



Multivariate approaches applied to optimization of an ultrasound-assisted extraction procedure for determination of essential elements in guarana samples by ICP OES

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Abstract

In the present work, a simple and high-throughput analytical procedure based on ultrasound-assisted extraction with diluted acid was proposed for the determination of Ca, Mg, K, P, S, Fe, Cu and Mn in guarana samples using inductively coupled plasma optical emission spectrometry. Two multivariate approaches were employed for optimization of the extraction procedure: mixture and Doehlert designs. The best experimental conditions were established by application of a multi-response function (overall desirability). An extractor medium composed of diluted nitric acid was selected for analytes extraction. Optimized conditions for ultrasound-assisted extraction followed the temperature of 60 °C, sonication time of 10 min and power of 100% applied to the ultrasonic bath. After the analytical validation step, the proposed procedure was successfully employed for determination of essential elements in thirty-three guarana samples from the state of Bahia, Brazil. Mass fractions higher than 0.42% (m m⁻¹) were found for potassium in all analyzed samples. For the other macro-elements, the mass fraction ranged from 514 mg kg⁻¹ (magnesium) to 0.19% m m⁻¹ (calcium). The mass fraction of micro-elements ranged from 5.1 to 91.3 mg kg⁻¹ for cooper and iron, respectively.

Keywords: ultrasonic energy; multi-element extraction; chemometric tools; guarana seeds; ICP OES.

Practical Application: Chemometric tools were successfully applied to develop a fast, inexpensive and greener analytical procedure for extracting essential minerals from guarana seeds aiming further determination by ICP-optical emission spectrometry.

1 Introduction

Guarana (*Paullinia cupana* Kunth) is a Brazilian plant, whose fruit is well-known by its stimulant property. Despite originally from Amazon, the cultivation has been expanded for other country areas, mainly along of Palm-Oil Coast region in the state of Bahia. The production increased rapidly in southern lowlands of State due to favorable characteristics such as hot and humid climate, adequate average annual precipitation, and soil fertility (Marques et al., 2019; Schimpl et al., 2013). Currently, this region is top-1 producer of guarana dry seeds in Brazil. Guarana has great economic value, especially in the beverages industry. It is estimated that most of the annual production is used for manufacture of non-alcoholic and energetic beverages (Marques et al., 2019).

The moderate consumption of guarana promotes an increase of energy-expenditure due to the large content of caffeine (2.5 up 6%) and smaller amounts of theobromine and theophylline (Machado et al., 2018; Lima & Farah, 2019). In addition, some works have been reported that guarana also contains other bioactive constituents including phenolic compounds, that represent a source of antioxidant for human diet (Silva et al., 2017;

Santana & Macedo, 2018). However, only a few researches were found in the scientific literature about the mineral composition of guarana samples. It is known that macro- and micro-elements such as Ca, Mg, K, P, S, Fe, Cu and Mn are essentials for human health, playing important roles in vital biochemical functions and enzymatic systems (World Health Organization, 2004).

Multi-elemental determination in foodstuff samples is routinely performed by using plasma-based instrumental methods such as microwave induced plasma optical emission spectrometry (MIP OES), inductively coupled plasma optical emission spectrometry (ICP OES) and inductively coupled plasma mass spectrometry (ICP-MS). All these analytical instrumentations normally require some type of sample pre-treatment before analyzing to destroy the organic matrix and convert in an adequate solution to sample introduction into spectrometer (Rocha et al., 2013; Williams et al., 2019).

Microwave-assisted digestion using nitric acid (alone or combined with hydrogen peroxide) is a well-established sample preparation method that combines high temperature and

Received 18 Dec., 2021

Accepted 25 Mar., 2022

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pressure conditions for the decomposition of organic samples in closed vessels (Bizzi et al., 2017). However, the high expense for acquisition and regular maintenance of the microwave furnaces is a non-desired characteristic associated with the use of microwave systems. In this sense, extraction procedures using ultrasonic-energy are possible alternatives to overcome the drawbacks of microwave-assisted digestion.

The ultrasound-assisted extraction procedure is based on leaching of ions from powdered samples by the action of high-intensity sonication in an acid solution, which the extraction of the analytes occurs due to a phenomenon known as acoustic cavitation (Santos et al., 2006; Tiwari, 2015). It has been demonstrated that the combination of ultrasound-assisted extraction and dilute acids is an effective strategy for the development of greener, fast and inexpensive sample preparation procedures (Gois et al., 2018; Gamela et al., 2020; Pohl et al., 2020).

Despite the simplicity of ultrasound apparatus, several parameters such as nature and concentration of extractor solution, sonication time, ultrasound power and temperature can influence the extraction process and, therefore, should be carefully evaluated (Bendicho et al., 2012). In this context, the Design of Experiments (DOE) appears as a powerful chemometric tool for variables study in ultrasound-assisted extraction to ensure greater extraction efficiency. DOE is a mathematical-statistical technique for multivariate approaches including the optimization of analytical methods by applying surface response methodologies such as Box-Behnken, central composite, Doehlert and mixture designs (Novaes et al., 2016).

Doehlert-matrix is a not-rotatable DOE which has the advantage of allowing the process optimization using a low number of experiments in comparison with Box-Behnken and central composite designs (Ferreira et al., 2004). The Doehlert-matrix has been recently employed for optimization of several analytical procedures for elemental determination in food-products, including dispersive liquid-liquid microextraction (Barreto et al., 2019), microwave-assisted digestion (Costa et al., 2019), extraction induced by emulsion breaking (Valasques et al., 2020) and ultrasound-assisted extraction (Santos et al., 2014; Almeida et al., 2019).

Mixture design is a type of DOE applied to obtain the optimal proportions of each component in a mixture in order to find the best response (Bezerra et al., 2020). For analytical purposes, mixture design has been successfully applied for optimization of the liquid-phase composition in slurry-sampling technique (Trindade et al., 2020), digesting solution (Moreira et al., 2019) and extractor medium in ultrasound-assisted extraction procedures for subsequent elemental-determination by spectroanalytical techniques (Santos et al., 2009; Costa et al., 2020).

Given the economic relevance and high consumption of guarana-based products worldwide, it is important to develop analytical procedures for assessment of the nutritional quality of guarana seeds. In this work, mixture and Doehlert designs combined with a multi-response function were used as chemometric tools for multivariate optimization of an ultrasound-assisted extraction aiming the determination of Ca, Mg, K, P, S, Cu,

Mn and Fe in guarana samples by inductively coupled plasma optical emission spectrometry (ICP OES).

