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Microwave-Assisted Digestion Using Diluted Nitric Acid for Multi-element Determination in Rice by ICP OES and ICP-MS

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Abstract In this work, microwave-assisted digestion using the diluted nitric acid procedure for trace elements determination in rice samples by inductively coupled plasma optical emission spectrometry (ICP OES) and inductively coupled plasma mass spectrometry (ICP-MS) was investigated in a multivariate way. The response surface methodology (RSM), based on the Box–Behnken design, was employed to obtain the optimum conditions of the significant parameters. The optimal conditions, for 250 mg of sample, could be obtained at a temperature of 200 °C, digestion time of 20 min, and 4.5 mol L^{-1} for nitric acid concentration. The accuracy of the optimized method was evaluated by analysis of the rice flour certified reference materials (NIST SRM 1568a) and spike recoveries. The results showed good agreement with the reference values of the CRM samples. The analytical method was applied to the determination of Al, As, Ca, Cd, Cu, Fe, K, Mg, Mn, Mo, Se, and Zn in rice samples. Considering some critical parameters such as cost, green chemistry, and analyst safety, the proposed method has advantages compared to classical microwave-assisted digestion procedures based on concentrated acids.

Keywords Microwave-assisted digestion · Diluted acid · Multi-element determination · Multivariate analysis · Rice · ICP-MS · ICP OES

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Introduction

Rice (*Oryza sativa*) is used as an energy source for human consumption due to its high concentration of starch. It also provides proteins, vitamins, and minerals. Because of the importance of rice in the diet of much of the world's population, its nutritional quality directly affects human health (Walter et al. 2008; Vieira et al. 2008). In this sense, the determination of chemical species in rice is important for the assessment of its nutritional capacity and to identify the presence of species that are toxic in the human diet (Erdemi and Gucer 2014; Antoine et al. 2012; Batista et al. 2011; Teixeira et al. 2012; Freschi et al. 2012).

Solid samples require pretreatment before they can be used in spectroscopy techniques with nebulization systems. The most common pretreatment before determination of inorganic species in food is acid digestion of the samples (Gonzalez et al. 2009). Acid digestion assisted by microwave radiation has been widely used in sample preparation, especially by employing the use of high temperatures and pressures in closed systems. These procedures allow the use of small volumes of reagents with minimal loss of volatiles, and the time taken for decomposition is reduced compared with decomposition by conventional heating (Nobrega et al. 2002; Gonzalez et al. 2009; Arruda and Santelli 1997). These advantages make it possible to reduce the acid concentration while keeping the efficiency of the digestion, decreasing the dilution factor prior to analysis, and generating less waste (Krug 2008; Bizzi et al. 2010; Santos et al. 2013), in accordance with the green analytical chemistry (Gałuszka et al. 2013; Lenardão 2003). However, optimization of the digestion is required in order to obtain satisfactory decomposition, when dilute acid solutions are employed (Castro et al. 2009).

The minerals are widespread in nature in different forms. Ingestion is the primary way to enter in the human

Table 1 Operating conditions for determinations by ICP-MS

Parameter	Value
RF incident power	1300 W
Plasma argon flow rate	13 L min^{-1}
Auxiliary argon flow rate	0.7 L min^{-1}
Nebulizer argon flow rate	0.87 L min^{-1}
Scanning mode	Peak jump
Resolution	Standard
Dwell time	10 ms
Sweeps	100
Number of readings per replicate	3
Conditions	$^{140}Ce^{16}O^+/^{140}Ce$ and $^{137}Ba^{++}/^{137}Ba^+ <2$ %

body. The chemical elements are classified according to their importance in human health: essential species such as Ca, K, Na, and Mg (needed in large quantities) or Fe, Co, Mn, and Zn (necessary for physiological functions, but at high concentrations can become toxic); and non-essential or toxic species such as Cd and Pb (no function known) (Leal et al. 2009; Naseri et al. 2015). Thus, the determination of chemical elements content in foods is important for the knowledge of their nutritional quality.

