



Multivariate Optimization for the Development of a Fast and Simple Ultrasound-Assisted Extraction Procedure for Multielemental Determination in Tea Leaves by Inductively Coupled Plasma Optical Emission Spectrometry (ICP OES)

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Abstract

The current study describes a fast and efficient procedure of ultrasound-assisted extraction for determination of Ca, Mg, K, Na, Cu, Zn, Mn, and Al in tea leaves by inductively coupled plasma optical emission spectrometry (ICP OES). The variables of procedure were optimized using the Box–Behnken design and the conditions selected were nitric acid concentration (1.0 mol L^{-1}), sonication time (7 min), and sonication temperature ($75 \text{ }^\circ\text{C}$). The extraction efficiency was calculated using the analyte concentration obtained by a total digestion procedure as reference. Accuracy was confirmed by analysis of certified reference material of apple leaves (NIST 1515) and spinach leaves (NIST 1570a) using the procedure proposed. A statistical evaluation using Student's *t* test showed that there is no significant difference between the value obtained with the proposed procedure and the certified value, at 95% confidence level. The proposed procedure was successfully applied and is a good alternative to conventional acid digestion procedure and can be applied to routine analysis for determination of Ca, Mg, K, Na, Zn, Mn, Cu, and Al in tea leaves used for the preparation of infusions.

Keywords Tea leaves · Ultrasound-assisted extraction · Multivariate optimization · Box–Behnken design · ICP OES

Introduction

Tea (*Camellia sinensis*) is the most popular non-alcoholic beverage worldwide because of its aroma, taste, smell, variety of types, and multiple positive health-promoting effects. In addition, it is an important source of several minerals and bioactive compounds such as methylxanthines, flavonoids,

and phenolic (Da Silva Pinto 2013; Diniz et al. 2015; Jeszka-Skowron et al. 2015). The health benefits related to tea consumption include the prevention of diseases, such as myocardial infarction, skin cancer, Parkinson disease, as well as the reduction of cholesterol levels in the blood and risk for type 2 diabetes (Huxley et al. 2009; Wang et al. 2011).

The tea is good source of macro (Ca, Mg, K, and Na) and micro (Zn, Mg, and Cu) elements, which are indispensable for health maintenance (Ashraf and Mian 2008). The content of these elements can be altered depending on the growing medium of the plant (Kartika et al. 2011). On the other hand, according to the acidophilic nature of the plant and the interaction with soil, some toxic elements, such as Pb and Al, may be present. These elements show high solubility in acid soils and, therefore, may be more easily absorbed by the plants and accumulate in the leaves (Han 2007).

Macro, micro, and toxic elements in tea leaves are usually quantified by atomic spectrometric techniques (Welna et al. 2013), such as graphite furnace atomic absorption spectrometry (GF AAS) (Pereira and Dantas 2016; Shaltout et al. 2013), inductively coupled plasma optical emission spectrometry (ICP

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OES) (Martins et al. 2014), and inductively coupled plasma mass spectrometry (ICP-MS) (Milani et al. 2015; Zhao et al. 2017). In general, these techniques require a sample pretreatment to convert the solid material to a homogeneous aqueous solution through the procedures of acid digestion (Korn et al. 2008; Krug and Rocha 2016). The most common treatment to converting solid samples to solutions is wet digestion using open systems with cold finger (Ferreira et al. 2012) and closed systems with microwave-assisted digestion (Castro and Silva 1997). However, some drawbacks can be observed in the use of these procedures, such as (i) loss of volatiles elements, (ii) use of large amounts of concentrated reagents (mainly acids), (iii) generation of residues, and (vi) time-consuming the overall analytical procedure (Krug and Rocha 2016).

In contrast to intensive sample preparation procedures involving high temperatures and pressures, acid extraction under mild conditions appears to be a promising alternative, particularly when associated with ultrasonic energy (Santos et al. 2006). Ultrasound-assisted techniques have been widely employed for extraction of essentials and contaminant elements (Lima et al. 2016; Santos et al. 2014; Villa et al. 2015) and can be considered an alternative for sample pretreatment, since ultrasound generates an auxiliary energy and accelerates some process, such as dissolution and leaching of substances from matrix (Armenta et al. 2015; Capote and De Castro 2007; Tiwari 2015).