2 Material and methods

2.1 Instrumentation

A model 710 ES axial view inductively coupled plasma optical spectrometer – ICP OES Varian (Mulgrave, Australia) equipped with concentric nebulizer and *single pass* cyclonic nebulization chamber was used for determination of the analytes. Argon 99.998% from White Martins-Praxair (Bahia, Brazil) was used for plasma generation, sample nebulization and auxiliary gas. Instrumental parameters were fixed in radiofrequency power of 1.3 kW; plasma, auxiliary and nebulizer flow rates at 15.0 L min⁻¹, 1.5 L min⁻¹ and 0.7 L min⁻¹, respectively. The analytical emission lines for each element were: Cu (I) 327.395 nm, Mn (II) 257.610 nm, Fe (II) 238.204 nm, Mg (II) 270.800 nm, Ca (II) 373.690 nm, K (I) 766.491 nm, P (I) 213.618 nm, S (I) 181.972 nm. A model AUW 220-D analytical balance Shimadzu (Kyoto, Japan) was used for weighing the samples. For extraction of analytes, a model P30H (P line) ultrasound bath Elma (Singen, Germany) operating at *Sweep* mode was used. A model AP59 Vortex Phoenix Luferto (São Paulo, Brazil) was used for samples agitation. A model SL700 centrifuge Solab (São Paulo, Brazil) was employed to separate the sample solid phase after extraction. A model Mars Xpress microwave furnace CEM (North Caroline, USA) equipped with an infrared temperature sensor and a rotor with 16 perfluoroalkoxy (PFA) vessels was used for samples digestion.

2.2 Reagents and solutions

The solutions were prepared with analytical grade reagents and ultrapure water with a resistivity of 18 MΩ.cm obtained through a Milli-Q purification system from Milipore (Bedford, USA). Nitric acid 65% (m m⁻¹) and hydrochloric acid 37% (m m⁻¹) from Merck (Darmstadt, Germany) were used for analytes extraction. The analytical calibration curves were prepared by using mono-element standard solutions from Merck (Darmstadt, Germany). A multielement standard solution High-Purity Standards (South Caroline, USA) was used for calibration of the ICP OES optical system. All glassware and plastic materials were washed with ultrapure water and decontaminated in a nitric acid bath 10% (v v⁻¹) by at least 24 h.

2.3 Sampling and pre-treatment

Thirty-three samples of guarana dry seeds were collected in guarana producing farms of different cities in the southern lowlands of the state of Bahia, Brazil: Nilo Peçanha (NP, n = 5), Camamu (Cm, n = 11), Taperoá (Tp, n = 11) and Valença (Va, n = 6). The samples were dried in an electronic oven at 50 °C for 16 h for moisture reduction. Then, the samples were ground in a ball mill constituted of stainless steel, transferred for plastic containers, and stored in a desiccator.

2.4 Optimization strategy for ultrasound-assisted extraction procedure

A synthetic sample was previously prepared by mixing several real samples for the procedure optimization step. Two multivariate methodologies were applied to establish the best experimental conditions for ultrasound-assisted extraction of Ca, Mg, K, P, S, Fe, Cu and Mn from guarana samples. First, the composition of the extractor solution was optimized through a simplex-centroid mixture design using 4.5 mol L⁻¹ nitric and hydrochloric acids, and ultrapure water as individual components. In this stage, the final volume of the mixture, sonication time, ultrasound temperature and power were fixed at 10.0 mL, 15 min, 40 °C and 90%, respectively. A total of nine experiments was performed (Table 1).

After definition of the extractor solution, a Doehlert-design was applied to optimize the sonication time (t), ultrasound temperature (T) and power (P) variables. From previous studies reported in the literature as well as the operational parameters of the equipment, the experimental domain was defined at 30-60 °C for temperature (seven levels), 1-13 min for sonication time (five

Table 1. Experimental matrix of mixture design applied to optimization of extractor solution.

| Experiment | Components | | | OD |
|------------|-----------------------|------------|-----------------------|------|
| | HNO ₃ (mL) | HCl (mL) | H ₂ O (mL) | |
| 1 | 0 (0.0) | 0 (0.0) | 1 (10.0) | 0.43 |
| 2 | 0 (0.0) | 1 (5.0) | 0 (5.0) | 0.39 |
| 3 | 1/2 (2.5) | 0 (0.0) | 1/2 (7.5) | 0.85 |
| 4 | 1/2 (2.5) | 1/2 (2.5) | 0 (5.0) | 0.65 |
| 5 | 1 (5.0) | 0 (0.0) | 0 (5.0) | 0.74 |
| 6 | 0 (0.0) | 1/2 (2.5) | 1/2 (7.5) | 0.82 |
| 7 (CP) | 1/3 (1.67) | 1/3 (1.67) | 1/3 (6.67) | 0.76 |
| 8 (CP) | 1/3 (1.67) | 1/3 (1.67) | 1/3 (6.67) | 0.86 |
| 9 (CP) | 1/3 (1.67) | 1/3 (1.67) | 1/3 (6.67) | 0.85 |

CP = central point; OD = overall desirability.

levels) and 80-100% for power (three levels). The experimental matrix with the 15 experiments, including the coded and real values (in bracket), is shown in Table 2.

In both designs, experimental and eventual lack-of-fit errors was evaluated by measurement of three central points. The maximization of the analytical signal (emission intensity) for each element was used as optimization criterion. To obtain the best experimental conditions, a multi-response optimization based on overall desirability function (Derringer & Suich, 1980; Candiotti et al., 2014) was used. The experimental data were processed by using the Statistica 12 and Octave 4.2.1 software.

2.5 Ultrasound-assisted extraction

Approximately 300 mg of guarana sample was weighted in a glass test tube (180 x 30 mm) and 10.0 mL of extractor solution composed of 3.1 mL of 4.5 mol L⁻¹ HNO₃ and 6.9 mL of ultrapure water was added. Samples were sonicated in an ultrasound bath operating at a frequency of 80 KHz and set to 60 °C by 10 min. The position and height of the tube (in relation to water level) on ultrasound bath were fixed by using Isopor® support. After the extraction procedure, the samples were centrifuged at 3,000 rpm by 5 min and 1 mL-aliquot of the supernatant was collected. Then, the samples were 10- and 2.5-fold diluted for macro and microelements, respectively. The resultant solution was analyzed by ICP OES using external calibration technique. All experiments were performed in triplicate.

2.6 Microwave-assisted digestion

As a reference method, guarana samples were acid-digested in a microwave system. A 300 mg sample mass was weighed in digestion vessel and 5.0 mL of HNO₃ 65% (m m⁻¹) and 2.0 mL of H₂O₂ 30% (m m⁻¹) was added. The vessels were heated by applying a heating program of 5 successive stages: i) a 2-minutes ramp up to 120 °C; ii) hold at 120 °C for 8 min; iii) a 5-minutes ramp up to 180 °C; iv) hold at 180 °C for 15 min; and v) cool-down for 15 min. Maximum power (1.6 kW) was used in the microwave

Table 2. Experimental matrix of Doehlert design applied to optimization of ultrasound-assisted extraction.

| Experiment | Factors | | | OD |
|------------|------------------|------------|-------------|------|
| | Temperature (°C) | Time (min) | Power (%) | |
| 1 | 0 (45) | 1 (13) | 0 (90) | 0.91 |
| 2 | 0.866 (60) | 0.5 (10) | 0 (90) | 0.89 |
| 3 | 0.289 (50) | 0.5 (10) | 0.817 (100) | 0.96 |
| 4 | 0 (45) | -1 (1) | 0 (90) | 0.93 |
| 5 | -0.866 (30) | -0.5 (4) | 0 (90) | 0.85 |
| 6 | -0.289 (40) | -0.5 (4) | -0.817 (80) | 0.86 |
| 7 | -0.866 (30) | 0.5 (10) | 0 (90) | 0.87 |
| 8 | -0.289 (40) | 0.5 (10) | -0.817 (80) | 0.82 |
| 9 | 0.866 (60) | -0.5 (4) | 0 (90) | 0.89 |
| 10 | 0.577 (55) | 0 (7) | -0.817 (80) | 0.93 |
| 11 | 0.289 (50) | -0.5 (4) | 0.817 (100) | 0.90 |
| 12 | -0.577 (35) | 0 (7) | 0.817 (100) | 0.90 |
| 13 (CP) | 0 (45) | 0 (7) | 0 (90) | 0.87 |
| 14 (CP) | 0 (45) | 0 (7) | 0 (90) | 0.95 |
| 15 (CP) | 0 (45) | 0 (7) | 0 (90) | 0.91 |

oven. After digestion, the samples were diluted to 25 mL with ultrapure water and analyzed by ICP OES. All experiments were performed in triplicate.