In recent years, multivariate optimization techniques have been widely used in the development of analytical methods which require the optimization of several variables simultaneously (Bezerra et al. 2008; Ferreira et al. 2007; Lopes et al. 2009; Khajeh et al. 2010). Among these techniques, the Box–Behnken design has been widely employed (Ferreira et al. 2007; Macedo et al. 2009; Khajeh and Sanchooli 2010; Almeida et al. 2015).

In this work, a microwave-assisted digestion procedure using the diluted nitric acid was optimized for trace elements determination in rice samples by inductively coupled plasma optical emission spectrometry (ICP OES) and inductively coupled plasma mass spectrometry (ICP-MS). The Box–Behnken design was employed to obtain the optimum conditions of the significant parameters: temperature and time for the final stage of digestion, and nitric acid concentration. The developed method was employed in the determination of 12 elements (Al, As, Ca, Cd, Cu, Fe, K, Mg, Mn, Mo, Se, and Zn) in rice samples.

Material and Methods

Apparatus

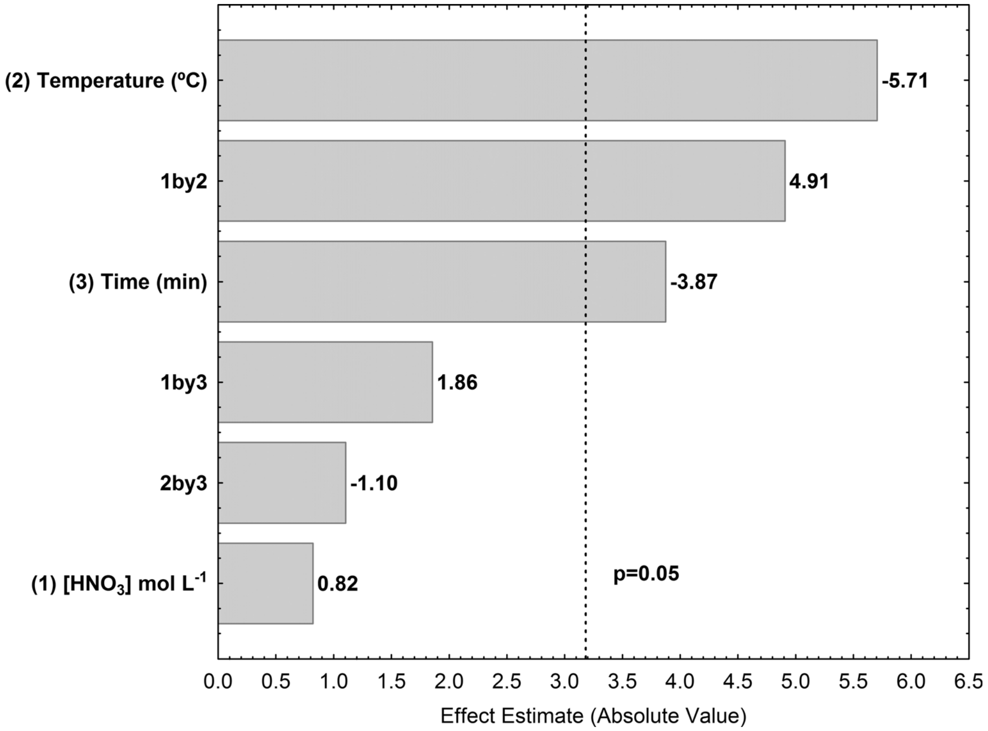
Acid digestion of the samples was performed using a commercial high-pressure laboratory microwave oven (Milestone Ethos 1600 Microwave Labstation, Sorisole, Italy) equipped with 10 vessels made of perfluoroalkoxy polymer (PFA) with a volume of 100 mL.