The procedures that involve ultrasound-assisted extraction are promising; but, several variables that affect the process of extraction, such as the physical characteristics of samples, analyte/sample interaction, extractor type, concentration of the extractor, sonication time, and temperature, should be studied (Santos et al. 2006). In this sense, multivariate optimization technique is a powerful tool because the variables affecting the extraction of the analytes and their interactions can be studied to obtain the optimal conditions of variable for all investigated analytes (Amorim et al. 2016; Amorim et al. 2017; Santos et al. 2009; Santos et al. 2014).

Multivariate techniques have been applied widely in the optimization of analytical chemistry methods (Bezerra et al. 2016; Novaes et al. 2016; Tarley et al. 2009) and present advantages, such as reduction in the number of experiments resulting in lower consumption of reagents and in analysis time. Furthermore, allowing the development of mathematical models that permit assessment of the relevance as well as statistical significance of the factor effects studied as well as evaluate the interaction effects among the factors (Bezerra et al. 2008; Ferreira et al. 2004). Among multivariate optimization tools for the development of analytical procedures, central composite (Pereira-Filho 2015), Box–Behnken (Ferreira et al. 2007), and Doehlert designs (Ferreira et al. 2004) are among the principal used. The application of Box–Behnken in analytical chemistry is smaller than the central composite and Doehlert designs (Bezerra et al. 2008; Ferreira et al. 2007).

However, this does not make it less important, and when compared to the central compost, it has a greater efficiency and a smaller number of experiments. Moreover, its use in extraction procedure is a field to be explored.

In this study, multivariate optimization using Box–Behnken design was applied in the development of an ultrasound-assisted extraction procedure for the determination of Ca, Mg, K, Na, Zn, Mn, Cu, and Al elements in tea leaves by inductively coupled plasma optical emission spectrometry (ICP OES).

Material and Methods

Instrumentation

The determination Ca, Mg, K, Na, Zn, Mn, Cu, and Al was performed using an inductively coupled plasma optical emission spectrometer with axial viewing—ICP OES (Vista Pro, Varian, Mulgrave, Australia) equipped with solid state detector, cyclonic spray chamber, and concentric nebulizer. The instrumental conditions were established as the manufacturer recommendations, as being power (1.2 kW), plasma gas flow (15.0 L min^{-1}), auxiliary gas flow (1.5 L min^{-1}), nebulizer gas flow (0.7 L min^{-1}), and sample introduction flow rate (2.1 ml min^{-1}). The elements and the emission lines used are atomic (I) and ionic (II), as follows: Ca II (317.933 nm), Mg II (285.213 nm), K I (766.465 nm), Na I (589.592 nm), Zn II (202.548 nm), Mn II (259.372 nm), Cu I (324.754 nm), and Al I (396.153 nm).

Reagents, Solutions, and Samples

Ultrapure water ($18.2 \text{ } \Omega \text{ cm}$ resistivity) produced by a Milli-Q® Plus Total Water System (Millipore Corp., Bedford, MA, USA) was used to prepare all the solutions. Nitric acid (HNO_3) (65%, v/v) and hydrogen peroxide (H_2O_2) (30%, v/v) supplied by Merck (Darmstadt, Germany) were used for digestion of the samples. All glassware and polypropylene flasks were washed with soap, soaked in 10% v/v HNO_3 for 24 h, rinsed with deionized water prior to use. The analyte solutions used for external calibration were prepared from 1000 mg L^{-1} standard solutions (Qhemis, Jundiaí, Brazil). Appropriate dilutions were made from the standard solutions and used for construction of the analytical curve for ICP OES measurements.

Five samples of different species of tea leaves were sampling in local markets in city of Itabuna, state of Bahia, Brazil. The samples acquired were Chile Bilberry (*Vaccinium myrtillus* L.), Spearmint (*Mentha spicata* L.), Lemongrass (*Cymbopogon citratus*), Chamomile (*Matricaria recutita*), and Lemon balm (*Melissa*

officinalis). In addition, certified reference materials (CRM) of apple leaves (NIST 1515) and spinach leaves (NIST 1570a) from the National Institute of Standards and Technology—NIST (Gaithersburg, MD, USA) were used to verify the accuracy of the proposed procedure.