2.7 Method validation

For validation of the proposed procedure, analytical parameters performance such as detection and quantification limits (LOD and LOQ, respectively), working linear range, precision and trueness were evaluated. Similar to the optimization step, the validation was performed using the synthetic sample. The limits of detection and quantification were calculated according to Equations 1-2, as recommended by IUPAC (Thompson et al., 2002).

$$LOD = (3 \times SD_{Br}) / slope \quad (1)$$

$$LOQ = (10 \times SD_{Br}) / slope \quad (2)$$

Where SD_{Br} is the standard deviation obtained of measurements of analytical blanks ($n = 10$) and slope is the inclination of the calibration curve.

Precision was estimated by the relative standard deviation (RSD) of seven determinations in the synthetic sample. The trueness of the method was evaluated by comparing the results obtained from the proposed procedure and microwave-assisted digestion.

3 Results and discussion

3.1 Optimization of the ultrasound-assisted extraction procedure

The extractor solution was established by applying a simplex-centroid mixture design to optimize the proportions of the components HNO_3 , HCl and H_2O . Table 1 presents the experimental matrix and obtained results in each experiment, express as emission intensities for the analytes. Optimization criteria was the maximization of the analytical signal for each element. In order to obtain a compromise condition for all responses simultaneously, the overall desirability was adopted as unique response. For this, individual desirability values (d_i) were initially calculated for each response (emission intensity) according to Equation 3 (Derringer & Suich, 1980; Bezerra et al., 2019).

$$d_i = (y_i - L_i / U_i - L_i)^s \quad (3)$$

Where y_i is the original response (analytical signal in emission intensity), L_i is the low value obtained for response, U_i is the high value of response and 's' is the established weight ($s = 1$) for each response.

Then, the overall desirability was calculated by geometric mean of the individual desirability values, as shown in Equation 4 (Derringer & Suich, 1980; Bezerra et al., 2019).

$$OD = \sqrt[n]{d_1 d_2 \dots d_n} \quad (4)$$

The quality of the obtained models was evaluated by analysis of variance (ANOVA). Among the tested mathematic models, the quadratic model presented the best fit to experimental data.

According to ANOVA (p -value < 0.05), the ratio between *Mean Square of Regression* (MSR) and *Mean Square of Residue* (MSRes) (F -calculated = 25.4) was higher than F -critical value (9.0) at the 95% confidence level (see Table S1). Additionally, the observed value for the ratio between *Mean Square of lack-of-fit* (MSlof) and *Mean Square of pure error* (MSpe) (F -calculated = 0.83) was less than F -critical (18.5), evidencing that the fitted model did not present lack-of-fit. Therefore, the quadratic model was adequate to describe the data generated by mixture design. Equation 5 shows the relationship between the proportions of the mixture components and the analytical response (overall desirability).

$$OD = 0.74 \pm 0.05 (HNO_3) + 0.39 \pm 0.05 (HCl) + 0.43 \pm 0.05 (H_2O) + 0.26 \pm 0.21 (HNO_3 \times HCl) + 0.98 \pm 0.21 (HNO_3 \times H_2O) + 1.56 \pm 0.21 (HCl \times H_2O) \quad (5)$$

The contour graph generated by the quadratic model is shown in Figure 1. It is possible to verify that the best response (higher OD) was obtained in the region of a binary mixture between nitric acid and water. The conditions that provided the better extraction of analytes were 3.1 mL of $4.5 \text{ mol L}^{-1} HNO_3$ and 6.9 mL of H_2O . These conditions were chosen as extractor medium for the proposed procedure. The use of diluted HNO_3 is desirable in analytical methods based on ICP-optical emission spectrometry because does not affect the sample introduction system of the spectrometer and can overcome non-spectral interferences caused by eventual transport effects (Stewart & Olesik, 1998; Todolí & Mermet, 2011). In addition, diluted solutions contribute to environmental-friendly methods, following Green Analytical Chemistry recommendations (Bizzi et al., 2017).

After the definition of extractor medium, the instrumental parameters of the ultrasound bath were optimized employing a Doehlert matrix. The studied variables and respective experimental domain were temperature (30 - $60 \text{ }^\circ\text{C}$), sonication time (1 - 13 min) and power (80 - 100%). As in mixture design, the maximization of analytical signal for each element was the

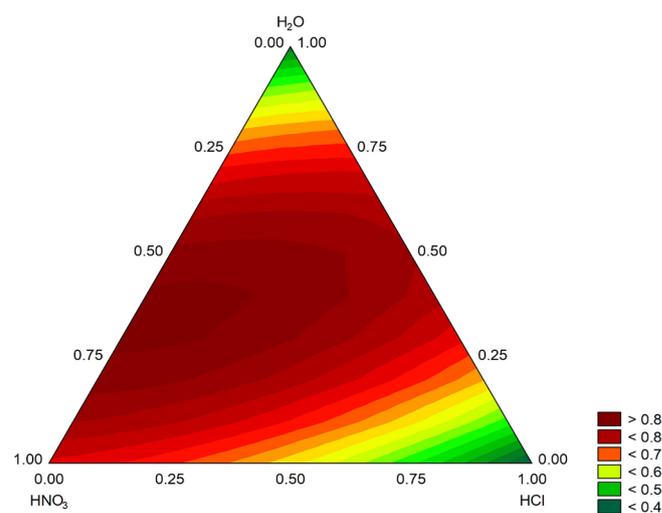


Figure 1. Contour graph generated from the mixture design for overall desirability.

criteria used for optimization. All responses were converted in individual desirability and subsequently combined in a unique response (overall desirability), according to Equations 3 and 4, respectively. Table 2 shows the experimental matrix and responses obtained by Doehlert design.

A quadratic model was fitted to describe the experimental data. According to ANOVA (p -value < 0.05) presented in Table S2, the regression was statistically significant in F test 1 (F -calculated, 5.05 > F -critical, 4.77) at a confidence level of 95%. Furthermore, the proposed model also did not present lack-of-fit, considering that F -calculated value (0.59) was less than F -critical (9.55) in F test 2. The Equation 6 shows the obtained second-order function with 10 regression coefficients and their respective confidence intervals (95% confidence level). Significant coefficients are highlighted in bold.

$$\begin{aligned}
 OD = & \mathbf{0.923} \pm \mathbf{0.032} + \mathbf{0.054} \pm \mathbf{0.027} (T) + 0.015 \pm \\
 & 0.027 (t) + 0.008 \pm 0.0278 (P) - 0.023 \pm 0.050 (T^2) - \\
 & \mathbf{0.053} \pm \mathbf{0.050} (t^2) - 0.025 \pm 0.048 (P^2) + 0.04 \pm \\
 & 0.06 (T \times t) + 0.028 \pm 0.071 (T \times P) - 0.008 \pm 0.071 (t \times P)
 \end{aligned} \quad (6)$$

Where T = temperature; t = sonication time; P = power.

