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The development and validation of a new method for the fast determination of Al, Ba, Ca, Cu, Fe, K, Mg, Mn, Na, Sr and Zn in rice by inductively coupled plasma optical emission spectrometry†

Pawel Pohl,* Krzysztof Greda, Maja Welna, Piotr Jamroz, Anna Dzimitrowicz and Anna Szymczycha-Madeja

An alternative method of rice sample preparation for measuring the total content of selected elements, *i.e.*, Al, Ba, Ca, Cu, Fe, K, Mg, Mn, Na, Sr and Zn, by ICP OES was developed. The proposed approach is based on the ultrasound-assisted extraction (USAE) of rice samples in the presence of a small amount of concentrated HNO_3. The optimal operating parameters were found using the design of experiments (DOE) approach, and the studied experimental factors were the temperature of the ultrasonic bath (*A*), the sonication time (*B*), and the volume of concentrated HNO_3 added per 0.5 g of a rice sample (*C*). Under the optimal conditions of the USAE procedure, *i.e.*, $A = 60$ °C, $B = 16$ min and $C = 4.0$ mL, the rice samples were readily solubilized, and the obtained sample solutions could be analyzed by ICP OES with the simple standard solution calibration (without matrix matching). The analysis of the certified reference material (rice flour, NIST SRM 1568b) confirmed the satisfactory trueness of the USAE-ICP OES method. Additionally, no statistically significant differences between the results obtained for the samples prepared by USAE and open-vessel wet digestion (WD, the reference method) were found. In comparison to the routinely used microwave-assisted digestion and open-vessel digestion, the USAE approach offers lower acid consumption, lower detection limits (LODs) of elements, ranging from 4.0 ng g^{-1} for Mn to 2.7 μg g^{-1} for K, and a much shorter time of sample preparation.

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1. Introduction

The consumption of rice globally, amounting to 517 million metric tons, plays a crucial role in feeding the world population. Almost 50% of people in the world, practically on all continents, base their diet on rice and/or rice flour.[1] Since this cereal is an important source of nutrients, including mostly proteins and minerals, its quality and safety are of the utmost importance.[2] Considering the presence of various minerals, including essential elements such as Ca and P (the formation of bones), Na and K (nerve transmission) as well as trace elements, including Cu, Fe and Zn, which play a very important role in the proper functioning of the body,[3] the element analysis of rice is completely obvious since it provides useful information on the mineral status of this food product as well as its possible contamination with the selected trace elements.

Apparently from the literature devoted to the element analysis of rice, two spectrometric methods are commonly applied, *i.e.*, inductively coupled plasma mass spectrometry (ICP MS)[2,4–10] and inductively coupled plasma optical emission spectrometry (ICP OES).[2,5,8–21] Both the mentioned methods need the rice samples to be digested before the measurements to decompose their organic matrix and quantitatively transfer the elements into the prepared sample solutions. This is commonly made with the aid of various microwave-assisted closed-vessel systems.[2,4–9,13–17] In this case, the rice samples are digested under the conditions of very high temperature (up to 200–280 °C) and very high pressure (up to 160–200 bars) and using oxidizing reagents such as concentrated HNO_3 alone,[6,11] or mixtures containing concentrated HNO_3 with concentrated (30%) H_2O_2,[4,5,7,12,15,17] or concentrated HCl (3 : 1).[16] In addition to this, concentrated H_2O_2 alone,[9] diluted (4.5 mol L^{-1}) HNO_3,[8] or diluted HNO_3, *i.e.*, at 0.1,[2] 1 or 8 mol L^{-1},[13,14] with concentrated H_2O_2 were also applied to decrease the usage of HNO_3. A mixture of diluted (2%) $HClO_4$ with diluted (4%) H_2O_2 was also used for this purpose.[15] Although quite popular and efficient, this type of wet digestion (WD) requires, however, a quite high economic outlay for the purchase of an appropriate microwave oven and appropriate accessories and spare parts. Moreover, although the microwave-assisted decomposition of rice samples is fast (taking up to a max. 30 min), the vessels used for this