Multivariate Optimization of Extraction Procedure

A Box–Behnken (Ferreira et al. 2007) design was used with the aim to study the following variables: nitric acid concentration (0.5, 1.0, and 1.5 mol L⁻¹), sonication time (2, 6, and 10 min), and sonication temperature (50, 75, and 100 °C). Furthermore, to evaluate the experimental error, the central point measurements were repeated three times, raising the total number of experiments to 15. All experiments were performed in random order.

In order to obtain a single condition to extraction of all elements, the multiple response (MR) was employed, which was obtained by evaluation of recovery percentages of the elements using the values obtained after total digestion by digester block using reflux system with cold finger as reference. The multiple response is given by (Eq. 1), where RM_n is analytical signal to an element in a particular experiment, and $R_{max} M_n$ is the maximum analytical signal in the set of experiments to that element n (Santos et al. 2009). The statistically significant effects of the variables were studied and interactions among them evaluated by analysis of variance (ANOVA) using the software Matlab 2017b (MathWorks, Natick, MA).

$$MR = \frac{(RM1)}{(R_{max1})} + \frac{(RM2)}{(R_{max2})} + \dots + \frac{(RMn)}{(R_{maxMn})} \quad (1)$$

Sample Preparation

Extraction Procedure

The sonication of the solutions was performed using an USC-1800 ultrasonic bath (Cortland, New York, USA). The equipment was filled with 1.0 L of water and glass tubes were placed in bath in the more intense cavitation region previously mapped according to literature recommendations (Nascentes et al. 2001). Extractions were performed in triplicate according to the following procedure: 100 mg of each sample was accurately weighed in glass tubes with capacity of 15.0 mL. Then it was added 10.0 mL of HNO₃ 1.0 mol L⁻¹ and the tubes were placed in ultrasonic bath for 7 min at 75 °C with frequency of 30 kHz and 100 W power. Then, the tubes were centrifuged for 5 min at 2000 rpm and the supernatant was filtrated and transferred to polyethylene flask. The final solutions were analyzed by ICP OES. To check the performance of the procedure, the CRMs of apple leaves (NIST 1515) and spinach leaves (NIST 1570a) were also submitted the extraction.

Total Digestion

For the digestion of the samples, a block digestion (Tecnal, Piracicaba, Brazil) with 40 channels, and thermostat for temperature control was used. This procedure was based in complete mineralization using digester block, according to the procedure described by (Andrade et al. 2017). The digestion procedure ($n = 3$) was performed by accurately weighing: 200 mg of each sample in the digestion vessels followed by the addition of 2.0 mL of 65%. The vessel was kept overnight (ca. 16 h) at room temperature. Then, 1.0 mL of 30% v/v H₂O₂ were added, and the solution was heated at 120 °C under reflux for 180 min using a digestion system with cold finger. After complete digestion, the solutions were transferred to volumetric flasks, and high-purity water was added to achieve a total volume of 20.0 mL. The final solutions were also analyzed by ICP OES. To check the performance of the procedure, the CRMs of apple leaves (NIST 1515) and spinach leaves (NIST 1570a) were also digested.

Results and Discussion

Optimization of the Procedure

Individual results to each element showed a tendency for efficient extractions in a common region for each obtained response (% recovery). In this sense, the multiple response (RM) was used to optimize an extraction single condition for the elements studied. The RM was calculated according to Eq. (1). The evaluation of recovery percentages of the elements using the values was obtained after total digestion by digester block using reflux system with cold finger as reference. The experimental matrix used, with recoveries for the studied elements and the multiple responses are shown in Table 1. The range of recoveries to each element were Ca (45–103%), Mg (44–92%), K (93–109%), Na (81–99%), Zn (47–103%), Mn (61–105%), Cu (49–94%), and Al (54–101%) showing a variable behavior for the elements studied due to different interactions analyte-matrix.

The optimized conditions for each variable were evaluated through contour graph obtained from Box–Behnken design after the evaluation of statistical model. If the model is well fitted to the experimental data, the mean square of lack of fit (MS_{lof}) should reflect only the random errors inherent to the system. Additionally, the mean square of pure error (MS_{pe}) should also be an estimative of these errors and it is assumed that these two values are not statistically different. Thus, it is possible to use the F distribution to assess whether there is any statistical difference between these two means.