The temperature was the more significant variable in the extraction procedure, with a positive effect. This means that better extractions are obtained when the temperature increases to a superior level. Indeed, the temperature has a relevant role in ultrasound-assisted extraction procedures because it kinetically favors the occurrence of reactions. It is known that temperatures above 50 °C promotes the decreasing of liquid surface tension and increasing the vapor pressure inside the cavitation bubbles, favoring sonochemical effects in the reaction medium (Padilha et al., 2011; Bendicho & Lavilla, 2013). In turn, the ultrasound power was non-significant, i.e., this variable does not influence the extraction process.

Contour plots generated from the Doehlert design for overall desirability are shown in Figure 2. By evaluating the profile for predicted values (data not shown), the obtained optimal conditions, decodified for real values, were: 59.5 °C, 8.8 min and 95% for temperature, sonication time and ultrasound power, respectively. Due to equipment operational limitations, the adopted values for procedure were temperature of 60 °C, 10 min for sonication and 100% of the power. The optimized conditions were employed for extraction of essential elements from guarana samples.

3.2 Analytical characteristics of the proposed procedure

Table 3 present the evaluated analytical parameters. LOD and LOQ values were relatively low, varying between 0.03 to 1.1 mg kg⁻¹ and 0.1 to 3.7 mg kg⁻¹ for Mn and Ca, respectively. These results indicate that the proposed method was adequate for quantification of Ca, Mg, K, P, S, Cu, Mn, and Fe in guarana samples by ICP OES. The precision was estimated by the repeatability (n = 7). RSD values were less than 8%, showing that the extraction procedure presented acceptable precision for all studied analytes.

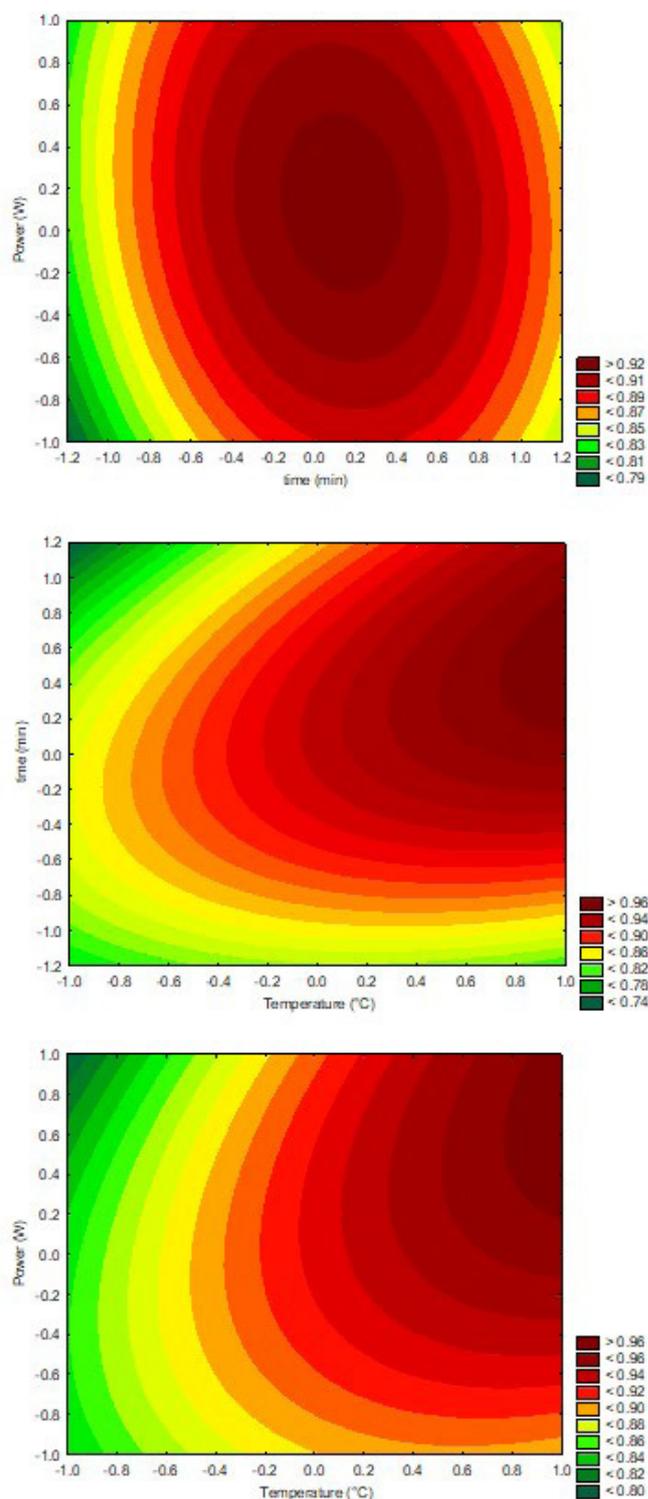


Figure 2. Contour graphs generated from the Doehlert-design for overall desirability.

The trueness of the procedure was evaluated by a statistical comparison between the results obtained using the ultrasound-assisted extraction and the microwave-assisted digestion (reference method). Initially, a F -test was applied in order to compare the standard deviations (SD) for the two methods. Since no significant differences were observed for all SD values

($F_{\text{calculated}} < F_{\text{critical}}$), a pooled standard deviation was previously estimated prior calculation of the t -value (Miller & Miller, 2010). The results are shown in Table 4. The statistical t -test showed a non-significant difference (at a 95% confidence level) between the determined mass fractions when both procedures were used, indicating that the ultrasound-assisted extraction presented good accuracy.

Table 3. Validation parameters of the proposed method.

| Element | LOD (mg kg ⁻¹) | LOQ (mg kg ⁻¹) | RSD (%) | Working linear range (mg L ⁻¹) |
|---------|----------------------------|----------------------------|---------|--|
| Cu | 0.25 | 0.83 | 7 | 0.025-2.0 |
| Mn | 0.03 | 0.10 | 3 | 0.0003-2.0 |
| Fe | 0.04 | 0.14 | 5 | 0.004-2.0 |
| Mg | 0.10 | 0.33 | 4 | 0.010-40 |
| Ca | 1.12 | 3.75 | 7 | 0.113-40 |
| K | 0.07 | 0.22 | 4 | 0.007-50 |
| P | 0.81 | 2.71 | 5 | 0.081-20 |
| S | 0.49 | 1.62 | 8 | 0.049-20 |

Table 4. Comparison between mass fraction of essential elements in guarana sample applying the proposed procedure and microwave-assisted digestion (average \pm standard deviation, $n = 3$).

