The flow rate for sample nebulization was 5.0 mL min^{-1}.

Phase separation was carried out in a Quimis Q222T centrifuge (São Paulo, Brazil). Ultrapure water (conductivity of 18 MΩ cm) was obtained from an Elga system (Purelab Classic). A digester block (Tecnal, model 040125, Piracicaba, Brazil) with glass tubes associated with a cold finger was used for sample decomposition; pH measurements were taken using a Quimis Q400 pH meter.

2.2. Reagents and samples

The chemicals used in all experiments carried out in this research were of analytical purity grade, and ultrapure water was used to prepare the used solutions. The stock solutions of Cu and Mn (1000 mg L^{-1}) were individually prepared from the dilution of the standard solution (Merck, Darmstadt, Germany). A 0.040% (m v^{-1}) Dithizone (1,5-diphenylthiocarbazone, Sigma-Aldrich, Milwaukee, USA) solution was prepared, dissolving a mass of 0.040 g of the chemical, diluting it in ethanol, and then transferring to a 100 mL volumetric flask; the volume was completed with ethanol (Exôdo Científica, São Paulo, Brazil). A 0.020% (m v^{-1}) 5-Br-PADAP (2-(5-Bromo-2-pyridylazo)-5- (diethylamino)-phenol, Sigma-Aldrich, Milwaukee, USA) solution was prepared by weighing 0.02 g of the chemical, diluting it in ethanol, and then transferred to a 100 mL volumetric flask; the volume was completed with ethanol. Buffer solutions (0.1 mol L^{-1}) were prepared for pH values 6.0, 7.0, 8.0 (citrate/phosphate buffer), 9.0 and 10.0 (boric acid /borate buffer). Decomposition was carried out in a hot plate using concentrate nitric acid and hydrogen peroxide (Êxodo Científica, São Paulo, Brazil). Studies on extraction induced by emulsion breaking were carried out using carbon tetrachloride (Merk, Darmstadt, Germany), chloroform (Química Moderna, Barueri, Brazil), Acetonitrile (Neon, Suzano, Brazil), acetone (Neon, Suzano, Brazil), ethyl alcohol (Exôdo Científica, São Paulo, Brazil) and methanol (Química Moderna, Barueri, Brazil).

2.3. Sample collection and preparation

Raw and industrialized coconut water samples were acquired in markets and fairs located in Jequié city (Bahia state, Brazil). The samples were digested with the aid of a hot plate. Concentrated nitric acid (2.0 mL) and hydrogen peroxide (1.0 mL) were added to 30.0 mL of the sample. The samples were digested in the temperature range of 110–120 °C for approximately 2 h. Digestion blanks were prepared in the same way as the digested samples. After cooling to room temperature, pH was adjusted with a concentrated sodium hydroxide solution before buffer addition.

2.4. DLLME optimization

The proportions of the mixture (extraction solvent, dispersive solvent, and complexing reagent) to carry out the DLLME were optimized using a constrained mixture design. The experimental mixture design matrix used in this procedure is shown in Table 1. Doehlert design was used for the optimization of the process variables. The variables studied were pH (6 to 10), volume of the 0.1 mol L^{-1} buffer solution (1.0 to 5.0 mL), both studied at five levels. The concentration of the 5% (mv^{-1}) NaCl solution (0 to 4.0 mL) was studied at three levels. The experimental matrix for the Doehlert design is shown in Table 2. The software Statistica® version 10.0 was used to generate experimental matrices, mathematical modeling and graphs. Microsoft Excel 2016® software was used to calculate basic statistical parameters, construction of bar graphs, and analytical curves.

2.5. Procedure for performing the DLLME after optimization

To perform the extractions, graduated centrifuge tubes (50.0 mL) of a conical bottom were used. A volume of 30.0 mL of the digested samples was put in the centrifuge tube with the pH previously adjusted with NaOH to a value close to that of the extraction pH. Subsequently, pH was adjusted and kept (4.0 for Cu and 9.5 for Mn) with buffer solution. In the next step, a NaCl solution (5%, mv^{-1}) and a complexing agent solution (0.7 mL of 0.020%, m v^{-1} 5-Br-PADAP) were added into the tube. The

Table 1
Experimental matrix and results of a constrained mixture design used in the optimization of dispersive liquid-liquid microextraction of copper and manganese.

