http://dx.doi.org/10.21577/0103-5053.20180095

Article

J. Braz. Chem. Soc., Vol. 29, No. 10, 2189-2196, 2018
Printed in Brazil - ©2018 Sociedade Brasileira de Química

Use of Constrained Mixture Design in the Optimization of a Method Based on Extraction Induced by Emulsion Breaking for the Determination of Ca, Mg, Mn, Fe and Zn from Palm Oil by Flame Atomic Absorption Spectrometry

Gisseli S. Valasques,[a] Ana M. P. dos Santos,[a] Darllen G. da Silva,[b] Juscelia P. S. Alves[b] and Marcos A. Bezerra*,[b]

[a]Instituto de Química, Universidade Federal da Bahia, Campus da Federação/Ondina,
Rua Barão de Geremoabo s/n, 40170-115 Salvador-BA, Brazil

[b]Departamento de Ciências e Tecnologias, Universidade Estadual do Sudoeste da Bahia,
Campus de Jequié, Rua José Moreira Sobrinho s/n, 45206-190 Jequié-BA, Brazil

In this study, it was developed a method for Ca, Mg, Mn, Fe and Zn determination in palm oil samples by flame atomic absorption spectrometry (FAAS) after ultrasound-assisted emulsification and extraction induced by emulsion breaking (EIEB). Optimization of the method was carried out by a constrained mixture design. The developed method has presented limits of detection (LOD) between 0.012 and 0.057 mg L^{-1}, limits of quantification (LOQ) between 0.039 and 0.19 mg L^{-1} and precision was expressed as repeatability (%RSD, n = 10) between 1.8 and 3.2% for the five studied metals. Method accuracy was assessed by the application of recovery tests (87 to 113%) and by comparison of concentration values with the dry ashing method, showing good agreement with the standard method. The developed methodology allows operational simplicity, multi-sample treatment, and low cost when compared with some methods based on decomposition. It was applied in palm oil samples collected in the Bahia State (Brazil). The concentrations (in mg L^{-1}) found in the samples were: 3.93-13.9 Ca, 0.37-2.26 Mg, > LOQ-0.32 Mn, 1.77-8.57 Fe and 0.38-2.54 Zn.

Keywords: palm oil, extraction induced by emulsion breaking, metals, FAAS

Introduction

Palm oil is extracted from the pulp of the *Elaeis guineensis* species. This oil has reddish yellow color and semi-solid consistency at room temperature, due to the high content of saturated fatty acids. Palm oil mainly consists of glycerides. Triglycerides are the main components, with small amounts of diglycerides and monoglycerides. It also consists of free fatty acids and practically do not present trans fatty acids.[1]

The physical and chemical characteristics of palm oil have been extensively studied due to the great industrial interest. It is widely used for the manufacture of margarine because of its consistency, besides not becoming rancid, and being excellent as cooking oil and fried foods; it is also used in the production of vegetable oil, suitable for making breads, cakes, pies, cookies, creams, etc. A major use of palm oil is as a raw material in the manufacture of soaps, washing powder detergent, etc.; it may also be used in fuel composition for diesel engines.[2]

The presence of metals in edible vegetable oils can be originated from the natural composition of the soil in which the planting is established, from the environmental pollution and from the contamination which can occur during extraction and conservation processes of these oils. The concentration of trace elements is an important criterion for quality assurance in flavor determination, half-life and rate of deterioration. In general, certain factors such as the presence of oxygen and trace metals, light exposure and storage temperature must be controlled to decrease oil oxidation.[3] There are many records showing that trace elements such as Fe, Cu, Mn and Ni affect the flavor and oxidative stability of oils, with catalytic effects on the self-oxidation mechanism.[4]

Foods with high-fat content, such as palm oil, are difficult to decompose, since they present a complex organic structure, as well as high concentrations of oily components.[3] Thus, the extraction induced by emulsion

---

*e-mail: mbezerra@uesb.edu.br

breaking (EIEB) technique is a very promising alternative for this type of samples.

When two immiscible liquids are placed in contact, there is a tendency for them to become dispersed in one another as globules (or droplets) when the action of a mechanical force is observed. However, when agitation ceases, these two liquids tend to separate. Emulsions are systems that remain dispersed in one another by a reasonable period (few seconds to several years). Emulsifying agents such as surfactants can be used to delay separation.[5,6]

The phase dispersed in an emulsion is called internal phase and the continuous phase is the external phase. They are commonly referred to as oil/water (o/w) systems, where the external phase is water, which is the continuous phase.[7,8] Emulsions are milky-looking systems consisting of droplets with sizes between 0.5 and 50 µm. They are thermodynamically unstable systems and show a tendency to separate into their immiscible components over time. O/w emulsions are the most applied in analytical chemistry due to some characteristics such as low viscosity, low organic compound loading, easiness of calibration with aqueous standards, adequate stability, etc., which make them compatible with most of the spectrometric techniques using aqueous solutions.[9,10]