Subsequently, the model was generated in function of multiple response to obtain the best description of the experimental region. To assess the quality of the model, the lack of fit

Table 1 Matrix Box–Behnken design and results (% recovery and multiple response) of optimization procedure for ultrasound-assisted extraction

Exp.	Variables			% recovery								MR
	C (mol L ⁻¹)	tS (min)	TS (°C)	Ca	Mg	K	Na	Zn	Mn	Cu	Al	
1	(-1) 0.5	(-1) 2	(0) 75	51	71	99	81	47	78	49	54	5.2
2	(+1) 1.5	(-1) 2	(0) 75	45	66	101	85	60	70	59	67	5.5
3	(-1) 0.5	(+1) 10	(0) 75	58	74	100	85	69	72	70	75	6.0
4	(+1) 1.5	(+1) 10	(0) 75	60	83	95	86	79	89	76	64	6.3
5	(-1) 0.5	(0) 6	(-1) 50	63	46	93	84	66	61	71	58	5.4
6	(+1) 1.5	(0) 6	(-1) 50	68	76	94	88	71	81	76	77	6.3
7	(-1) 0.5	(0) 6	(+1) 100	72	59	109	90	67	69	81	65	6.1
8	(+1) 1.5	(0) 6	(+1) 100	73	44	104	89	86	89	71	75	6.6
9	(0) 1.0	(-1) 2	(-1) 50	61	65	93	86	72	78	82	74	6.1
10	(0) 1.0	(+1) 10	(-1) 50	76	81	101	87	86	88	74	84	6.7
11	(0) 1.0	(-1) 2	(+1) 100	80	88	106	90	76	75	74	74	6.6
12	(0) 1.0	(+1) 10	(+1) 100	83	91	99	96	93	91	78	88	7.1
13	(0) 1.0	(0) 6	(0) 75	97	91	102	99	103	99	89	92	7.7
14	(0) 1.0	(0) 6	(0) 75	103	92	104	99	98	105	94	93	7.8
15	(0) 1.0	(0) 6	(0) 75	98	90	98	98	101	94	85	101	7.6

C (mol L⁻¹), nitric acid concentration; tS (min), sonication time; TS (°C), sonication temperature

was verified. According to analysis of variance (ANOVA) presented in Table 2, the model did not show lack of fit $F_{\text{calculated}} (3.76) < F_{\text{tabulated}} (19.16)$, at 95% confidence level demonstrating have a good predictive capability.

The quality of the model was also evaluated by analyzing the graph of values predicted versus observed, as shown in Fig. 1a. Thus, it is possible to observe that the model is well adjusted with 99% regression percentage. This observation confirms the good fit of the model that was verified in Table 2. Another parameter to be observed is the behavior of the residues, that is, the difference between the experimental and predicted values. In Fig. 1b is presented a graph of predicted values versus residues showing a normal distribution of

residues, confirming again the quality of the model. Thus, the model obtained is well fit to the data collected by the Box–Behnken design and can be represented by the quadratic model shown in Eq. (2) that presents the significant coefficients and your respective confidence intervals.

$$\begin{aligned} \text{MR} = & 6.15 \pm 0.13 + 0.15 \pm 0.16 (C_{\text{HNO}_3}) \\ & + 0.34 \pm 0.16 (tS) + 0.25 \pm 0.16 (TS) \\ & + 0.62 \pm 0.12 (C_{\text{HNO}_3})^2 + 0.35 \pm 0.12 (tS)^2 \\ & + 0.18 \pm 0.12 (TS)^2 \end{aligned} \quad (2)$$

where MR represents the multiple response, C_{HNO_3} is the nitric acid concentration, tS is the sonication time, and TS is the sonication temperature. The model showed a maximum response for the following experimental conditions (critical points): nitric acid concentration = 1.0 mol L⁻¹; sonication time = 7 min, and sonication temperature = 75 °C. The contour graphs are presented in (Fig. 2a–c). The optimized experimental conditions were used for to validate the procedure of extraction Ca, Mg, K, Na, Zn, Mn, Cu, and Al from tea leave samples.