A quadrupole ICP-MS X series II (Thermo, Germany) equipped with a hexapole collision cell (CCT) was used for all determinations. In order to obtain optimal accuracy and precision, the internal standards were chosen as close in mass number as possible to that of the analyte element. Thus, ^{74}Ge and ^{103}Rh isotopes were selected to be used as internal standards. The CRM NIST 1568a was analyzed twice. Firstly, the standard mode (XT), normal mode of operation of the equipment, was tested and, then, hexapole collision cell operation mode (CCT) was tried, to eliminate possible polyatomic interference. Taking into account the agreement with the certified values, the XT mode was selected for the determination of all the elements. The equipment was configured with a Peltier cooled, quartz impact bead spray chamber, glass concentric nebulizer, and single piece, 1.5-mm i.d. injector torch. This

Table 2 Experiments and multiple responses (MR) obtained from the full factorial design 2^3

Experiment	HNO_3 concentration (mol L^{-1})	Temperature (°C)	Time (min)	MR
1	14 (1)	210 (1)	25 (1)	3.98
2	14 (1)	210 (1)	15 (−1)	4.10
3	14 (1)	190 (−1)	25 (1)	3.97
4	14 (1)	190 (−1)	15 (−1)	4.28
5	2 (−1)	210 (1)	25 (1)	2.96
6	2 (−1)	210 (1)	15 (−1)	3.90
7	2 (−1)	190 (−1)	25 (1)	4.42
8	2 (−1)	190 (−1)	15 (−1)	4.70
9	8 (0)	200 (0)	20 (0)	3.94
10	8 (0)	200 (0)	20 (0)	4.20
11	8 (0)	200 (0)	20 (0)	4.22
12	8 (0)	200 (0)	20 (0)	3.96

Fig. 1 Pareto chart for the full factorial design 2^3 (95 % confidence level)



spray chamber is usually used with conventional or low-flow pneumatic nebulizers to reduce the amount of solvent entering the plasma. The daily optimization procedure involved xyz alignment of the torch, and determination of the optimum nebulizer gas flow rate and the ion lens voltage to maximize the 115In$^+$ signal and obtain low oxide (140Ce16O$^+$/140Ce$^+$) and double charged ions (137Ba^{++}/137Ba$^+$). The detector was operated in dual mode and cross-calibration was performed weekly. Samples were introduced via a peristaltic pump with an uptake rate of 0.8 mL min^{-1}. Table 1 presents the ICP-MS operational conditions.

A Varian Vista (Mulgrave, Australia) simultaneous ICP OES with axial viewing and a charge coupled device (CCD) detector was used for Al, Ca, Cu, Fe, K, Mg, Mn, and Zn determinations. The ICP OES was calibrated with a multi-element stock solution, and the optical alignment was adjusted using a solution containing 5.0 mg L^{-1} Mn. Emission lines were selected according to the absence of spectral interferences and adequate sensitivity for the determination of the elements at low and high concentrations. The optimal values for the instrumental parameters were radio frequency power of 1.3 kW, plasma gas flow rate of 15 L min^{-1}, auxiliary gas flow rate of 1.5 L min^{-1}, nebulizer gas flow rate of 0.7 L min^{-1}, replicate reading time of 1 s, instrument stabilization delay of 15 s, replicates (n = 3), and pump rate of 15 rpm. The analytical wavelengths (nm) employed were Al (I) 237.312, Ca (II) 396.847, C (I) 193.024, Cu (I) 327.395, Fe (II) 238.204, K (I) 766.491, Mg (I) 285.213, Mn (II) 257.610, and Zn (II) 206.200.

Reagents, Solutions, and Samples

All labware was soaked in a HNO_3 acid bath (65 % *w*/*w*, diluted 1/10 with high-purity water) for 24 h and rinsed with high-purity water. Subsequently, all materials were dried under clean-air conditions at ambient temperature. All solvents and reagents were of the highest commercially available purity.

High-purity deionized water (resistivity 18.2 MΩ cm), from a Milli-Q water purified system (Millipore, Bedford, MA, USA), was employed to prepare all standard and sample solutions. Suprapur grade 65 % HNO_3 (*w*/*w*) and 30 % H_2O_2 (*w*/*w*) (Merck, Darmstadt, Germany) were used for sample digestion. The plasma torch argon purity was higher than 99.99 %. Mono-elemental, high-purity grade 1 g L^{-1} stock solutions of 75As, 111Cd, 95Mo, and 82Se and a 100 mg L^{-1} multi-element solution of Bi, Ge, In, Tl, Rh, and Sc were purchased from Merck (Darmstadt, Germany). Element determination by ICP-MS was performed using external calibration. The reference analytical solutions and the samples were adjusted to an acid concentration 0.288 mol L^{-1} HNO_3, as recommended by the manufacturer.