In the formation of an emulsion or interfacial surface, the area between the continuous and dispersed phase largely increases and interface properties are important in determining the easiness of emulsification and stability. Not only is this interface exchange phenomenon of substances between phases favored by increasing contact area, but also by interaction forces dependent on the nature of this substance (polar or nonpolar).[9]

Extraction induced by emulsion breaking[10] has been applied in edible oils for the determination of Cr and Mn by graphite furnace atomic absorption spectrometry (GFAAS),[11] in edible oils from Turkey for the determination of Cd, Cr, Cu, Fe, Mn, Ni, Pb and Zn using inductively coupled plasma optical emission spectrometry (ICP OES),[12] trace concentrations of Cu, Mn and Ni in biodiesel by GFAAS,[13] Cu, Fe and Mn in used lubricating oils by flame atomic absorption spectrometry (FAAS),[14] zinc from diesel after multivariate optimization[15] and edible oils by FAAS.[8]

This study proposes the application of EIEB for the determination of Ca, Mg, Mn, Fe and Zn from palm oil samples by FAAS. The developed method is simple, fast, efficient, and results in a preconcentration step (in some cases) due the quantitative transfer of metals to a small volume of aqueous phase, which is easier to handle and submit to measurements than the original oil sample.

Experimental

Instrumentation

The determination of metals (Ca, Mg, Mn, Fe and Zn) in the aqueous phase obtained from the EIEB, as well as in the solution obtained after dry ash digestion/dissolution, was carried out using a PerkinElmer AAnalyst 200 (Norwalk, CT, USA) flame atomic absorption spectrometer equipped with a deuterium lamp for background correction. Hollow cathode lamps were used in accordance with the recommendations of the manufacturer operating at the following values: 248.33, 279.48, 213.86, 422.67 and 285.21 nm for wavelength; 30, 15, 15, 20 and 20 mA for lamp current and 1.35, 0.60, 1.80, 0.60 and 1.05 nm for bandpass for Fe, Mn, Zn, Ca and Mg determination, respectively. Flame was consisted of acetylene (flow rate 2.0 L min^{-1}) and air (flow rate 13.5 L min^{-1}). Flow rate used for the nebulizer was 5.0 mL min^{-1}.

A Cristofoli (Campo Mourão, Brazil) ultrasonic bath was used for emulsion formation. The ultrasound bath equipment was filled with about 3.0 L of water and glass centrifuge tubes were used as container to promote the emulsification.

Sample dry ashing was carried out in an EDGCON 3P muffle oven (EDG Equipamentos, São Carlos, Brazil). A Tecnal hot plate (model TE 0851, Piracicaba, Brazil) was used for ash solubilization with HNO_3 and H_2O_2.

Reagents

Nitric and hydrochloric acid solutions were prepared by direct dilution with deionized water from the concentrated solutions. All chemicals used were of the highest available purity and analytical reagent grade. Solutions of 10% (m/v) Triton X-114 surfactant (Sigma-Aldrich, Milwaukee, USA) were prepared in high purity deionized water. Ultrapure water was obtained from Purelab Classic® purification system (Elga, High Wycombe, UK). Concentrated nitric, sulfuric acid and standard stock solutions (1000 mg L^{-1}) of Ca, Mg, Mn, Fe and Zn were purchased from Merck (Darmstadt, Germany). Working standard solutions of these metals ranging from 0.1 to 3.0 mg L^{-1} were prepared daily by dilution of the 1000 mg L^{-1} stock solution in aqueous media with surfactant (1% v/v Triton X-114) and 4.6% (m/v) nitric acid solution. Analytical curves and their parameters were plotted using the Excel® (Microsoft) software. Statistica® software[16] was used to modeling and evaluation of mathematical models fitted to experimental data provided from mixture design application. An oil blank solution was prepared from a sample after five exhaustive sections of extraction.

Procedure for dry ashing and sample solubilization

The adopted procedure was adapted from the American Section of the International Association for Testing Materials (ASTM).[17] Triplicates of each sample with a volume of about 0.3 mL of palm oil was placed in a porcelain crucible and brought to the oven at 150 °C for 1 h, and then at 300 °C for 2 h. The crucible was removed from the oven, cooled to room temperature, then it was added 1 mL of H_2SO_4 and taken back to the oven at 300 °C for 2 h. After, the crucible was cooled, it was taken, with the remaining ashes, to a hot plate and 2 mL of concentrated HNO_3 were added and heated to 100 °C with the addition of drops of hydrogen peroxide until clarification. After cooling, the final digest was quantitatively transferred to a 10.0 mL volumetric flask and its volume was set with ultrapure water. A blank digest was carried out in the same way as the samples of interest. Determination of the elements was performed using a flame atomic absorption spectrometer.