Analytical Features

The limits of detection (LOD) and quantification (LOQ) of the developed were calculated as $3 \times \text{BEC} \times \text{RSD}/100$ and $10 \times \text{BEC} \times \text{RSD}/100$, respectively, where RSD is the relative standard deviation from ten blank measurements and BEC is the background equivalent concentration (average blank signal/slope of the analytical curve) (IUPAC, Analytical Chemistry

Table 2 Analysis of variance (ANOVA) for quadratic model fitted to multiple response with a 95% confidence level

Quadratic model					
Source of variation	SS	df	MS	$F_{\text{Calculated}}$	p value
(1) C (mol L ⁻¹) L + Q	6.296	2	3.148	266.05	0.003
(2) tS (min) L + Q	2.783	2	1.391	117.63	0.008
(3) TS(°C) L + Q	1.020	2	0.510	43.14	0.022
1*2	0.000	1	0.000	0.033	0.871
1*3	0.024	1	0.024	2.042	0.289
2*3	0.002	1	0.002	0.221	0.684
Lack of fit	0.133	3	0.044	3.764	0.216
Pure error	0.023	2	0.011		
Total adjusted	9.521	14			

$F_{\text{tabulated}} = 19.16$; SS, sum of square; df, degree of freedom; MS, media of square; L, linear; Q, quadratic

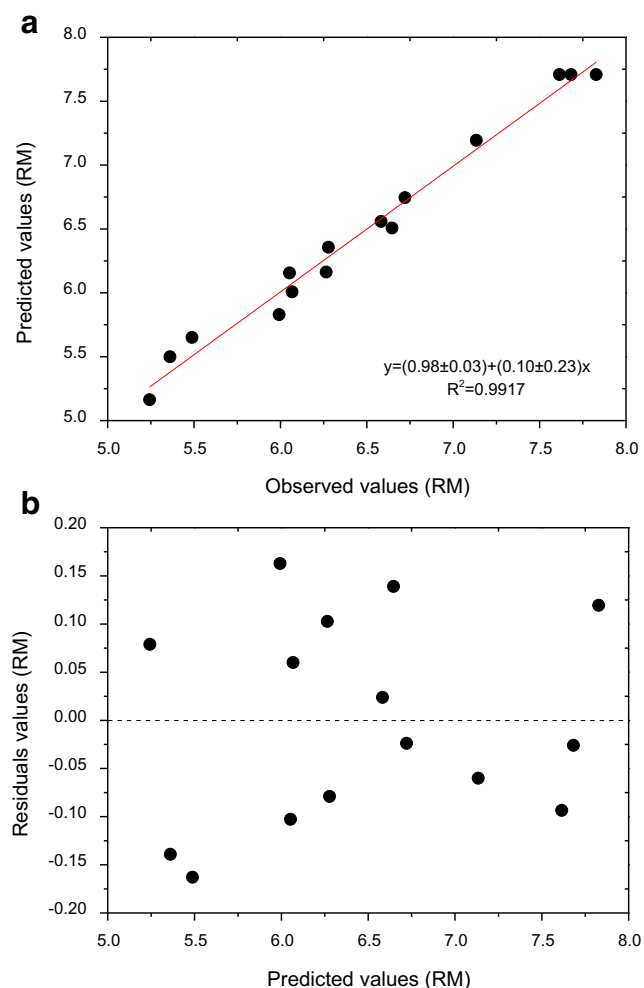


Fig. 1 Evaluation of the quadratic model fitted to multiple response (RM). **a** Values observed versus predicted values. **b** Values predicted versus residual values

Division. Commission on Spectrochemical and Optical 484 Procedures for Analysis, 1978). The LOD and LOQ calculated to proposed procedure and reference procedure of total digestion are provided in Table 3. The precision of the proposed procedure was evaluated in terms of repeatability for seven distinct extractions of a single sample and the values of RSD % ($n = 7$) obtained were 3.5 (Ca), 4.9 (Mg), 4.5 (K), 2.9 (Na), 2.3 (Zn), 2.5 (Mn), 1.8 (Cu), and 2.0% (Al).

To verify the accuracy of the procedure for determining Ca, Mg, K, Na, Zn, Mn, Cu, and Al in tea leaves, these analytes were also determined in the certified references materials (CRMs) of apple leaves (NIST 1515) and spinach leaves (NIST 1570a). After comparison between the certified and the determined ($n = 3$) concentrations, the obtained recovery values were in the range of 93 to 108% and results are shown in Table 4. Statistical evaluation, using the Student t test, showed there is no significant difference between values obtained and the certified value at 95% confidence level, confirming the accuracy of this procedure.