The optimized procedure was used in the analysis of 23 rice samples (10 parboiled, 8 white, and 5 brown rice) purchased in markets in Salvador City, Brazil. Dried samples were ground in a ball mill with a tungsten carbide vial set (Model 8000 M, Spex Sample Prep, USA) and stored in clean polyethylene vials inside a desiccator at room temperature.

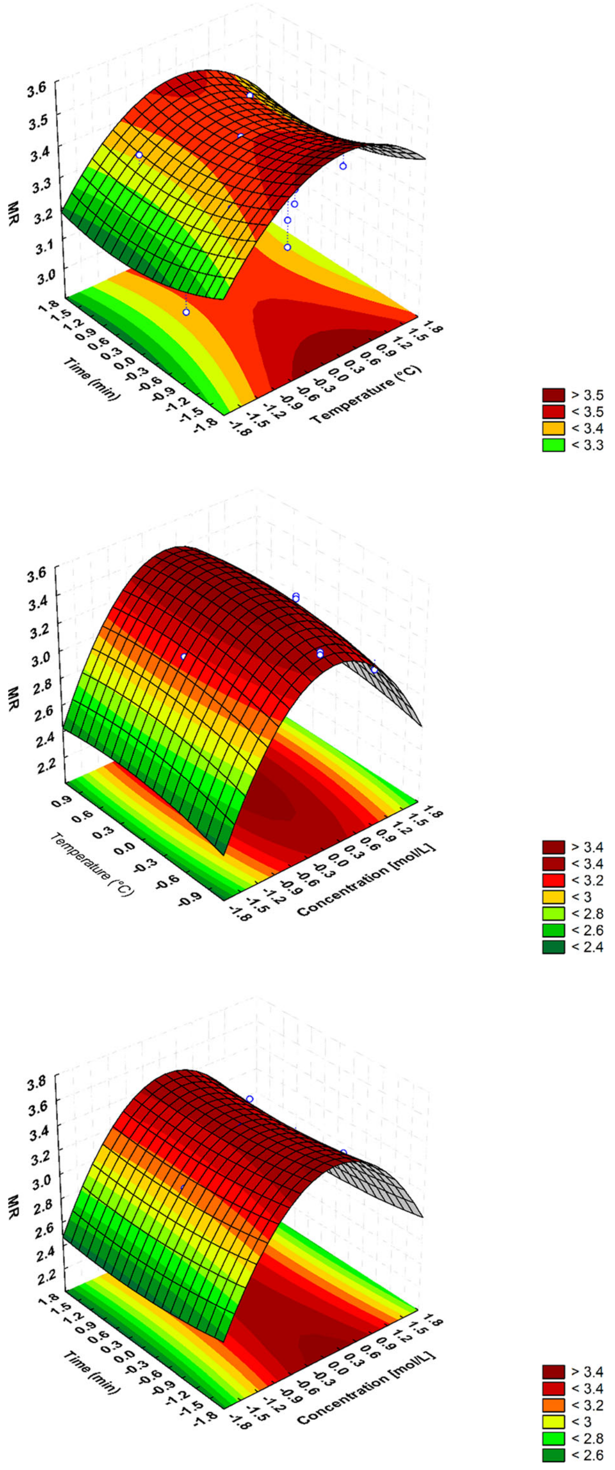


Fig. 2 Response surface curves for the effects of temperature, time, and concentration of nitric acid in multiple responses obtained from the Box–Behnken design

Optimization of Sample Digestion

Sample masses of 250 mg of each dried and ground rice sample were weighed in a 100-mL microwave closed vessel and 7.0 mL nitric acid solution at different concentrations (2.0; 4.5, and 7.0 mol L^{-1}) and 1.0 mL of 30 % (*w/w*) H_2O_2 were also added to each vessel. The heating program was performed in four successive steps. In the first step, the temperature was increased linearly to 90 °C over a period of 4 min. In the second step, the temperature was kept at 90 °C for 2 min. In the third step, the temperature was increased linearly to 200 °C over a period of 10 min. For the fourth step, the temperature and time were optimized. After digestion and cooling, the digests were transferred to plastic flasks and made up to a final volume of 15.0 mL with deionized water. Blanks were prepared in each batch of samples.