Optimization of emulsion breaking extraction

Proportions among sample and chemicals (10% m/m surfactant solution and concentrated nitric acid) for EIEB were optimized using a constrained mixture design.[18] The use of constraints is justified, since the presence of three components is always necessary for emulsion formation and posterior extraction.

Table 1 presents low and high constraints established for each component. Table 2 presents the experimental matrix for this constrained mixture design. The proportion of each component in each experiment is established by the mixture design matrix used. In this step, method variables such as extraction time and temperature were fixed at 12 min and 80 °C.

Table 1. Low and high constraints for mixture components for the optimization of extraction induced by emulsion breaking from palm oil samples

Mixture variable	Low constraint	High constraint
Sample volume / mL	4	7
Concentrate HNO_3 volume / mL	1	3
10% (v v^{-1}) Triton X-114 volume / mL	1	3

To evaluate the effect of extraction time (defined as time to which the emulsion was submitted to ultrasound energy), this variable was studied in the range from 5 to 50 min. Optimal proportions found applying mixture design (6 mL of sample, 2.5 mL of 10% m/m surfactant solution and 2.5 mL concentrate nitric acid) and breaking temperature of 90 °C were used. Breaking temperature and the breaking time effects on the turbidity of extract and the analytical signal were also studied in the optimum proportions found by mixture design application.

Table 2. Experimental matrix applied for the optimization of extraction induced by emulsion breaking from palm oil samples

Experiment	Sample / mL	Triton X-114 / mL	HNO_3 / mL
1	7	1	2
2	7	2	1
3	6	3	1
4	6	1	3
5	4	3	3
6	7	1.5	1.5
7	6.5	1	2.5
8	5	3	2
9	6.5	2.5	1
10	5	2	3
11	6	2	2

In order to allow the simultaneous optimization of the five obtained responses (metal absorbance), a multi-response approach was used. It is based on desirability functions applied in the optimization of several responses.[19] The approach consists of converting each response y_i into an individual desirability function d_i, which varies within the range $0 \leq d_i \leq 1$. If the response is the desired, $d_i = 1$, and if the response is not within the acceptable region, $d_i = 0$. Thus, factor levels are chosen to maximize the overall desirability (D), given by the expression:

$$D = \sqrt[m]{d_1 d_2 \ldots d_m} \qquad (1)$$

where m is the number of response variables (in this case, 5). If the target value T is a maximum, d_i will be:

$$d = \begin{cases} 0, \text{ if } y < L \\ \left(\dfrac{y - L}{T - L}\right)^s, \text{ if } L \leq y \leq T \\ 1, \text{ if } y > T \end{cases} \qquad (2)$$

where L is the lowest acceptable value for the response, and s is the weight (for linear desirability function, s = 1). In this study, L values were the lowest recoveries found in a set of experiments for each metal and T values were the highest recoveries for each metal.[20]

General procedure for EIEB after optimization

The extraction of studied metals from palm oil samples was carried out using the EIEB procedure developed in two steps: (*i*) emulsification: 6.0 mL of the palm oil sample was put into a glass conic centrifuge tube of 50 mL of capacity. Then, 2.5 mL of concentrate nitric acid solution is added, the tube is manually stirred and, posteriorly, it was also added 1.5 mL of 10% (v/v) Triton X-114 surfactant. This mixture was submitted to ultrasound energy for 30 min to form the emulsion; (*ii*) emulsion breaking: after the emulsion formation, the glass tube was transferred to a water bath to keep the temperature at 90 °C by sufficient time (about 30 min) to promote the phase separation. The aqueous phase, containing the extracted analytes, was collected with the aid of a pipette and stored in polyethylene bottle (with its volume set to 10.0 mL) until the determination by FAAS.

Analytical features assessment

The calculation of limits of detection (LOD) for the determination of Ca, Mg, Mn, Fe and Zn was carried out using the standard deviation from 10 replicate measurements of blank solution, multiplied by three and by the division of the obtained value by the slope of the analytical curve. Similarly, the limit of quantification (LOQ) is the concentration that gives a response equivalent to 10 times the standard deviation of the blank signal (n = 10), also divided by the slope of the analytical curve.[21] Precision, expressed as repeatability, was assessed as percent relative standard deviation (%RSD), by determination of ten replicate measurements from solutions of 0.5 and 2 mg L^{-1} for each studied metal. Analytical curves (ranging from 0.1 to 3.0 mg L^{-1}) were obtained with aqueous standard solutions of each metal in surfactant and nitric acid media using a flame atomic absorption spectrometer.

Results and Discussion

The optimization of the analytical method proposed in this study was carried out by multivariate methodology, employing a mixture design. Two types of responses were evaluated: the turbidimetric signal, expressed as –log T (where T is the transmittance) and the set of absorption signals for the studied metals. These absorption signals were grouped in a unique response using a desirability function. Turbidimetric measurements allow evaluating the efficiency of emulsion breaking, since it can be considered that radiation scattering is proportional to the amount of emulsion that remains in the aqueous solution. Thus, the lower the turbidimetric signal, the better the breaking efficiency of the studied emulsion. To optimize sample proportions, acid and surfactant solutions were used in a constrained mixture design. Responses for each experimental condition are presented in Table 3.