Application

The proposed procedure was applied for the determination of Ca, Mg, K, Na, Cu, Zn, Mn, and Al elements in five samples of tea leaves used for the preparation of infusions and the results are shown in Table 5. The elements Ca, Mg, K, Na, and Zn are considered essential and their intake are required at levels of milligrams per kilogram level to maintain the human organisms free from deficiency effects (ANVISA 2005). Additionally, elements as Cu and Mn are needed at trace levels in the human diets. Toxic elements are those that can cause hazardous effects in human health, and in this work, were investigated the levels of Pb and Al (Marqués et al. 2016).

Among the macro elements, it can be seen that K presents the higher concentrations in the analyzed samples, in ranges of (3233–9428 mg kg⁻¹) followed by Ca (1987–4328 mg kg⁻¹), Mg (735–2445 mg kg⁻¹), and Na (184–338 mg kg⁻¹). These ranges of values are highly consistent with the levels obtained in the leaves of the studied tea plants already reported in the literature (Chen et al. 2009; Karak and Bhagat 2010; Szymczycha-Madeja et al. 2012). According to Marschner (1995), the higher levels of K in the tea plants occur due to the fact that nutrient elements such as N, P, and K that are highly mobile in the tea plant tissue and are translocated from old leaves to young leaves. Kumar et al. (2005) have also reported a higher concentration of K and suggested that it may be specifically incorporated with in a binding ligand in the tea leaves. The concentrations of Ca and Mg were lower in relation of K and are consistent with other works (Chen et al. 2009; Yemane et al. 2008). According Solomon et al. (2001) this mainly occurs in regions with high rainfall and causing extensive leaching of Ca and Mg rendering these metals to exist at lower levels. Among the major elements, the Na generally is found in lower concentration in tea leaves, and in this study, the concentration range was 184–338 mg kg⁻¹. According to Yemane et al. (2008), in tea leaves, independently of variety, contain higher levels of K in relation the Ca, Mg, and Na.

Regarding the minor elements, the Mn presented the higher concentration ranges in the tea leaves analyzed, with a range of 35–94 mg kg⁻¹. These results which confirm the suggestion made by Dambiec et al. (2013) that tea is a potential Mn accumulator. In addition, in work proposed by Bezerra et al. (2010) was evaluated the concentration de Mn in different tea leaves and range found varied from 42 to 118 mg kg⁻¹. The concentrations of Zn and Cu were found in range of 10–64 mg kg⁻¹ and 2.01–12 mg kg⁻¹, respectively. In a study proposed by Bezerra et al. (2010) concentrations of Zn in tea leaves in the range of 18.6–54.1 mg kg⁻¹ were determined. Miranda and Pereira-Filho (2013) evaluated the concentration of Cu in different tea leaves, and the range varied from 9.5–14.6 mg kg⁻¹. In addition, Diniz et al. (2015) evaluated the concentrations of Zn and Cu in tea leaves, and the range found was 4.5–34.9 mg kg⁻¹ for Zn and 0.58–27.6 mg kg⁻¹ for Cu.

Fig. 2 Contour graph obtained from the Box–Behnken design to the **a** nitric acid concentration versus sonication time and **b** sonication temperature versus nitric acid concentration. **c** Sonication time versus sonication temperature