A full two-level factorial design (2^3) was used in order to verify the influence and interactions of the variables. At this stage, a rice sample was prepared in large quantities, with the aim of using a single sample in all experiments. Three variables were regarded as factors in the optimization study: the time (15, 20 e 25 min) and temperature (190, 200 e 210 °C) of digestion in the fourth step of the sample digestion and the concentration of HNO_3 (2.0; 8.0, and 14 mol L^{-1}). Table 2 shows the experimental design with the minimum, maximum, and central point levels for each factor (coded and real values). The factorial design totalized 12 experiments (experiments 01–12), including four replicates at the central point.

Additional experiments employing a Box–Behnken design were applied to determine the optimum conditions for the sample digestion (Table 3). The Box–Behnken design included 15 experiments (experiments 13–27), including three replicates at the central point. All digestion procedures were also evaluated by comparing the residual carbon content of the digests and the recoveries of the analytes. Multiple responses (MR) were employed in both designs for elements quantified, using a mathematical tool based on the Eq. 1(Santos et al. 2009):

$$\mathrm{MR} = \left(\frac{\mathrm{R}_{M1}}{R_{\max\ \mathrm{M1}}}\right) + \left(\frac{\mathrm{R}_{M2}}{R_{\max\ \mathrm{M2}}}\right) + \ldots + \left(\frac{\mathrm{R}_{M\mathrm{n}}}{R_{\max\ \mathrm{Mn}}}\right) \quad (1)$$

where R_{Mn} is the recovery of each analyte in the experiment and $\mathrm{R}_{\max\ Mn}$ is the maximum recovery of the analyte in the design.

Determination of the Acidity and Residual Carbon Content of the Digests

To determine the final acidity, acid-base titrations of the digests were performed. The titrations were carried out with a standard solution of sodium hydroxide (0.0997 mol L^{-1}) and phenolphthalein (1.0 % m v^{-1} in ethanol). The residual carbon content (RCC) was measured in the ICP OES with axial configuration, using the line emission for C(I) at 193.025 nm (Bizzi et al. 2010). Carbon reference solutions (25–500 mg L^{-1}) used for external calibration were prepared by dissolution of citric acid (Merck) in water.

Table 3 Box–Behnken design for multivariate optimization of rice sample digestion

Experiment	HNO_3 concentration (mol L^{-1})	Temperature (°C)	Time (min)	MR
13	2 (−1)	190 (−1)	20 (0)	2.965
14	7 (1)	190 (−1)	20 (0)	3.095
15	2 (−1)	210 (1)	20 (0)	3.155
16	7 (1)	210 (1)	20 (0)	3.204
17	2 (−1)	200 (0)	15 (−1)	3.193
18	7 (1)	200 (0)	15 (−1)	3.281
19	2 (−1)	200 (0)	25 (1)	3.003
20	7 (1)	200 (0)	25 (1)	3.262
21	4.5 (0)	190 (−1)	15 (−1)	3.399
22	4.5 (0)	210 (1)	15 (−1)	3.373
23	4.5 (0)	190 (−1)	25 (1)	3.378
24	4.5 (0)	210 (1)	25 (1)	3.418
25	4.5 (0)	200 (0)	20 (0)	3.415
26	4.5 (0)	200 (0)	20 (0)	3.451
27	4.5 (0)	200 (0)	20 (0)	3.441

Quality Assurance and Quality Control

All of the samples were digested in triplicate and all measurements were run in triplicate for each sample. Element concentrations were calculated and expressed in μg g^{-1} dry weight. The accuracy of the analytical method was verified by analyzing a certified reference material (Rice Flour—NIST SRM 1568a—National Institute of Standard and Technology, USA). At least one sample of the SRM 1568a and three blanks (reagents and digestion blanks) were included in each analytical batch. The precision of the method, defined as the closeness of agreement between mutually independent test results, was expressed in terms of relative standard deviation (RSD%).