Linear, quadratic, special cubic and full cubic equations were fitted to the data generated by the turbidimetric and global desirability obtained from atomic absorption measurements. While all models have shown lack of fit, it was noted that the quadratic model is the simplest model that better explains the behavior of the data set. Using the quadratic model, it is possible to obtain the two response surfaces shown in Figures 1a and 1b. The surface in Figure 1a indicates that turbidimetric signals are minor in the region between the points 4 and 7. Taking into account the overall desirability, the data treatment

Table 3. Constrained mixture matrix applied for optimization of components of the mixture and responses as turbidity (–log T) and corrected analytical signal for the studied metals

Experiment	Sample / mL	Triton X-114 / mL	HNO_3 / mL	Turbidity	Responses / (absorbance mL^{-1})				
					Mn	Fe	Zn	Mg	Ca
1	7	1	2	2.36 / 2.24	0.00417 / 0.00467	0.0415 / 0.0395	0.00817 / 0.00617	0.117 / 0.119	0.0212 / 0.0225
2	7	2	1	30.2 / 30.5	0.0140 / 0.0148	0.0527 / 0.0535	0.0538 / 0.0530	0.147 / 0.148	0.0400 / 0.0412
3	6	3	1	0.854 / 0.852	0.00733 / 0.00701	0.0383 / 0.0403	0.0267 / 0.0278	0.118 / 0.119	0.0330 / 0.0302
4	6	1	3	0.0813 / 0.0824	0.0115 / 0.0118	0.0643 / 0.0653	0.0592 / 0.0531	0.157 / 0.156	0.0527 / 0.531
5	4	3	3	0.790 / 0.810	0.00517 / 0.00583	0.0290 / 0.0295	0.104 / 0.102	0.0950 / 0.0962	0.0263 / 0.0247
6	7	1.5	1.5	29.9 / 29.5	0.0118 / 0.0123	0.0580 / 0.0587	0.0473 / 0.0463	0.140 / 0.138	0.0390 / 0.0398
7	6.5	1	2.5	0.110 / 0.112	0.0123 / 0.0126	0.104 / 0.138	0.0622 / 0.0612	0.152 / 0.151	0.0587 / 0.0528
8	5	3	2	0.942 / 0.943	0.00700 / 0.00650	0.0365 / 0.0353	0.0282 / 0.0265	0.0930 / 0.0918	0.0220 / 0.0187
9	6.5	2.5	1	3.98 / 3.95	0.0300 / 0.0308	0.106 / 0.107	0.0402 / 0.0412	0.137 / 0.139	0.0423 / 0.0473
10	5	2	3	0.889 / 0.885	0.00950 / 0.00967	0.0412 / 0.0408	0.00933 / 0.0108	0.116 / 0.115	0.0292 / 0.0287
11	6	2	2	0.808 / 0.811	0.0143 / 0.0148	0.0315 / 0.0303	0.0163 / 0.0155	0.132 / 0.131	0.0406 / 0.0401

T: transmittance.

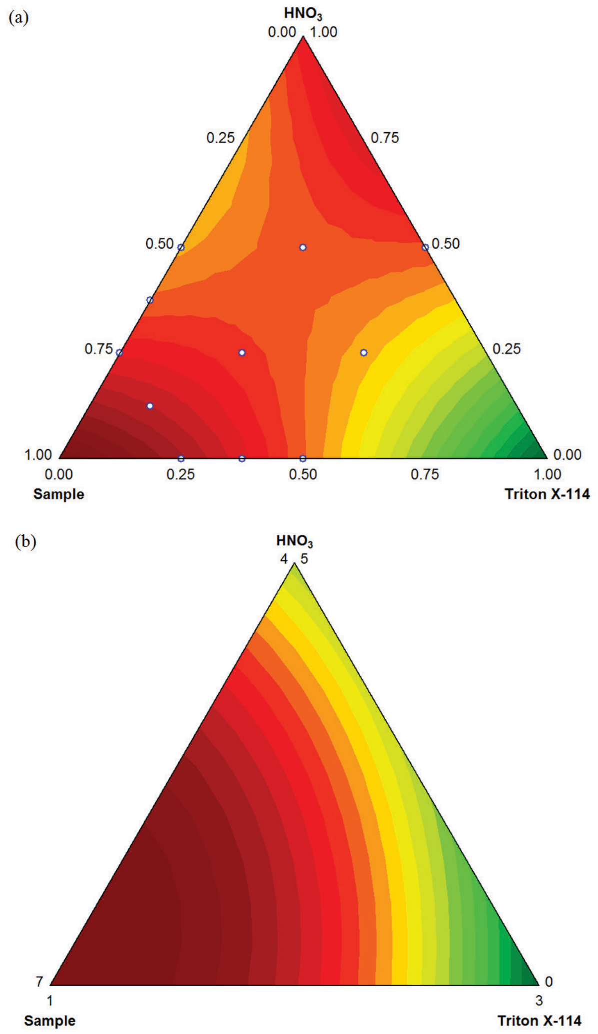

Figure 1. Response surface obtained after fitting quadratic models to (a) turbidity expressed as –log T and (b) overall desirability.