Exp.	Acetonitrile volume (μL)	Chloroform volume (μL)	Complexing volume (μL)	Absorbances	
				Cu	Mn
1	4000 (0.800)	500 (0.100)	500 (0.100)	0.075/0.063/0.062	0.018/0.029/0.015
2	3500 (0.700)	1000 (0.200)	500 (0.100)	0.011/0.011/0.014	0.005/0.004/0.002
3	3500 (0.700)	500 (0.100)	1000 (0.200)	0.037/0.032/0.052	0.027/0.017/0.022
4	3750 (0.750)	750 (0.150)	500 (0.100)	0.026/0.019/0.022	0.008/0.007/0.006
5	3750 (0.750)	500 (0.100)	750 (0.150)	0.073/0.067/0.064	0.029/0.034/0.032
6	3500 (0.700)	750 (0.150)	750 (0.150)	0.021/0.017/0.021	0.006/0.006/0.009
7	3667 (0.733)	666 (0.133)	667 (0.133)	0.029/0.026/0.023	0.009/0.010/0.010
8	3833 (0.767)	583 (0.117)	583 (0.117)	0.040/0.042/0.032	0.010/0.010/0.010
9	3583 (0.717)	833 (0.167)	583 (0.117)	0.021/0.018/0.016	0.005/0.005/0.003
10	3583 (0.717)	583 (0.117)	833 (0.167)	0.022/0.029/0.028	0.013/0.012/0.013

Table 2
Doehlert design and responses for Cu and Mn in the optimization of process variables in the DLLME procedure.

Exp.	pH	Buffer volume (mL)	NaCl volume (mL)	Absorbances	
				Cu	Mn
1	8	5	2	0.024/0.021	0.010/0.009
2	7	4	0	0.029/0.025	0.003/0.002
3	7	4	4	0.032/0.031	0.001/0
4	9	4	0	0.024/0.021	0.019/0.018
5	9	4	4	0.028/0.028	0.018/0.020
6	6	3	2	0.049/0.045	0/0.001
7	8	3	2	0.025/0.024	0.016/0.015
8	10	3	2	0.018/0.021	0.014/0.012
9	7	2	0	0.034/0.033	0.002/0.002
10	7	2	4	0.027/0.028	0.002/0.002
11	9	2	0	0.031/0.031	0.025/0.021
12	9	2	4	0.018/0.017	0.023/0.022
13	8	1	2	0.022/0.024	0.002/0.001

extraction solvent (acetonitrile 3.8 mL) and dispersive solvent (ethanol 0.5 mL) were added. The mixture was manually stirred to facilitate solvent dispersion, where it was possible to observe the turbidity of the solution. Afterwards, the samples were centrifuged at 5000 rpm for 5 min to promote phase separation. The supernatant was discarded, and the sedimented organic phase containing the analytes was transferred to a vial and posteriorly analyzed by FAAS.

3. Results and discussion

3.1. Preliminary studies

Preliminary studies were carried out to select the most effective extraction solvents (chloroform or carbon tetrachloride). Acetonitrile, acetone, ethanol and methanol were tested as dispersive solvents. The complexing agents tested were 5-Br-PADAP and dithizone. The experiments were carried out with 30 mL of a 10 μg L^{-1} metal solution at pH 9. The results of this study are presented in the form of a bar graph in Fig. 1. It is noted that the mixture chloroform, acetonitrile, and Br-PADAP resulted in the best extractions, both for copper and manganese. Thus, these substances were chosen to perform the DLLME.

Another study carried out was on the amount of the enriched phase obtained after applying DLLME injected into the flame atomic absorption spectrometer. The amount of extract injected into the flame can be very large and destabilize the flame, extinguishing it. If the amount of the enriched phase injected is small, the signal generated may be shallow, which would deteriorate the analytical characteristics of the method. Thus, the volume of the extraction phase injected into the spectrometer was studied, varying the volume of chloroform between 20 and 60 μL. The results show that the highest absorbances for copper and manganese occur when 40 and 60 μL are used, respectively (Fig. S1). However, when making successive determinations with 40 μL, it was possible to notice a high signal oscillation for both elements. Instability in the flame and a significant variation in the signal was observed for volumes of 60 μL. Besides, the flame was frequently extinguished. Thus, the selected amount of extraction solvent was 50 μL, since the responses obtained were more accurate and increasing, and flame instability decreased.