Table 4 Analysis of a rice flour certified reference material (NIST SRM 1568a) by ICP-MS and ICP OES after microwave-assisted digestion using diluted nitric acid (mean ± SD, $n = 3$)

Element	Certified (% mg g^{-1} dry wt.)	Found (% mg g^{-1} dry wt.)
Ca	0.0118 ± 0.0006	0.0101 ± 0.0002
K	0.1280 ± 0.0008	0.1079 ± 0.0028
Mg	0.056 ± 0.002	0.056 ± 0.001
Element	Certified (μg g^{-1} dry wt.)	Found (μg g^{-1} dry wt.)
Al	4.4 ± 1.0	4.5 ± 0.7
As	0.29 ± 0.03	0.24 ± 0.01
Cd	0.022 ± 0.02	0.0207 ± 0.002
Cu	2.4 ± 0.3	1.9 ± 0.1
Fe	7.4 ± 0.9	7.1 ± 0.2
Mn	20.0 ± 1.6	17.6 ± 0.1
Mo	1.46 ± 0.08	1.41 ± 0.05
Se	0.38 ± 0.04	0.31 ± 0.02
Zn	19.4 ± 0.5	16.6 ± 0.1

Results and Discussion

The efficiency of decomposition in the microwave oven was evaluated by three variables: acid concentration, digestion time, and temperature. Firstly, a full two-level factorial design experiment (2^3) was carried out in order to verify the influence and interactions of these variables on the digestion of rice samples. The results obtained from this design are shown in Table 2 and the Pareto chart (Fig. 1). The temperature and time factors (negative effect) and the interaction of temperature and concentration of nitric acid (positive effect) were significant in the experimental domain studied.

A Box–Behnken design was then used in order to adjust the digestion procedure, using a quadratic model to identify the optimum conditions. Considering that good recoveries were obtained with diluted nitric acid solution, lower concentrations of acid were used in Box–Behnken design. The Box–Behnken design was performed employing the MR. The residual carbon concentrations and residual acidity were also determined in all the samples in the experiment. According to Nobrega et al. (2002), a residual carbon content of up to 13 % did not cause interference in the determination of metals by ICP OES. The residual carbon concentrations in the present study were between 2.21 and 18.4 % (m/m), and only experiments 2 and 3 had concentrations greater than 13 %. Low residual acidity solutions

Table 5 Recovery ranges obtained by previous methods for the determination of different elements in rice samples

Analyte	Detection	Agreement with the CRM (%)[a]	Recovery range (%)	Reference
Hg	CV-AFS	86.4–134.5	94–98	Silva et al. 2010
Ag, Al, As, B, Ba, Br, Ca, Cd, Ce, Co, Cr, Cs, Cu, Eu, Fe, Hf, Hg, K, La, Mg, Mn, Mo, Na, P, Rb, S, Sb, Sc, Se, Sm, Sr, Th, Ti, U, V, and Zn	INAA, ICP OES, F AAS, and TXRF	91.7–115.8	–	Antoine et al. 2012
Ca, K, Mg, Na, P, Fe, Mn, and Zn	ICP OES	96.9–101.7	–	Silva et al. 2013
Pb	HR-CS GF AAS	111.9	–	Gunduz and Akman 2013
As, Ba, Ca, Cd, Cr, Cu, Fe, Mg, Mn, Ni, Pb, Se, Sr, Zn	DRC-ICP-MS	85–108	–	Wei et al. 2014
Cr, Fe, Cu, Zn, and Se	ETV-DRC-ICP-MS	81.6–102.5	–	Huang et al. 2014
Cd, Cr, Co, Pb, and Ni	GF AAS	87.5–107	–	Naseri et al. 2015
As, Cd, Pb, and Se	GF AAS	93.1–109.1	90.3–106.0	Oliveira et al. 2016
As and Hg	ICP-MS	86.2 and 103.1	85.33–119.35 and 72.57–96.82	Fang et al. 2016
Al, As, Ca, Cd, Cu, Fe, K, Mg, Mn, Mo, Se, and Zn	ICP-MS and ICP OES	80–102 %	92–115	This work