| Analyte | Microwave-assisted digestion (mg kg ⁻¹) | Ultrasound-assisted extraction (mg kg ⁻¹) | F | F _{tab} | t | t _{tab} |
|---------|---|---|------|------------------|------|------------------|
| Cu | 10.0 \pm 1.0 | 9.8 \pm 0.5 | 4.00 | 19.00 | 0.31 | 2.78 |
| Mn | 25.8 \pm 0.5 | 26.3 \pm 0.7 | 1.96 | | 1.01 | |
| Fe | 39.8 \pm 2.7 | 41.8 \pm 1.7 | 2.52 | | 1.09 | |
| Mg | 711 \pm 31 | 697 \pm 23 | 1.82 | | 0.63 | |
| Ca | 591 \pm 25 | 577 \pm 14 | 3.19 | | 0.85 | |
| K | 7,083 \pm 137 | 7,311 \pm 172 | 1.58 | | 1.80 | |
| P | 1,437 \pm 31 | 1,380 \pm 89 | 8.24 | | 1.05 | |
| S | 1,239 \pm 124 | 1,151 \pm 178 | 2.06 | | 0.70 | |

F_{tab} = tabulated value for F ($p = 0.05$); t_{tab} = tabulated value for t ($p = 0.05$).

Table 5. Mass fraction for essential macro- and micro-elements in guarana seeds samples (average \pm standard deviation, $n = 3$).

| Sample | Mass fraction \pm standard deviation (mg kg ⁻¹) | | | | | | | |
|--------|---|----------------|-----------------|----------------|----------------|----------------|----------------|---------------|
| | Cu | Mn | Fe | Mg | Ca | K | P | S |
| Cm-01 | 12.7 \pm 1.0 | 15.2 \pm 0.2 | 19.4 \pm 0.7 | 552 \pm 11 | 1319 \pm 50 | 4872 \pm 12 | 1779 \pm 17 | 1474 \pm 6 |
| Cm-02 | 13.4 \pm 0.9 | 13.8 \pm 0.6 | 22.0 \pm 1.4 | 899 \pm 42 | 990 \pm 17 | 5341 \pm 367 | 809 \pm 51 | 703 \pm 21 |
| Cm-03 | 6.1 \pm 0.6 | 18.2 \pm 1.3 | 37.3 \pm 1.5 | 1057 \pm 80 | 1207 \pm 117 | 4468 \pm 151 | 1418 \pm 63 | 903 \pm 28 |
| Cm-04 | 13.7 \pm 0.8 | 17.7 \pm 1.7 | 22.7 \pm 1.9 | 725 \pm 39 | 698 \pm 3 | 4783 \pm 201 | 822 \pm 47 | 1041 \pm 17 |
| Cm-05 | 12.6 \pm 0.2 | 12.1 \pm 1.8 | 23.3 \pm 0.9 | 716 \pm 92 | 496 \pm 69 | 5299 \pm 538 | 912 \pm 72 | 1140 \pm 17 |
| Cm-06 | 12.9 \pm 0.5 | 14.5 \pm 0.8 | 43.9 \pm 1.2 | 946 \pm 32 | 811 \pm 34 | 6549 \pm 160 | 1317 \pm 21 | 1251 \pm 13 |
| Cm-07 | 15.8 \pm 0.8 | 17.9 \pm 0.7 | 31.9 \pm 3.1 | 871 \pm 44 | 689 \pm 5 | 5142 \pm 174 | 1034 \pm 54 | 1252 \pm 25 |
| Cm-08 | 6.2 \pm 0.8 | 16.9 \pm 0.9 | 22.2 \pm 0.6 | 890 \pm 117 | 642 \pm 81 | 4885 \pm 481 | 892 \pm 74 | 716 \pm 34 |
| Cm-09 | 6.1 \pm 0.3 | 17.0 \pm 1.7 | 15.7 \pm 0.2 | 742 \pm 27 | 547 \pm 85 | 4996 \pm 553 | 895 \pm 56 | 759 \pm 32 |
| Cm-10 | 9.4 \pm 0.7 | 26.2 \pm 1.7 | 36.5 \pm 1.5 | 771 \pm 18 | 957 \pm 38 | 6816 \pm 51 | 1328 \pm 19 | 1174 \pm 16 |
| Cm-11 | 12.8 \pm 0.4 | 12.7 \pm 1.8 | 74.2 \pm 10.6 | 1352 \pm 7 | 1953 \pm 317 | 4569 \pm 75 | 1421 \pm 57 | 1230 \pm 16 |
| NP-01 | 12.2 \pm 0.0 | 21.1 \pm 1.9 | 66.6 \pm 3.7 | 1070 \pm 147 | 1762 \pm 152 | 4838 \pm 79 | 1149 \pm 23 | 1180 \pm 17 |
| NP-02 | 12.9 \pm 0.1 | 15.7 \pm 0.4 | 18.9 \pm 1.5 | 562 \pm 88 | 1275 \pm 68 | 4224 \pm 562 | 879 \pm 130 | 559 \pm 31 |
| NP-03 | 5.8 \pm 0.6 | 24.7 \pm 2.9 | 31.8 \pm 4.5 | 1070 \pm 147 | 638 \pm 95 | 8002 \pm 948 | 1287 \pm 151 | 868 \pm 47 |
| NP-04 | 14.4 \pm 0.1 | 25 \pm 0.2 | 23.5 \pm 0.7 | 819 \pm 4 | 783 \pm 21 | 5009 \pm 81 | 1003 \pm 9 | 1231 \pm 2 |
| NP-05 | 11.4 \pm 0.3 | 19.9 \pm 0.6 | 17.9 \pm 0.5 | 681 \pm 12 | 552 \pm 47 | 4328 \pm 83 | 1101 \pm 31 | 985 \pm 12 |
| Tp-01 | 8.5 \pm 0.1 | 13.7 \pm 2.2 | 72.6 \pm 12.0 | 1060 \pm 41 | 1986 \pm 330 | 4478 \pm 277 | 1148 \pm 76 | 906 \pm 36 |

Cm = Camamu ($n = 11$); NP = Nilo Peçanha ($n = 5$); Tp = Taperoá ($n = 11$); Va = Valença ($n = 6$).

4 Application of the proposed method in guarana seed samples

The proposed method was applied for determination of Ca, Mg, K, P, S, Cu, Mn, and Fe in thirty-three guarana seeds samples from the southern lowlands of the state of Bahia. The results (express in mg kg⁻¹) are shown in Table 5. High mass fractions of potassium were found for all analyzed samples, ranging from 4,225 to 8,432 mg kg⁻¹. For macro-elements calcium and magnesium, the found mass fractions ranged from 496 to 1,987 mg kg⁻¹ and 515 to 1,352 mg kg⁻¹, respectively. Similar results were obtained by Santos et al. (2019) for guarana seeds from the state of Bahia after samples digestion in closed-vessels microwave system followed by determination by ICP OES.