The extraction efficiency in DLLME also depends on the ionic strength of the medium since, with the addition of highly soluble salts in the system (such as NaCl, $CaCl_2$ and $AlCl_3$), they are dissociated and hydrolyzed, forming anions and cations. Water creates a hydration sphere around these ions, reducing water availability to solvate the analyte molecules of interest in the aqueous phase, decreasing the solubility of the analytes in the aqueous phase, and favoring their partition into the extraction phase, an effect known as salting out. However, care should be taken when optimizing this parameter, as this effect is worse when the analyte is very polar. Very polar analyte ions can participate in electrostatic interactions with the salt ions in solution and, as a result, reduce the extraction capacity of the extraction solvent (Viñas et al., 2014). The addition of salt can also increase the volume of the sedimented phase due to the reduction in the solubility of the extraction solvent in the aqueous phase. An increase in the amount of sedimented phase negatively affects the enrichment factor. In preliminary experiments, it was observed that the addition of 5% (mv^{-1}) NaCl solution improved Cu and Mn extractions using DLLME.

3.2. Optimization step

For optimizing the proportions of the mixture components (dispersive solvent, extraction solvent and solution of the complexing agent), a constrained mixture design for three components was applied (Table 1). The restrictions were used to delimit the experimental region, avoiding conditions in which the proportions between the solvents are inefficient.

The two obtained responses are located at a common optimum region for maximization. Thus, the desirability function was used as a simultaneous optimization tool. This function is based on transforming the responses obtained into individual desirabilities (d_i), varying from 0 to 1. A single response, called overall desirability (D), is defined as the

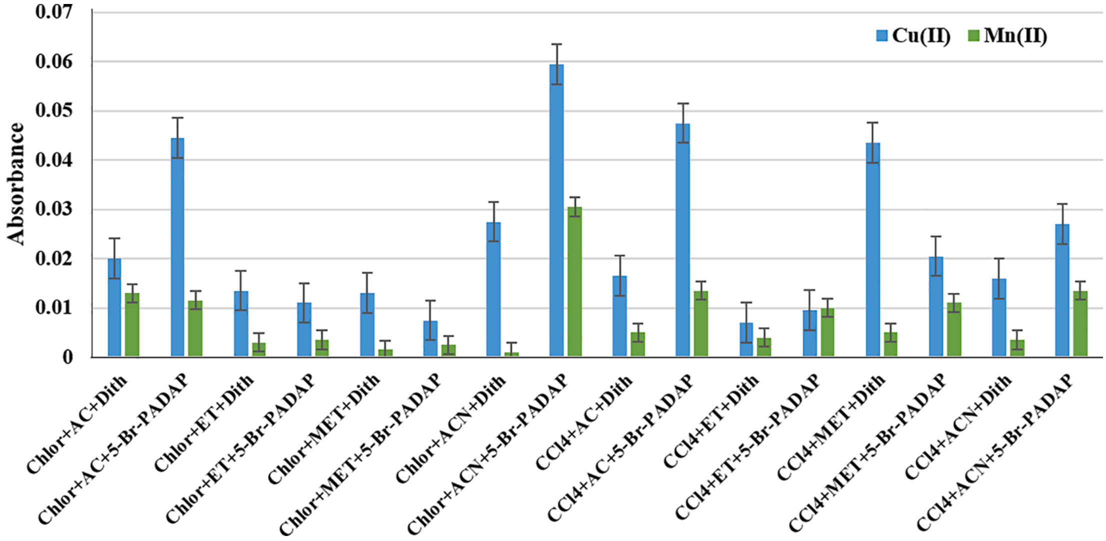

Fig. 1. Study of extraction solvent, dispersive solvent and complexing agent for the determination of Cu and Mn by dispersive liquid-liquid microextraction. Chlor: chloroform, AC: acetone; Dith: dithizone; ET: ethanol, MET: methanol, ACN: acetonitrile.