CRM Certified Reference Material, *INAA* instrumental neutron activation analysis, *ICP OES* inductively coupled plasma optical emission spectrometry, *F AAS* flame atomic absorption spectrophotometry, *TXRF* total reflection X-ray fluorescence, *CV-AFS* cold vapor atomic fluorescence spectrometry method, *ICP-MS* inductively coupled plasma mass spectrometry, *GF AAS* graphite furnace atomic absorption spectrometry, *HR-CS GF AAS* high resolution continuum source graphite furnace atomic absorption spectrometry

[a] (Observed/certified) × 100

are recommended for elemental determination by spectrometric techniques, because acidity affects the sample introduction system and low residual acidity solutions result in better detection (Todolí and Mermet 1999). The residual acidity obtained after the digestions, as expected, was highest in the samples digested with highly concentrated solutions. The residual acidity of the diluted digests varied from 0.9 to 3.2 mol L^{-1}.

The Box–Behnken design confirmed that the temperature and concentration of HNO_3 had a positive effect on digestion, as can be seen in the response surface (Fig. 2). As can be seen in Table 3, the highest MR values were obtained at the central point. These experiments were performed with an acid concentration of 4.5 mol L^{-1}, which correspond to a volume of 2 mL of concentrated HNO_3 per 250 mg of sample. This condition conforms to the

Table 6 Mean concentrations and standard deviations of trace elements ($n = 3$, μg g^{-1}) in different types of rice from the Brazilian market: White rice (WR, $n = 8$), Integral rice (IR, $n = 5$), Parboiled rice (PR, $n = 10$)

Elements	WR (mean ± SD (min–max))	IR (mean ± SD (min–max))	PR (mean ± SD (min–max))
Al	5.2 ± 2.5 (<2.4–8.57)	4.0 ± 2.4 (<2.4–7.8)	7.2 ± 5.8 (<2.4–15.3)
As	0.135 ± 0.082 (<0.17–0.32)	0.196 ± 0.047 (<0.17–0.24)	0.159 ± 0.043 (<0.17–0.17)
Ca	50.9 ± 38.5 (<5.0–114.8)	140.0 ± 25.7 (98.0–155.0)	24.7 ± 14.5 (<5.0–16.0)
Cd	0.011 ± 0.005 (<0.006–0.017)	0.013 ± 0.004 (<0.006–0.017)	0.009 ± 0.003 (0.01–0.017)
Fe	2.1 ± 1.8 (<0.3–7.2)	14.0 ± 2.7 (10.5–17.4)	2.6 ± 3.5 (<0.3–12.5)
K	649.7 ± 75.7 (530–720)	1989.0 ± 87.0 (1940–2090)	1453.0 ± 50.8 (1390–1520)
Mg	282.1 ± 165.9 (145–720)	1535.7 ± 103.7 (1370–1620)	302.1 ± 314.7 (200–460)
Mn	8.2 ± 2.3 (5.33–12.4)	28.1 ± 4.5 (23.7–34.9)	4.7 ± 1.3 (2.78–6.60)
Mo	0.39 ± 0.19 (0.30–0.81)	0.49 ± 0.21 (0.38–0.53)	0.37 ± 0.11 (<0.06–0.45)
Cu	0.66 ± 0.76 (<0.3–2.18)	0.55 ± 0.18 (<0.3–0.73)	0.270 ± 0.06 (<0.3–0.33)
Se	0.081 ± 0.215 (<0.06–0.117)	0.072 ± 0.017 (<0.06–0.079)	0.059 ± 0.07 (<0.06–0.271)
Zn	9.1 ± 4.3 (8.3–14.9)	15.7 ± 5.0 (15.0–17.1)	5.0 ± 2.3 (4.8–7.8)

max maximum value, *min* minimum value recommendation of Krug (2008) to use between 0.4 and 2.0 mL acid per 200 mg of sample. Thus, the central point conditions proved to be suitable for the digestion of rice samples, confirmed by the values calculated by the software Statistica 6.0 for the critical points: an acid concentration of 4.8 mol L^{-1} HNO_3, a temperature of 208 °C, and a digestion time of 21 min.