The mass fraction of manganese ranged from 6.5 a 26.0 mg kg⁻¹. Mass fractions less than 16 mg kg⁻¹ were found for cooper in all guarana samples. However, a relatively large variation was observed for the mass fraction of iron (13.0 to 91.3 mg kg⁻¹), possibly due to presence of soils with high contents of iron oxides in some regions of the southern lowlands in state of Bahia

Table 5. Continued...

| Sample | Mass fraction ± standard deviation (mg kg ⁻¹) | | | | | | | |
|--------|---|------------|-------------|------------|------------|-------------|------------|------------|
| | Cu | Mn | Fe | Mg | Ca | K | P | S |
| Tp-02 | 9.1 ± 0.3 | 14.1 ± 1.2 | 28.8 ± 0.5 | 1259 ± 150 | 1349 ± 86 | 4270 ± 103 | 814 ± 85 | 995 ± 8 |
| Tp-03 | 9.2 ± 0.7 | 14.7 ± 0.9 | 13.8 ± 0.9 | 1219 ± 9 | 1375 ± 80 | 7668 ± 464 | 829 ± 19 | 1137 ± 90 |
| Tp-04 | 10.3 ± 1.4 | 13.5 ± 0.5 | 25.4 ± 3.1 | 913 ± 24 | 1371 ± 47 | 4824 ± 419 | 831 ± 29 | 964 ± 84 |
| Tp-05 | 5.9 ± 0.3 | 10.4 ± 0.0 | 55.5 ± 0.2 | 1136 ± 25 | 1152 ± 172 | 8432 ± 152 | 970 ± 52 | 808 ± 41 |
| Tp-06 | 9.4 ± 0.2 | 8.1 ± 0.2 | 69.7 ± 1.7 | 923 ± 7 | 739 ± 18 | 6858 ± 82 | 1540 ± 24 | 1312 ± 25 |
| Tp-07 | 5.7 ± 0.0 | 12.8 ± 0.3 | 13.2 ± 0.2 | 1029 ± 3 | 992 ± 58 | 7543 ± 10 | 93.2 ± 4.0 | 993 ± 13 |
| Tp-08 | 6.3 ± 0.8 | 25.7 ± 2.7 | 43.8 ± 3.6 | 1175 ± 4 | 922 ± 33 | 8069 ± 639 | 1439 ± 125 | 1033 ± 52 |
| Tp-09 | 12.1 ± 0.2 | 25.2 ± 1.5 | 22.5 ± 3.9 | 514 ± 39 | 1292 ± 77 | 5070 ± 232 | 816 ± 44 | 810 ± 54 |
| Tp-10 | 12.4 ± 0.4 | 17.3 ± 0.2 | 24.6 ± 0.8 | 698 ± 14 | 496 ± 26 | 5072 ± 50 | 1115 ± 172 | 1140 ± 42 |
| Tp-11 | 10.4 ± 0.1 | 6.5 ± 0.2 | 43.3 ± 1.6 | 699 ± 24 | 1356 ± 87 | 7261 ± 246 | 1271 ± 29 | 1213 ± 31 |
| Va-01 | 11.1 ± 1.4 | 11.8 ± 1.7 | 91.3 ± 14.8 | 930 ± 32 | 1694 ± 351 | 4765 ± 281 | 1276 ± 71 | 968 ± 106 |
| Va-02 | 10.2 ± 0.8 | 14.7 ± 2.9 | 23.4 ± 2.0 | 592 ± 38 | 570 ± 12 | 5035 ± 155 | 964 ± 60 | 843 ± 3 |
| Va-03 | 5.4 ± 0.5 | 14.3 ± 0.6 | 29.1 ± 0.6 | 1037 ± 2 | 869 ± 113 | 8314 ± 473 | 803 ± 60 | 975 ± 107 |
| Va-04 | 11.7 ± 0.2 | 12.1 ± 0.9 | 16.4 ± 0.6 | 598 ± 30 | 547 ± 38 | 4642 ± 121 | 849 ± 15 | 1038 ± 87 |
| Va-05 | 5.1 ± 0.4 | 20.4 ± 2.1 | 27.6 ± 2.9 | 809 ± 128 | 544 ± 46 | 8035 ± 1029 | 994 ± 149 | 1098 ± 135 |
| Va-06 | 12.8 ± 0.2 | 16.1 ± 0.8 | 22.1 ± 1.6 | 587 ± 13 | 1189 ± 58 | 5503 ± 129 | 999 ± 17 | 968 ± 39 |

Cm = Camamu (n = 11); NP = Nilo Peçanha (n = 5); Tp = Taperoá (n = 11); Va = Valença (n = 6).

(Santos et al., 2019). In recent work, Adolfo et al. (2020) reported that the mass fraction of Fe ranged from 21.3 to 144 mg kg⁻¹ in guarana samples purchased in the state of Rio Grande do Sul, Brazil, after direct analysis by high resolution continuum source graphite furnace atomic absorption spectrometry.

Other studies have been performed in order to evaluate the content of essential macro- and micro-elements in commercial guarana powder samples (Leal et al., 2013; Gois et al., 2016). The average values for Ca, K, Mg, Fe and Mn were like those found in the present study. In general, variations observed for the mass fraction of elements in guarana samples analyzed in this work can be related to several factors such as soil characteristics, genetic diversity of cultivated *P. cupana* plants as well as non-standardization of seeds post-harvest processing in southern lowlands of the state of Bahia.

5 Conclusion

The proposed procedure for the extraction of essential elements using ultrasonic irradiation proved to be an excellent alternative for sample preparation of guarana samples, showing advantages such as simplicity, high analytical frequency, and low cost. The employed mixture design enabled the use of dilute nitric acid (1.40 mol L⁻¹) for efficient extraction of Ca, Mg, K, P, S, Cu, Mn, and Fe. Additionally, Doehlert matrix was effective to optimize the instrumental parameters studied in the ultrasound-assisted procedure, allowing satisfactory extractions for all analytes in a short time. The ultrasound-based method showed good sensitivity, precision, and trueness. It was demonstrated in this work that the use of ultrasound-assisted extraction and diluted HNO₃ was an adequate strategy for the development of a greener analytical method for multi-element determination in guarana seeds samples by using ICP OES.

Conflict of interest

There are no conflicts to declare.

Acknowledgements

The authors acknowledge the financial support provided by Fundação de Amparo à Pesquisa do Estado da Bahia (FAPESB), Conselho Nacional de Desenvolvimento Científico e Tecnológico (CNPq), T.O. PNE 014/2014, and Coordenação de Aperfeiçoamento de Pessoal de Nível Superior (CAPES, Finance Code 001).