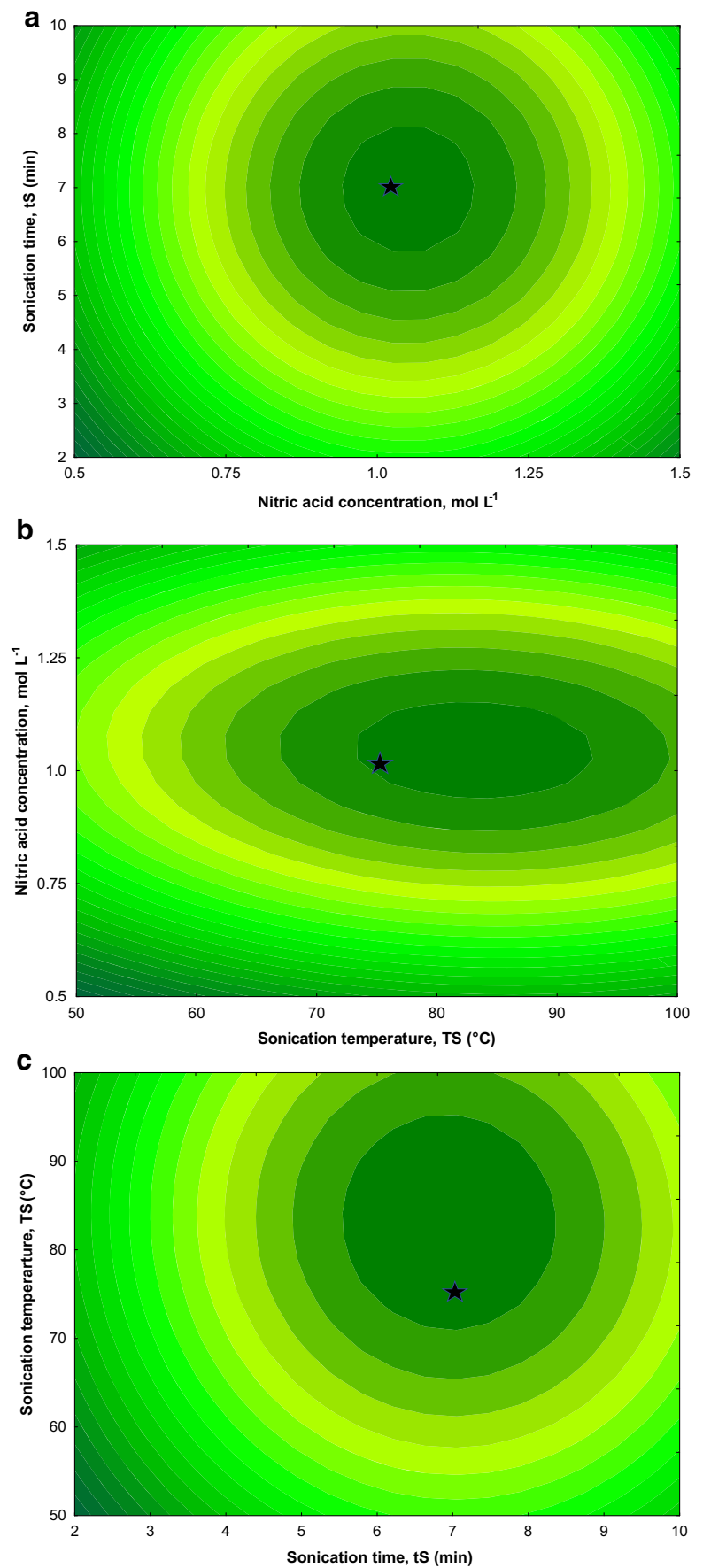


Table 3 Limits of detection and quantification (mg kg^{-1}) for proposed procedure and total digestion

Element	Proposed procedure		Total digestion	
	LOD (mg kg^{-1})	LOQ (mg kg^{-1})	LOD (mg kg^{-1})	LOQ (mg kg^{-1})
Ca	5.8	20	6.3	21
Mg	1.3	4.3	1.8	6.0
K	4.1	14	3.8	13
Na	0.9	3.0	1.2	4.0
Zn	1.0	3.3	0.8	2.6
Mn	0.2	0.7	0.3	1.0
Cu	0.4	1.4	0.4	1.3
Al	2.0	6.7	2.2	7.3

Table 4 Analyte determinations (mg kg^{-1}) in apple leaves (NIST 1515) and spinach leaves (NIST 1570a) by proposed procedure (mean \pm standard deviation, $n = 3$; and recovery, %)

Element	Concentration (mg kg^{-1})			
	Apple leaves (NIST 1515)		Spinach leaves (NIST 1570a)	
	Certified values	Proposed procedure	Certified values	Proposed procedure
Ca	15,260 \pm 150	15,670 \pm 310 (102)	15,270 \pm 410	14,480 \pm 470 (95)
Mg	2710 \pm 80	2820 \pm 120 (104)	8900 ^a	8600 \pm 400 (97)
K	16,100 \pm 200	17,500 \pm 410 (108)	29,030 \pm 520	28,870 \pm 1030 (99)
Na	24.4 \pm 1.2	22.8 \pm 0.7 (93)	18,180 \pm 430	17,777 \pm 367 (98)
Zn	12.5 \pm 0.3	11.9 \pm 0.2 (95)	82 \pm 3	80 \pm 2 (98)
Mn	54 \pm 3	56 \pm 1 (103)	75.9 \pm 2	70.3 \pm 1 (93)
Cu	5.64 \pm 0.24	5.77 \pm 0.08 (102)	12.2 \pm 0.86	11.5 \pm 0.20 (95)
Al	286 \pm 9.0	281 \pm 5.0 (98)	310 \pm 11	316 \pm 4.1 (102)