geometric mean of these individual desirabilities (d_{is}), according to Eq. (1), where i is the number of responses studied in the optimization process

$$D = \sqrt[i]{d_1 d_2 \cdots d_i} \tag{1}$$

Mathematical models, such as linear, quadratic, special cubic and complete cubic, were fitted to the global desirability to describe data behavior within the experimental region studied. Lack of fit tests were applied to assess the quality of the fitted models. All fitted models showed a significant lack of fit (p values < 0.05 at 95% confidence). However, the complete cubic and special cubic models showed a better ability to describe data behavior, even with a significant lack of fit. Residues are smaller and less likely when these two models are applied. Thus, the special cubic model was chosen to indicate the optimal conditions. The adjusted response surface is shown in the graph in Fig. 2. The optimal proportions of the reagents that made up the extraction mixture were 3800 μL (76%) of acetonitrile, 500 μL (10%) of chloroform, and 700 μL (14%) of the 0.020% (mv^{-1}) Br-PADAP complexing solution. These proportions simultaneously satisfy all the responses considered in this design to extract both metals, applying the DLLME.

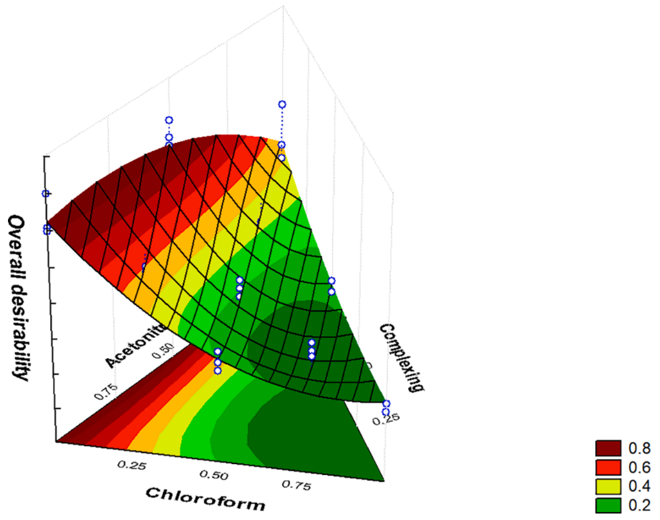

Fig. 2. Response surface obtained by fitting the special cubic model to the overall desirability in the optimization of the simultaneous extraction of Cu and Mn in coconut water by DLLME.

For optimizing the process variables, the Doehlert matrix (presented in Table 2 together with the obtained responses) was applied. In this case, to describe data behavior, it is only possible to fit, using least square regression, the linear and quadratic models due to the number of experimental points available. The desirability function was also used to try to simultaneously optimize the two responses. However, the overall desirability value obtained was very small, indicating no experimental region that simultaneously satisfies both responses. Thus, it was decided to perform the optimization of these two responses separately. Therefore, at the end of the process, there will be two different copper and manganese methods.

The linear and quadratic models were then separately fitted to the Cu and Mn absorbance signals. Although both the quadratic and the linear models have a significant lack of fit, the first model leaves fewer residuals between the predicted and observed values. For this reason, it was chosen to find the optimal values for extraction of the analytes. Fig. 3 shows the partial response surfaces for the studied metals. It is observed that the optimal values for the extraction of Mn are, respectively, the following: pH (9.5); buffer volume (2.8 mL) and volume of the NaCl solution (1.9 mL).

The analysis of partial surfaces obtained for copper revealed a behavior that indicates that the optimum point is outside the delimited experimental region, mainly for pH. The analytical signal significantly increases when going to low pH regions. It was decided to move the design to lower pH values to find the best experimental conditions. Although the quadratic model still presents significant lack of fit ($p = 0.000424 < 0.05$), it was used to indicate trends in data behavior and to indicate optimal conditions, which are as follows: pH (4.0); buffer volume (3.0 mL) and NaCl solution volume (2.0 mL).

Control experiments were carried out under optimal conditions to compare and evaluate the values predicted by the mathematical model used. The signals obtained for absorbance for copper (0.046 ± 0.004) and for manganese (0.024 ± 0.006) were found, showing the predictive capacity of the adopted mathematical model.