References

- Adolfo, F. R., Nascimento, P. C., Leal, G. C., Bohrer, D., Viana, C., & Carvalho, L. M. (2020). Simultaneous determination of Fe and Ni in guarana (*Paullinia cupana* Kunth) by HR-CS GF AAS: comparison of direct solid analysis and wet acid digestion procedures. *Journal of Food Composition and Analysis*, 88, 103459. <http://dx.doi.org/10.1016/j.jfca.2020.103459>.
- Almeida, J. S., Santos, G. L., Brandão, G. C., Korn, M. G. A., & Teixeira, L. S. G. (2019). Multivariate optimization of ultrasound-assisted extraction using Doehlert matrix for simultaneous determination of Fe and Ni in vegetable oils by high-resolution continuum source graphite furnace atomic absorption spectrometry. *Food Chemistry*, 273, 130-135. <http://dx.doi.org/10.1016/j.foodchem.2018.01.112>. PMID:30292358.
- Barreto, J. A., Assis, R. S., Cassella, R. J., & Lemos, V. A. (2019). A novel strategy based on in-syringe dispersive liquid-liquid microextraction for the determination of nickel in chocolate samples. *Talanta*, 193, 23-28. <http://dx.doi.org/10.1016/j.talanta.2018.09.082>. PMID:30368293.
- Bendicho, C., & Lavilla, I. (2013). *Reference module in chemistry, molecular sciences and chemical engineering*. Vigo: Elsevier. Ultrasound-assisted metal extractions. Online. Retrieved from <https://www.sciencedirect.com/science/article/pii/B9780124095472049532?via%3Dihub#fn0010>
- Bendicho, C., Calle, I., Pena, F., Costas, M., Cabaleiro, N., & Lavilla, I. (2012). Ultrasound-assisted pretreatment of solid samples in the context of green analytical chemistry. *Trends in Analytical Chemistry*, 31, 50-60. <http://dx.doi.org/10.1016/j.trac.2011.06.018>.
- Bezerra, M. A., Ferreira, S. L. C., Novaes, C. G., Santos, A. M. P., Valasques, G. S., Cerqueira, U. M. F. M., & Alves, J. P. S. (2019).

- Simultaneous optimization of multiple responses and its application in analytical chemistry – a review. *Talanta*, 194, 941-959. <http://dx.doi.org/10.1016/j.talanta.2018.10.088>. PMID:30609628.
- Bezerra, M. A., Lemos, V. A., Novaes, C. G., Jesus, R. M., Souza, H. R. Fo., Araújo, S. A., & Alves, J. P. S. (2020). Application of mixture design in analytical chemistry. *Microchemical Journal*, 152, 104336. <http://dx.doi.org/10.1016/j.microc.2019.104336>.
- Bizzi, C. A., Pedrotti, M. F., Silva, J. S., Barin, J. S., Nóbrega, J. A., & Flores, E. M. M. (2017). Microwave-assisted digestion methods: towards greener approaches for plasma-based analytical techniques. *Journal of Analytical Atomic Spectrometry*, 32(8), 1448-1466. <http://dx.doi.org/10.1039/C7JA00108H>.
- Candiotti, L. V., Zan, M. M., Cámara, M. S., & Goicoechea, H. C. (2014). Experimental design and multiple response optimization. Using the desirability function in analytical methods development. *Talanta*, 124, 123-138. <http://dx.doi.org/10.1016/j.talanta.2014.01.034>. PMID:24767454.
- Costa, F. S., Leal, R. V. P., Pacheco, C. S. V., Amorim, F. A. C., Jesus, R. M., Santos, L. N., & Silva, E. G. P. (2020). Multivariate optimization of ultrasound-assisted extraction procedure for the determination of Cu, Fe, Mn, and Zn in plant samples by flame atomic absorption spectrometry. *Analytical Methods*, 12(19), 2509-2516. <http://dx.doi.org/10.1039/D0AY00554A>. PMID:32930241.
- Costa, V. C., Pinheiro, F. C., Amorim, F. A. C., Silva, E. G. P., & Pereira-Filho, E. R. (2019). Multivariate optimization for the development of a sample preparation procedure and evaluation of calibration strategies for nutrient elements determination in handmade chocolate. *Microchemical Journal*, 150, 104166. <http://dx.doi.org/10.1016/j.microc.2019.104166>.
- Derringer, G., & Suich, R. (1980). Simultaneous optimization of several response variables. *Journal of Quality Technology*, 12(4), 214-219. <http://dx.doi.org/10.1080/00224065.1980.11980968>.
- Ferreira, S. L. C., Santos, W. N. L., Quintella, C. M., Barros, B. No., & Bosque-Sendra, J. M. (2004). Doehlert matrix: a chemometric tool for analytical chemistry - review. *Talanta*, 63(4), 1061-1067. <http://dx.doi.org/10.1016/j.talanta.2004.01.015>. PMID:18969534.
- Gamela, R. R., Costa, V. C., & Pereira-Filho, E. R. (2020). Multivariate optimization of ultrasound-assisted extraction procedure for the determination of Ca, Fe, K, Mg, Mn, P, and Zn in pepper samples by ICP OES. *Food Analytical Methods*, 13(1), 69-77. <http://dx.doi.org/10.1007/s12161-019-01524-5>.
- Gois, J. S., Almeida, T. S., Andrade, R. M., Toaldo, I. M., Bordignon-Luiz, M. T., & Borges, D. L. G. (2016). Direct solid analysis for the determination of Mn, Ni, Rb and Sr in powdered stimulant plants using high-resolution continuum source atomic absorption spectrometry followed by chemometric classification based on elemental composition, polyphenol content and antioxidant activity. *Microchemical Journal*, 124, 283-289. <http://dx.doi.org/10.1016/j.microc.2015.08.020>.
- Gois, J. S., Lucena, I. O., Cezario, P. S. D. O., Silva, A. P., Lima, I. C. A., & Luna, A. S. (2018). A high-throughput method for multi-element determination in green coffee beans using diluted nitric acid and ultrasound energy. *Analytical Methods*, 10(14), 1656-1661. <http://dx.doi.org/10.1039/C8AY00331A>.
- Leal, A. S., Prado, G., Gomes, T. C. B., Sepe, F. P., & Dalmázio, I. (2013). Determination of metals in medicinal plants highly consumed in Brazil. *Brazilian Journal of Pharmaceutical Sciences*, 49(3), 599-607. <http://dx.doi.org/10.1590/S1984-82502013000300022>.
- Lima, J. P., & Farah, A. (2019). Methylxanthines in stimulant foods and beverages commonly consumed in Brazil. *Journal of Food Composition and Analysis*, 78, 75-85. <http://dx.doi.org/10.1016/j.jfca.2019.02.001>.
- Machado, K. N., Freitas, A. A., Cunha, L. H., Faraco, A. A. G., Pádua, R. M., Braga, F. C., Vianna-Soares, C. D., & Castilho, R. O. (2018). A rapid simultaneous determination of methylxanthines and proanthocyanidins in Brazilian guaraná (Paullinia cupana Kunth.). *Food Chemistry*, 239, 180-188. <http://dx.doi.org/10.1016/j.foodchem.2017.06.089>. PMID:28873557.
- Marques, L. L. M., Ferreira, E. D. F., Paula, M. N., Klein, T., & Mello, J. C. P. (2019). Paullinia cupana: a multipurpose plant – a review. *Brazilian Journal Pharmacognosy*, 29(1), 77-110. <http://dx.doi.org/10.1016/j.bjpp.2018.08.007>.
- Miller, J. N., & Miller, J. C. (2010). *Statistics and chemometrics for analytical chemistry* (6th ed.). Harlow: Pearson Education Limited.
- Moreira, L. S., Chagas, B. C., Pacheco, C. S. V., Santos, H. M., Menezes, L. H. S., Nascimento, M. M., Batista, M. A. S., Jesus, R. M., Amorim, F. A. C., Santos, L. N., & Silva, E. G. P. (2019). Development of procedure for sample preparation of cashew nuts using mixture design and evaluation of nutrient profiles by Kohonen neural network. *Food Chemistry*, 273, 136-143. <http://dx.doi.org/10.1016/j.foodchem.2018.01.050>. PMID:30292359.
- Novaes, C. G., Bezerra, M. A., Silva, E. G. P., Santos, A. M. P., Romão, I. L. S., & Santos, J. H. No. (2016). A review of multivariate designs applied to the optimization of methods based on inductively coupled plasma optical emission spectrometry (ICP OES). *Microchemical Journal*, 128, 331-346. <http://dx.doi.org/10.1016/j.microc.2016.05.015>.
- Padilha, C. C. F., Moraes, P. M., Garcia, L. A., Pozzi, C. M. C., Lima, G. P. P., Valente, J. P. S., Jorge, S. M. A., & Padilha, P. M. (2011). Evaluation of Cu, Mn, and Se in vegetables using ultrasonic extraction and GFAAS quantification. *Food Analytical Methods*, 4(3), 319-325. <http://dx.doi.org/10.1007/s12161-010-9169-x>.
- Pohl, P., Dzimitrowicz, A., Lesniewicz, A., Welna, M., Szymczycha-Madeja, A., Jamroz, P., & Cyganowski, P. (2020). Multivariable optimization of ultrasound-assisted solvent extraction of bee pollen prior its element analysis by FAAS. *Microchemical Journal*, 157, 105009. <http://dx.doi.org/10.1016/j.microc.2020.105009>.
- Rocha, D. L., Batista, A. D., Rocha, F. R. P., Donati, G. L., & Nóbrega, J. A. (2013). Greening sample preparation in inorganic analysis. *Trends in Analytical Chemistry*, 45, 79-92. <http://dx.doi.org/10.1016/j.trac.2012.12.015>.
- Santana, Á. L., & Macedo, G. A. (2018). Health and technological aspects of methylxanthines and polyphenols from guarana: a review. *Journal of Functional Foods*, 47, 457-468. <http://dx.doi.org/10.1016/j.jff.2018.05.048>.
- Santos, D. C. M. B., Carvalho, L. S. B., Lima, D. C., Leão, D. J., Teixeira, L. S. G., & Korn, M. G. A. (2014). Determination of micronutrient minerals in coconut milk by ICP OES after ultrasound-assisted extraction procedure. *Journal of Food Composition and Analysis*, 34(1), 75-80. <http://dx.doi.org/10.1016/j.jfca.2014.02.008>.
- Santos, D. Jr., Krug, F. J., Pereira, M. G., & Korn, M. (2006). Currents on ultrasound-assisted extraction for sample preparation and spectroscopic analytes determination. *Applied Spectroscopy Reviews*, 41(3), 305-321. <http://dx.doi.org/10.1080/05704920600620436>.
- Santos, H. M., Coutinho, J. P., Amorim, F. A. C., Lôbo, I. P., Moreira, L. S., Nascimento, M. M., & Jesus, R. M. (2019). Microwave-assisted digestion using diluted HNO₃ and H₂O₂ for macro and microelements determination in guarana samples by ICP OES. *Food Chemistry*, 273, 159-165. <http://dx.doi.org/10.1016/j.foodchem.2017.12.074>. PMID:30292363.
- Santos, W. P. C., Castro, J. T., Bezerra, M. A., Fernandes, A. P., Ferreira, S. L. C., & Korn, M. G. A. (2009). Application of multivariate