^a According with certificate of the reference material, insufficient information is available to assess the uncertainty associated with the value; therefore, no uncertainty is provided

The content of Al in all the tea samples ranged among 176–802 mg kg^{-1} , and similar result can be found in the literature. Diniz et al. (2015) found concentrations of Al in black tea in the range of 291–1231 mg kg^{-1} and in green tea in the range of 440–2169 mg kg^{-1} . Tea plants can be containing a higher concentration of Al than many other plants, and, because tea beverages are consumed in large quantities worldwide, a high

incidence of Al exposure comes through drinking tea (Karak and Bhagat 2010). Different studies have indicated relatively high levels of Al in several types of teas. This element has been associated to Alzheimer's disease, and its main route of absorption by humans has been linked to consumption of Al-containing food over a prolonged period of time (Krewski et al. 2007; Yokel and Florence 2008). In fact, the tea plant

Table 5 Analyte determinations (mg kg^{-1}) in tea leaves by proposed procedure (mean \pm standard deviation, $n = 3$)

Samples	Concentration (mg kg^{-1})							
	Ca	Mg	K	Na	Zn	Mn	Cu	Al
Chile Bilberry	3985 \pm 61	1387 \pm 21	3233 \pm 51	338 \pm 8	64 \pm 1	49 \pm 0.8	3.51 \pm 0.05	176 \pm 2
Spearmint	4328 \pm 65	1094 \pm 26	9428 \pm 81	251 \pm 5	23 \pm 0.5	83 \pm 2	9.2 \pm 0.2	802 \pm 11
Lemongrass	2731 \pm 49	2445 \pm 89	8279 \pm 70	184 \pm 4	18 \pm 0.1	42 \pm 0.5	8.38 \pm 0.07	545 \pm 5
Chamomile	2785 \pm 43	1123 \pm 31	7654 \pm 45	201 \pm 5	10 \pm 0.8	94 \pm 2	12 \pm 0.1	402 \pm 3
Lemon balm	1987 \pm 23	735 \pm 12	5554 \pm 98	254 \pm 5.5	42 \pm 0.1	35 \pm 0.6	2.01 \pm 0.02	348 \pm 4

can be considered an Al accumulator, and this will cause a special increase in concentration in older plants.

High concentrations of Al found in tea leaves may be related to soil pH. Plants grown in soils with (pH < 4.5) favors the extraction of elements such as Al and its fixation in tea leaves. The concentrations of Al in tea leaves grown in acid soil can vary from 20 to 13,000 mg kg⁻¹, and in some extreme cases can reach levels of up to 27,000 mg kg⁻¹ (Szymczycha-Madeja et al., 2016; Wong et al. 2003).

Conclusions

The application of Box–Behnken design allowed the development of analytical procedure for the determination of macro (Ca, Mg, K, and Na), micro (Cu, Zn, and Mn), and contaminant (Al) elements in tea leaves samples by ICP OES, based on ultrasound-assisted extraction, using a smaller number of experiments. The procedure showed to be a fast and simple alternative to conventional acid digestion procedure for multielemental determinations and can be used in routine analysis due to high analytical frequency and low reagent consumption that means lower cost and less residue generated.

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Compliance with Ethical Standards

This is an original research article that has neither been published previously nor considered presently for publication elsewhere.

All authors named in the manuscript are entitled to the authorship and have approved the final version of the submitted manuscript.

Conflict of Interest Vinicius Câmara Costa declares that he has no conflict of interest. Wesley Nascimento Guedes declares that he has no conflict of interest. Antonio de Santana Santos declares that he has no conflict of interest. Madson Moreira Nascimento declares that he has no conflict of interest.

Ethical Approval This article does not contain any studies involving human participants or animals performed by any of the authors.

Informed Consent Informed consent was obtained from all individual participants included in the study.

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