indicates the following coordinates as optimal points: 6.5 mL (sample); 2.5 mL (10% surfactant solution) and 1.0 mL (nitric acid). However, under these experimental conditions, a slight turbidity is still observed, showing a non-efficient emulsion breaking. By surface superposition, it was observed that there is a region where the two optimums (minimum turbidity and maximum overall desirability) intersect. This point is characterized by the following experimental conditions: 6.0 mL (sample), 1.5 mL (surfactant solution) and 2.5 mL (nitric acid). Under these conditions, an efficient emulsion breaking is noted, with no loss in metal signals. These conditions allow obtaining the maximum absorbance of the metals. Thus, they were chosen as optimum proportions to carry out the next studies (nebulization and transport efficiency, extraction time, influence of breaking temperature and breaking time) and the analytical characteristics were assessed, based on these optimum proportions.

Nebulization and transport efficiency

Surfactants lower the surface tension of the medium and facilitate the process of nebulization and transport of the analytes to the flame and this phenomenon can increase the analytical signal. However, experiments carried out with addition of standard solutions in the aqueous phase obtained after emulsion breaking show that the amount of remaining surfactant does not alter the analytical signal obtained concerning the aqueous standard.

Extraction time

Metal transference from oil to aqueous phase can demand different extraction times, according to the sample matrix. The sample was submitted to ultrasound energy from 5 to 50 min aiming to evaluate the sonication time that provides the best extractions. In this experiment, the optimum conditions found in the mixture design were used. Results from these studies can be observed in Figure 2. The temperature of 90 °C was considered for emulsion breaking. It was noted that extraction efficiency increased with an increasing sonication time, mainly for Zn (Figure 2a). After 30 min, the maximum extraction is observed for all five studied metals. A sonication time of 30 min was then chosen to perform the extraction procedure.

Influence of breaking temperature

The temperature of the water bath used for emulsion breaking ranged from 70-90 °C. It was observed that, from the temperature of 80 °C, it is possible to efficiently break the emulsions (Figure 2b). This is evidenced by the low turbidity in the aqueous phase. Regarding the extraction of the studied metals, it was observed that, from 80 °C, the normalized signal is stabilized (Figure 2c). Another observation was in relation to the time for emulsion breaking. It was observed that breaking occurs in a shorter time (Figure 3) when it was used the temperature of 90 ºC. Therefore, 90 °C was chosen as the optimum temperature, since it allows good extraction efficiency, a better throughput time, provides a greater operational confidence and it does not work under the limit conditions as happens when the breaking is carried out at 80 °C.

Analytical features of the developed procedure

The obtained analytical features for the developed method based on extraction induced by emulsion breaking were assessed after the optimization and are presented in

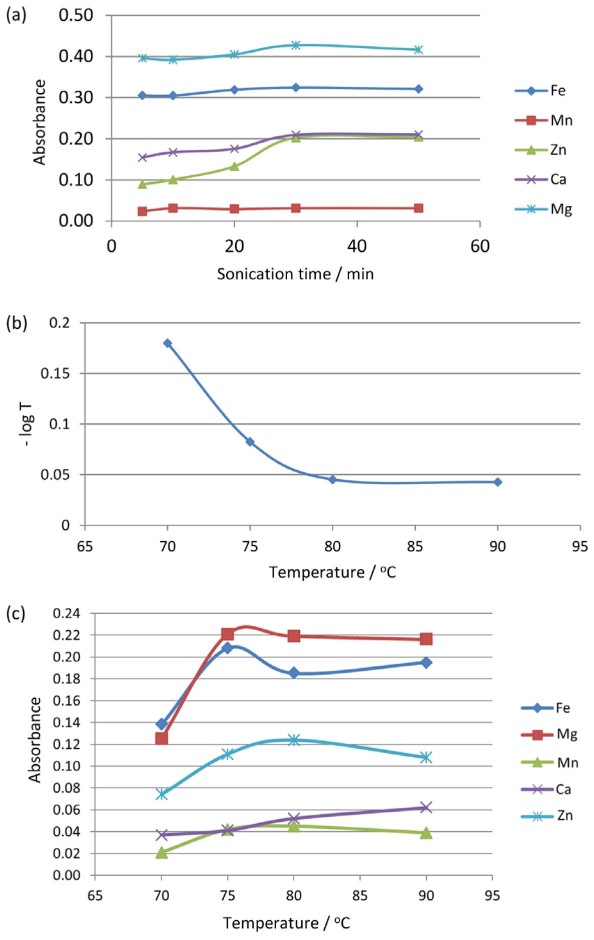

Figure 2. Evaluation of (a) sonication time and breaking temperature effect on (b) turbidimetric measurements and (c) absorbance of metals. Working conditions: sample volume: 6.0 mL; HNO_3 volume: 2.5 mL; 10% Triton X-114 volume: 1.5 mL; ultrasound time: 30 min; emulsion breaking time: 30 min.