- optimization in the development of an ultrasound-assisted extraction procedure for multielemental determination in bean seeds samples using ICP OES. *Microchemical Journal*, 91(2), 153-158. <http://dx.doi.org/10.1016/j.microc.2008.10.001>.
- Schimpl, F. C., Silva, J. F., Gonçalves, J. F. D. C., & Mazzafera, P. (2013). Guarana: revisiting a highly caffeinated plant from the Amazon. *Journal of Ethnopharmacology*, 150(1), 14-31. <http://dx.doi.org/10.1016/j.jep.2013.08.023>. PMID:23981847.
- Silva, G. S., Canuto, K. M., Ribeiro, P. R. V., Brito, E. S., Nascimento, M. M., Zocolo, G. J., Coutinho, J. P., & Jesus, R. M. (2017). Chemical profiling of guarana seeds (*Paullinia cupana*) from different geographical origins using UPLC-QTOF-MS combined with chemometrics. *Food Research International*, 102, 700-709. <http://dx.doi.org/10.1016/j.foodres.2017.09.055>. PMID:29196003.
- Stewart, I. I., & Olesik, J. W. (1998). The effect of nitric acid concentration and nebulizer gas flow rates on aerosol properties and transport rates in inductively coupled plasma sample introduction. *Journal of Analytical Atomic Spectrometry*, 13(11), 1249-1256. <http://dx.doi.org/10.1039/a804966a>.
- Thompson, M., Ellison, S. L. R., & Wood, R. (2002). Harmonized guidelines for single-laboratory validation of methods of analysis (IUPAC technical report). *Pure and Applied Chemistry*, 74(5), 835-855. <http://dx.doi.org/10.1351/pac200274050835>.
- Tiwari, B. K. (2015). Ultrasound: a clean, green extraction technology. *Trends in Analytical Chemistry*, 71, 100-109. <http://dx.doi.org/10.1016/j.trac.2015.04.013>.
- Todoí, J. L., & Mermet, J. M. (2011). Fundamentals and practical aspects of nonspectroscopic interferences in inductively coupled plasma atomic spectrometry. In R. A. Meyers (Ed.), *Encyclopedia of analytical chemistry: applications, theory and instrumentation* (pp. 1-29). Chichester: Wiley. <http://dx.doi.org/10.1002/9780470027318.a9184>.
- Trindade, A. C., Araújo, S. A., Amorim, F. A. C., Silva, D. S., Alves, J. P. S., Trindade, J. S., Aguiar, R. M., & Bezerra, M. A. (2020). Development of a method based on slurry sampling for determining Ca, Fe, and Zn in coffee samples by flame atomic absorption spectrometry. *Food Analytical Methods*, 13(1), 203-211. <http://dx.doi.org/10.1007/s12161-019-01578-5>.
- Valasques, G. S., Santos, A. M. P., Souza, V. S., Teixeira, L. S. G., Alves, J. P. S., Santos, M. J., Santos, W. P. C., & Bezerra, M. A. (2020). Multivariate optimization for the determination of cadmium and lead in crude palm oil by graphite furnace atomic absorption spectrometry after extraction induced by emulsion breaking. *Microchemical Journal*, 153, 104401. <http://dx.doi.org/10.1016/j.microc.2019.104401>.
- Williams, C. B., Amais, R. S., Fontoura, B. M., Jones, B. T., Nóbrega, J. A., & Donati, G. L. (2019). Recent developments in microwave-induced plasma optical emission spectrometry and applications of a commercial Hammer-cavity instrument. *Trends in Analytical Chemistry*, 116, 151-157. <http://dx.doi.org/10.1016/j.trac.2019.05.007>.
- World Health Organization – WHO. Food and Agriculture Organization of the United Nations – FAO (2004). *Vitamins and mineral requirements in human nutrition* (2nd ed.). Bangkok: WHO.

Supplementary Material

Supplementary material accompanies this paper.

Table S1. Analysis of variance for the model fitted to overall desirability obtained from the mixture design.

Table S2. Analysis of variance for the model fitted to overall desirability obtained from the Doehlert-design.

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