Division of Analytical Chemistry and Chemical Metallurgy, Faculty of Chemistry, Wroclaw University of Science and Technology, Wybrzeze Wyspiansgiego 27, 50370, Wroclaw, Poland. E-mail: pawel.pohl@pwr.edu.pl

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process need to be washed every time. The washing procedure should be carried out once or twice, using conditions similar to those employed during the sample decomposition step. This is just to prevent possible memory effects and any uncontrolled contamination of the subsequent samples. In consequence, appropriate washing programs are additionally run, which, however, extends the sample preparation time.

Traditional open-vessel WD is also willingly applied at the step of the sample preparation of rice before the element analysis by ICP OES and ICP MS.[10,18–21] In this case, the treatment of the samples at lower temperatures 110–130 °C is, however, longer, *i.e.*, 2 h and more. Considering the reaction mixtures applied to treat the samples, it can be concentrated HNO_3 with concentrated HCl (3 : 1)[18] or concentrated HNO_3 with concentrated H_2O_2,[20,21] as well as more complex mixtures of the concentrated reagents, *e.g.*, HNO_3, HCl with H_2SO_4 (ref. 19) or HNO_3, HF, $HClO_4$ with HCl.[10] Unfortunately, the longer preparation time and the use of the open-vessel system increase the risk of contamination of the analyzed samples and/or the loss of the analytes.

Both of the aforementioned cases result in the necessity of searching for entirely new procedures for sample preparation. The ideal approach would be to make these procedures more environmentally friendly (greenish) by reducing the amount of concentrated and toxic reagents used, as well as by using energy-efficient equipment, or significantly reducing the time required for sample preparation. All these efforts certainly reduce the costs of the analysis itself. In the case of rice samples, due to the sample matrix, such searches for a new alternative to WD procedures are rather uncommon. The studies in which concentrated HNO_3 is replaced with its diluted solutions[2,8,13,14] or by other reagents (concentrated[9] or diluted[15]) can be partially considered as such, because in all these cases very high temperatures and pressures are needed, which are only ensured by the application of closed-vessel microwave-assisted systems. Therefore, appropriate mineralization devices are required and their use, apart from the generally known benefit – quick decomposition, has its disadvantages such as preparing polytetrafluoroethylene (PTFE) vessels and their covers each time before use.

The literature reports sample preparation procedures based on ultrasound-assisted extraction (USAE), but this is extremely exceptional and rare. The USAE procedure for rice samples with an alkaline (pH > 10) EDTA solution was used to determine the concentration of P, K, Mg, Ca, Zn, Mn, Cu and Mo in rice using ICP OES.[16] In another study, an alkaline (pH = 8) solution of pancreatin was taken to treat the rice sample before the determination of As, Cd, Mn and Zn by ICP MS.[17] The experiments were carried out at room temperature, and the procedure lasted 20 min. Finally, USAE was also applied to prepare rice samples with concentrated HNO_3 before the determination of the concentrations of Cd, As, Pb and Se by GF-AAS.[22] However, although the treatment was carried out at 80 °C, the procedure was very long (up to 2 h) and, hence, the authors recommended at the end WD in a reflux system in a digestion block (for 90 min and at 120 °C with concentrated HNO_3).[22]

For all these reasons, the present work was aimed at developing a new sample preparation procedure for rice, omitting completely WD in open- or closed-vessel microwave-assisted systems. Instead, the USAE of rice samples was proposed while the optimal working conditions of this procedure, *i.e.*, the temperature of water filling an ultrasonic bath (*A*, in °), the sonication time (*B*, in min), and the volume of a concentrated HNO_3 solution added per 0.5 g of rice (*C*, in mL), were selected based on the design of experiments (DOE) approach with the Box–Behnken response surface design along with the desirability functions ($d_{element}$s) and the overall desirability (*D*) approach. The multiresponse of the system was the concentration of 11 elements (Al, Ba, Ca, Cu, Fe, K, Mg, Mn, Na, Sr and Zn) determined in the prepared sample solutions. The newly developed ICP OES method with the USAE sample preparation was validated and applied for the analysis of different types of rice.