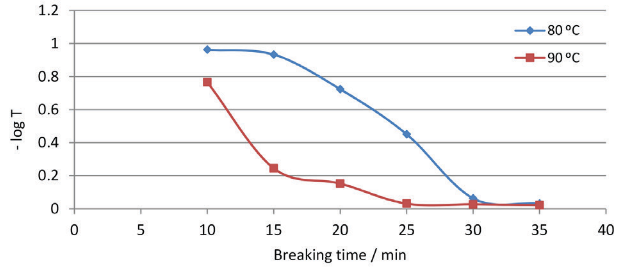

Figure 3. Breaking time studies at optimum conditions using a breaking temperature of 80 and 90 °C. Working conditions: sample volume: 6.0 mL; HNO_3 volume: 2.5 mL; 10% Triton X-114 volume: 1.5 mL; ultrasound time: 30 min.

Table 4. Analytical curves (based on external standard and standard addition) were compared, in order to evaluate the matrix effect. Confidence intervals of the slopes were evaluated at 95% confidence level using parallelism test (critical t = 2.31 for n = 12 and degrees of freedom (d.f.) = 8) and it was found that there are no differences between the slopes of the two types of analytical curves for Ca (t = 0.098), Mg (t = 2.2), Mn (t = 0.80), Fe (t = 0.25) and Zn (t = 0.29). Thus, external standardization was chosen for metals determination due to its simplicity and commodity.

As it can be noted by the obtained LODs and LOQs, the proposed method is able to determine low concentrations of the studied metals in comparison with other published works that use extraction induced by emulsion breaking. Bakircioglu *et al.*[9] have obtained LOD of 0.010 mg L^{-1} for Zn determination using flow injection coupled to FAAS. This value is very similar to the presented in this work. In another research, Robaina *et al.*[11] have determined Mn with LOD of 0.12 mg L^{-1} using ETAAS (electrothermal atomic absorption spectrometry) and He *et al.*[22] have determined Mg, Mn, Fe and Zn (among others) by ICP-MS (inductively coupled plasma-mass spectrometry) with LODs of 0.093, 0.052, 0.271 and 0.177 ng L^{-1}, respectively. These two last works present LODs lower than the proposed method. However, they demand analytical techniques highly sensible and expensive.

Table 4. Comparison between two calibration strategies and LOD, LOQ and repeatability (%RSD) for the developed method, based on extraction induced by emulsion breaking

Metal	Calibration strategy	Analytical curve	LOD / (mg L^{-1})	LOQ / (mg L^{-1})	Repeatability (%RSD)
Ca	external standard	$A = 0.035\ C_{Ca} + 0.001$, $R^2 = 0.9990$	0.057	0.19	2.5
	standard addition	$A = 0.033\ C_{Ca} + 0.223$, $R^2 = 0.9992$			
Mg	external standard	$A = 1.042\ C_{Mg} + 0.022$, $R^2 = 0.9960$	0.054	0.18	2.2
	standard addition	$A = 0.957\ C_{Mg} + 0.312$, $R^2 = 0.9971$			
Mn	external standard	$A = 0.173\ C_{Mn} + 0.004$, $R^2 = 0.9990$	0.012	0.039	1.8
	standard addition	$A = 0.181\ C_{Mn} + 0.025$, $R^2 = 0.9985$			
Fe	external standard	$A = 0.048\ C_{Fe} + 0.003$, $R^2 = 0.9980$	0.042	0.14	3.2
	standard addition	$A = 0.045\ C_{Fe} + 0.142$, $R^2 = 0.9991$			
Zn	external standard	$A = 0.118\ C_{Zn} - 0.001$, $R^2 = 0.9991$	0.017	0.058	2.8
	standard addition	$A = 0.110\ C_{Zn} - 0.028$, $R^2 = 0.9988$			

LOD: limit of detection; LOQ: limit of quantification; RSD: relative standard deviation.