Analytical Performance

The limits of detection (LOD) and quantification (LOQ) of each analyte were calculated as the analyte concentration corresponding to three and ten times, respectively, the standard deviation of ten independent measurements of the blank, divided by the slope of the calibration curve employing sample mass of 250 mg and final volume of 15.0 mL after digestion. The LODs for Al, Ca, Cu, Fe, K, Mg, Mn, and Zn (elements determined by ICP OES) were 0.8, 1.5, 0.1, 0.1, 0.7, 2.3, 0.1 and 0.2 μg g^{-1}, respectively. When ICP-MS was employed, the LODs for As, Cd, Mo, and Se determinations were 0.05, 0.002, 0.02, and 0.02 μg g^{-1}, respectively.

In order to evaluate the accuracy of the proposed procedure, a CRM sample (NIST 1568a, Rice Flour) was digested by the proposed procedure and the analytes were determined by ICP OES and ICP-MS. The results are presented in Table 4 and show that the obtained values were in agreement with certified values (80–102 %). The worst results were for Ca, K, As, Cu, Se, and Zn (between 80 and 85 %); however, these results are acceptable for mg g^{-1} or μg g^{-1}concentration levels as reported in previous works concerning the determination of metals in food samples (AOAC SMPR 2012; Mohd-Taufek et al. 2016; Leme et al. 2014; Ni et al. 2016). Additionally, the evaluation of the analytical performance of procedure was also made by a spike recovery study at two concentration levels: 0.25 and 3.0 mg L^{-1}. The recovery results ranged from 92 to 115 %. The recoveries obtained confirmed that the proposed procedure showed good analytical performance. Table 5 shows the recovery ranges obtained by previous methods for the determination of different elements in rice samples. Moreover, the procedure resulted in solutions with low residual acidity after dilution (2.0 mol L^{-1}) and carbon (7.2 ± 2.5 %), which are important prerequisites for multi-element determination using ICP-MS and ICP OES.

Analytical Application in Rice Samples

The proposed method was applied to the determination of trace elements in 23 rice samples purchased from different local markets in Salvador, Bahia, Brazil (10 parboiled, 8 white, and 5 brown rice). The concentration ranges, i.e., the minimum and maximum values, for each type of rice are shown in Table 6. The average concentration of the analytes differed according to the type of rice, with brown rice showing the highest levels of the nutrients Ca, Mg, Fe, Mn, and Zn. This difference in concentration is related to differences in the processing of the rice. Brown rice is only subjected to a stripping step which does not lead to removal of these species from the grains. The determined concentrations of the analytes were also compared with values published in the literature, and the results were in good agreement with them (Silva et al. 2013; Teixeira et al. 2012; Walter et al. 2008; Oliveira et al. 2012; Okada et al. 2007).

Comparing the range of concentration of the analytes in three types of rice studied with the concentration regulated by Brazilian Agency for Sanitary Surveillance (Brazil 2005), it can be seen that all the element contents were below the maximum tolerated.

Conclusions

The microwave-assisted digestion procedure using dilute nitric acid was successfully applied for multi-element determination in rice samples by ICP OES and ICP-MS. The optimal conditions for analyte extraction from rice samples were obtained using a response surface methodology based on Box–Behnken experimental design, resulting in a fast and efficient method of optimization. Considering some critical parameters such as cost, minimization of residues, and analyst safety, the proposed procedure has advantages compared to classical digestion procedures.

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Compliance with Ethical Standards

Conflict of Interest Taiana B. Tarantino declares that he has no conflict of interest. Isa S. Barbosa declares that he has no conflict of interest. Daniel de C. Lima declares that she has no conflict of interest. Madson de G. Pereira declares that he has no conflict of interest. Leonardo S. G. Teixeira declares that he has no conflict of interest. Maria Graças A. Korn declares that he has no conflict of interest.

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

Informed Consent Not applicable.

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