3.3. *Matrix effect*

The need to digest the coconut water sample was evaluated before performing the DLLME. The results showed that, when the extraction is done without sample digestion, there is a strong matrix effect corresponding to a low analytical signal (a decrease ranging from 42 to 53% and from 30 to 56% for Cu and Mn, respectively) when compared to the

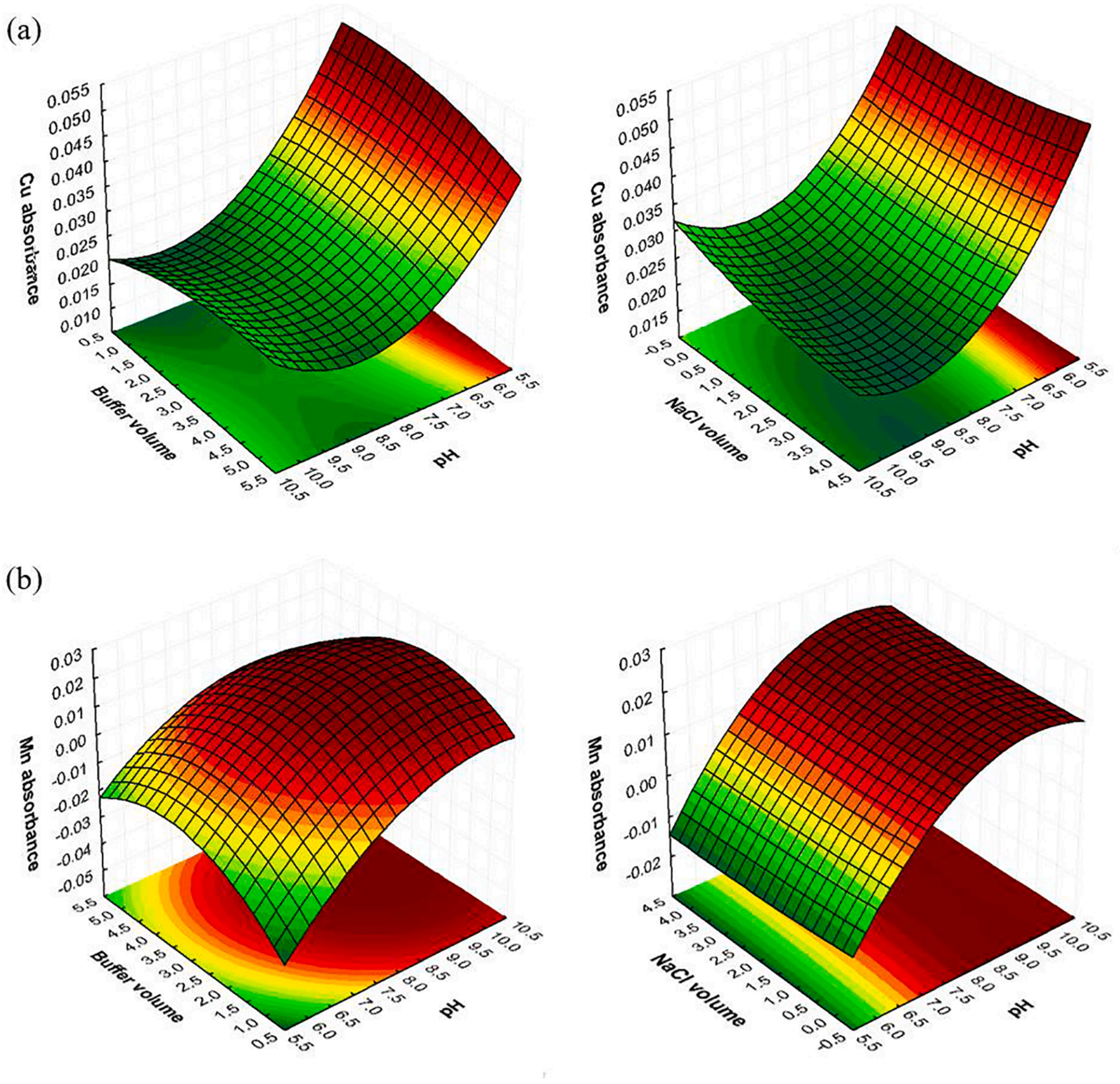

Fig. 3. Partial response surfaces obtained by fitting quadratic models to Doehlert design data for (a) copper and (b) manganese, using DLLME optimization.

extraction using the digested sample. This fact probably happens due to complex organic substances and lipids that bind to the analytes or cause difficulties in the action of the complexing agent. Therefore, digestion is always recommended before the extraction procedure is applied.