Application of the developed methodology and accuracy evaluation

The methodology based on induced extraction by emulsion breaking was used for the determination of Ca, Mg, Mn, Fe and Zn in palm oil samples collected in a supermarket from Jequié and Salvador cities (Bahia, Brazil). The results are presented in Table 5. Since there are no available certified reference materials for palm oil, the accuracy of the developed method was evaluated from two methodologies: (*i*) using addiction/recovery tests, where the five studied metals are spiked (using aqueous and organic standards) in the samples and extracted using the developed analytical method, and (*ii*) comparing the results generated by extraction induced by emulsion breaking with the results obtained using an alternative and consolidated method, such as the sample dry ashing and posterior solubilization with HNO_3 on a hot plate. The proposed method presents a good accuracy. Recoveries of added metals were satisfied and values between 87 and 113% were obtained. Using another palm oil sample, paired *t*-test (95% confidence level) was applied to compare metal concentrations found by the proposed method and the results found by the dry ashing method[17] (Table 6). According to this statistical test, it was not possible to observe a significant difference between data generated by the two methods. The *t* values found respectively for Ca, Mg, Mn, Fe and Zn were –1.30, –0.38, 0.65, –1.42 and 4.12. All these values are below the tabulated value (4.30), indicating that, at this confidence level, the results found for both methods are not statistically different.

Conclusions

The application of constrained mixture design and additional studies of process variables allowed the efficient development of a reliable method for the determination of Ca, Mg, Mn, Fe and Zn from palm oil

Table 5. Concentrations, amounts added and recoveries of metals spiked in palm oil samples using extraction induced by emulsion breaking

Sample	Ca / (mg L^{-1})			Mg / (mg L^{-1})			Mn / (mg L^{-1})			Fe / (mg L^{-1})			Zn / (mg L^{-1})		
	Before addition	After addition[a]	Recovery / %	Before addition	After addition[b]	Recovery / %	Before addition	After addition[c]	Recovery / %	Before addition	After addition[d]	Recovery / %	Before addition	After addition[e]	Recovery / %
1	5.95 ± 1.3	11.2 ± 1.1	105	0.72 ± 0.18	0.98 ± 0.08	87	0.11 ± 0.01	0.25 ± 0.07	93	1.77 ± 0.02	4.88 ± 0.32	104	0.38 ± 0.09	0.67 ± 0.07	97
2	5.14 ± 1.1	9.93 ± 0.61	96	0.74 ± 0.02	1.03 ± 0.04	97	< LOQ	0.16 ± 0.07	107	3.97 ± 0.41	6.72 ± 0.08	92	0.52 ± 0.19	0.83 ± 0.04	103
3	5.19 ± 0.47	9.84 ± 0.46	93	0.37 ± 0.01	0.66 ± 0.05	97	0.15 ± 0.01	0.32 ± 0.01	113	3.94 ± 0.69	6.82 ± 0.21	96	0.71 ± 0.02	1.05 ± 0.06	113
4	6.52 ± 1.0	11.6 ± 0.71	102	1.94 ± 0.01	2.26 ± 0.07	107	0.17 ± 0.07	0.33 ± 0.02	107	5.97 ± 0.09	8.69 ± 0.33	91	1.14 ± 0.01	1.42 ± 0.05	93
5	13.9 ± 0.99	18.8 ± 0.22	98	2.24 ± 0.07	2.56 ± 0.06	107	0.32 ± 0.02	0.45 ± 0.01	87	8.57 ± 0.06	11.8 ± 0.78	108	2.54 ± 0.22	2.80 ± 0.24	87
6	3.93 ± 0.98	8.85 ± 1.2	98	0.55 ± 0.06	0.84 ± 0.02	97	0.13 ± 0.01	0.29 ± 0.02	107	6.98 ± 0.32	9.57 ± 0.06	86	0.94 ± 0.08	1.22 ± 0.13	93
7	9.87 ± 0.30	15.28 ± 0.84	108	1.49 ± 0.04	1.77 ± 0.08	93	0.25 ± 0.04	0.39 ± 0.05	93	7.86 ± 0.36	10.87 ± 0.71	100	1.78 ± 0.25	2.05 ± 0.21	90
8[f]	7.15 ± 0.14	12.01 ± 0.51	97	0.54 ± 0.05	0.81 ± 0.05	90	0.21 ± 0.04	0.34 ± 0.03	87	2.62 ± 0.08	5.54 ± 0.51	97	0.58 ± 0.11	0.86 ± 0.15	93

[a]Ca added: 5.0 mg L^{-1}; [b]Mg added: 0.30 mg L^{-1}; [c]Mn added: 0.15 mg L^{-1}; [d]Fe added: 3.0 mg L^{-1}; [e]Zn added: 0.30 mg L^{-1}; [f]addiction of oil based standard. LOQ: limit of quantification.

Table 6. Concentrations of Ca, Mg, Mn, Fe and Zn found in the analyzed palm oil samples using extraction induced by emulsion breaking and dry ashing digestion

Metal	EIEB method / (mg L^{-1})	Dry ashing method / (mg L^{-1})	Calculated *t*
Ca	4.87 ± 0.23	5.11 ± 0.09	–1.30
Mg	1.19 ± 0.52	1.28 ± 0.12	–0.38
Mn	0.61 ± 0.15	0.58 ± 0.07	0.65
Fe	7.95 ± 0.22	8.04 ± 0.11	–1.42
Zn	2.47 ± 0.26	2.01 ± 0.11	4.12

Critical *t* (n = 3): 4.30. EIEB: extraction induced by emulsion breaking.

based on ultrasonic emulsification and extraction induced by emulsion breaking. The proposed method presents several advantages in relation to digestion and dilution methods, such as simplicity, the use of aqueous standards for calibration and low possibilities of analyte losses and contamination. This method also contributes to the economy of chemical reagents, since it avoids the use of large volumes of oxidizing acids, hydrogen peroxide and organic solvents. The determination of the studied analytes from palm oil samples was successfully carried out, showing that the developed method presents suitable analytical characteristics that allow its application to oily samples.

Acknowledgments

The authors acknowledge the financial support of the Fundação de Amparo à Pesquisa do Estado da Bahia (FAPESB), the Coordenação de Aperfeiçoamento de Pessoal de Nível Superior (CAPES) and Conselho Nacional de Desenvolvimento Científico e Tecnológico (CNPq).

References

1. Akpanabiatu, M. I.; Ekpa, O. D.; Mauro, A.; Rizzo, R.; *Food Chem.* **2001**, *72*, 173.
2. Hameed, B. H.; Lai, L. F.; Chin, L. H.; *Fuel Process. Technol.* **2009**, *90*, 606.
3. Cabrera-Vique, C.; Bouzas, P. R.; Oliveras-Lopez, M. J.; *Food Chem.* **2012**, *134*, 434.
4. Choe, E.; Min, D. B.; *Compr. Rev. Food Sci. Food Saf.* **2006**, *5*, 169.
5. Rosen, M. J.; Kunjappu, J. T.; *Surfactants and Interfacial Phenomena*; Wiley: New Jersey, 2012.
6. Viana, C.; Bohrer, D.; Carvalho, L. M.; Nascimento, P. C.; Rosa, M. B.; *TrAC, Trends Anal. Chem.* **2014**, *53*, 49.
7. Daltin, D.; *Tensoativos: Química, Propriedades e Aplicações*; Edgard Blucher: São Paulo, 2011.
8. Myers, D.; *Surfaces, Interfaces and Colloids: Principles and Applications*; Wiley-VCH: Weinheim, 1999.
9. Bakircioglu, D.; Topraksever, N.; Kurtulus, Y. B.; *Food Chem.* **2014**, *151*, 219.
10. Valasques, G. S.; Santos, A. M. P.; Teixeira, L. S. G.; Cerqueira, U. M. F. M.; Souza, V. S.; Bezerra, M. A.; *Appl. Spectrosc. Rev.* **2017**, *52*, 729.
11. Robaina, N. F.; Brum, D. M.; Cassella, R. J.; *Talanta* **2012**, *99*, 104.
12. Bakircioglu, D.; Kurtulus, Y. B.; Yurtsever, S.; *Food Chem.* **2013**, *138*, 770.
13. Pereira, F. M.; Zimpeck, R. C.; Brum, D. M.; Cassella, R. J.; *Talanta* **2013**, *117*, 32.
14. Caldas, L. F. S.; Brum, D. M.; Paula, C. E. R.; Cassella, R. J.; *Talanta* **2013**, *110*, 27.
15. Cassella, R. J.; Brum, D. M.; Lima, C. F.; Caldas, L. F. S.; Paula, C. E. R.; *Anal. Chim. Acta* **2011**, *690*, 79.
16. *Statistica Software*, version 7; Statsoft, Tulsa, USA, 2007.
17. ASTM D7455-14: *Standard Practice for Sample Preparation of Petroleum and Lubricant Products for Elemental Analysis*, ASTM International: West Conshohocken, PA, 2014.
18. Bezerra, M. A.; Castro, J. T.; Macedo, R. C.; Silva, D. G.; *Anal. Chim. Acta* **2010**, *670*, 33.
19. Bezerra, M. A.; Santelli, R. E.; Oliveira, E. P.; Villar, L. S.; Escaleira, L. A.; *Talanta* **2008**, *76*, 965.
20. Barros, J. M.; Bezerra, M. A.; Valasques, G. S.; Nascimento, B. B.; Souza, A. S.; Aragão, N. M.; *An. Acad. Bras. Cienc.* **2013**, *85*, 891.
21. Thompson, M.; Ellison, S. L. R.; Wood, R.; *Pure Appl. Chem.* **2002**, *74*, 835.
22. He, Y. M.; Chen, J. J.; Zhou, Y.; Wang, X. J.; Liu, X. Y.; *Anal. Methods* **2014**, *6*, 5105.

Submitted: December 31, 2017