3.4. Analytical characteristics and applications

The developed method, based on DLLME, had its analytical characteristics accessed after the optimization process. The limits of quantification (LOQ) were calculated based on the expression LOQ = 10 s_b/m, where s_b is the standard deviation obtained from the determination of ten blanks and m is the slope of the analytical curve of each metal. The limits of quantification found for Cu and Mn were 4.83 and 3.32 μg L^{-1}, respectively. Accuracy was assessed in terms of repeatability and expressed as % RSD (N = 10). The values found were 6.6 (Cu) and 6.0% (Mn). The linearity of the analytical curves was accessed in the form of determination coefficient (R^2). The values found for R^2 were 0.9957 and 0.9972, for Cu and Mn, respectively. The enrichment factors were calculated by the ratio between the angular coefficients of the analytical curves obtained by the preconcentration of the metal standard solution and the analytical curves obtained by the direct reading of the element standard solution. The enrichment factors found for Cu and Mn were, respectively, 11 and 8 times. Accuracy was assessed by addition/recovery tests (Table 3). Recoveries between 98 and 120% were found for the studied metals. These recoveries are considered satisfactory for analytes at trace levels. The developed method was applied in the determination of Cu and Mn in samples of natural (NCW) and

Table 3
Results for the determination of copper and manganese (μg L^{-1}) by FAAS in coconut water samples (N = 3) by the developed method.

Samples	Metal	Added (μg L^{-1})	Found (μg L^{-1})	Recovery (%)
NCW 1	Cu	0	11 ± 0.4	120
		30	47 ± 0.4	
	Mn	0	13.9 ± 0.5	107
		30	46 ± 0.6	
NCW 2	Cu	0	22 ± 1	–
	Mn	0	16.8 ± 0.3	–
ICW 1	Cu	0	44 ± 2	98
		30	73 ± 1	
	Mn	0	8.0 ± 1	107
		30	40 ± 1	
ICW 2	Cu	0	51.4 ± 1.9	–
	Mn	0	17.6 ± 0.8	–
ICW 3	Cu	0	41 ± 1	–

industrialized (ICW) coconut water. The concentrations found are shown in Table 3. Cu concentrations ranged from 11.0 to 51.4 μg L^{-1}, and Mn concentrations ranged from 8.0 to 17.6 μg L^{-1}.

Sousa et al. (2006) determined Ca, Mg, Mn, Fe, Zn, and Cu in samples of processed and natural coconut water with detection by inductively coupled plasma optical emission spectrometry (ICP OES). Sample preparation consisted only of the filtration step followed by dilution in nitric acid (2% vv^{-1}). In the procedure performed, it was impossible to quantify Cu in natural coconut water samples. The quantification of this element is only possible in processed coconut water samples (140 μg L^{-1}). For Mn, the mean found was 280 μg L^{-1}, much higher than the value found in this study. This article described for the first time the application of DLLME in the separation and preconcentration of Cu and Mn in coconut water samples, aiming at its determination by FAAS. DLLME applications in coconut waters found dealt with its use to extract cadmium and lead in industrialized coconut water (Paixão et al., 2019) and to determine pesticides (Deme et al., 2013, Ferreira et al., 2016).

4. Conclusions

The application of multivariate optimization techniques allowed the fast and efficient optimization of a sensitive method for determining Cu and Mn in coconut water samples after dispersive liquid–liquid microextraction of these metals. Constrained mixture design revealed the best proportions between complexing reagent, dispersive and extraction solvents. In contrast, the Doehlert design complemented the optimization process by finding the best conditions for the process variables (pH, buffer and NaCl concentration). The analytical characteristics of the DLLME-FAAS procedure proved to be satisfactory and suitable for carrying out the task for which it is intended. Low quantification limits were reached for both analytes.

The developed method proved to be a powerful tool in increasing the detectability power of FAAS aiming to determine metals at trace amounts, and not only could it analyze coconut water, but also other complex matrices. A perspective for other studies is to increase the amount of metals that can be simultaneously pre-concentrated in the most diverse types of samples that are currently of interest to society.

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Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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Appendix A. Supplementary data

Supplementary data to this article can be found online at https://doi.org/10.1016/j.foodchem.2021.130473.

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