2. Experimental

2.1. Reagents and materials

Merck (Germany) Emsure ACS grade 65% (m/m) HNO_3 and 30% H_2O_2 were used to wet digest the rice samples in a digestion block. To calibrate an ICP OES instrument, multielement working standard solutions within the concentration range of 0.010–10 μg g^{-1} were applied. They were prepared by diluting a bulk (1000 μg g^{-1}) standard solution, ICP no. IV, obtained from Merck as well. In addition, Merck bulk (1000 μg g^{-1}) single-element standard solutions of Ba, Na and Sr were applied at the stage of the spike-and-recovery experiment.

Considering the experimental material, rice samples, commercially available in local stores and distributed by leading retailers in Poland, were taken. All of them were sold in bulk packages containing 4 to 6 individual 100 g bags. In the case of each rice material, including white rice (WR1, WR2, WR3, WR4, and WR5), basmati rice (BR1 and BR2), jasmine rice (JR1 and JR2), parboiled rice (PBR1 and PBR2) and red rice (RR1 and RR1), 5 individual bags from different bulk packages were taken and combined. 50 g of such prepared laboratory samples of WR, BR, JR, PBR and RR were ground using a Fritsch planetary micro mill, model Pulverisette 7 premium line, with agate grinding balls (fi 15 mm) and an 80 mL grinding bowl. The resulting ground rice material was kept in screwed polypropylene (PP) containers in the dark. In addition, for the whole optimization study of the USAE sample preparation procedure, which was carried out using the response surface design, another WR (WR0) was selected and prepared in the same way as the other rice samples.

To validate the ICP OES methods with the sample preparation by open-vessel WD in a digestion block (the reference method) as well as with USAE (the new, alternative method), a NIST certified reference material (CRM) of rice flour, *i.e.*, SRM 1568b, was applied.

2.2. Instrumentation

To determine the concentrations of the studied elements (Al, Ba, Ca, Cu, Fe, K, Mg, Mn, Na, Sr and Zn) in the prepared

solutions of the samples and the working standards, an Agilent ICP optical emission spectrometer, model 5110, was used. It was a synchronous dual view (SVDV) instrument with a solid-state radio frequency (SSRF) system and a vertically oriented, easy-to-fit demountable quartz torch (with a 1.8 mm injector) to sustain and stably operate the Ar plasma. A glass single-pass cyclonic spray chamber and a glass SeaSpray concentric nebulizer, tolerating a high content of the dissolved solids in the solutions, were used to introduce the solutions into the plasma torch. To acquire the radiation emitted by the Ar ICP, an Echelle polychromator along with a Vista Chip II CCD detector were used. The operating conditions of the instrument used in this work were those recommended by the manufacturer and given in the instrument software ICP Expert (see Table 1S†).

For the WD of the selected rice samples, a SCP Science (Canada) digestion block, model DigiPREP Jr, was used. It was equipped with a timer and a temperature controller.

In the case of the rice samples subjected to the USAE procedure, a Polsonic (Poland), model Sonic 36, 48 L ultrasonic bath with an ultrasonic power of 2 × 900 W at 40 kHz, a temperature controller (0–80 °C) for heating water filling its tank, and a timer (0–30 min) was used. The resulting sample solutions were centrifuged, if necessary, to separate any insoluble remnants of the rice samples, and a Medical Instruments (Poland) centrifuge, model MPW-352, was used for that.

2.3. Sample preparation

2.3.1. Wet digestion. The open-vessel WD of the rice samples in a mixture of the oxidizing reagents, followed by the analysis of the resulting sample solutions by ICP OES, was selected as the reference method, providing the reference concentrations (C_{REF}s) of Al, Ba, Ca, Cu, Fe, K, Mg, Mn, Na, Sr and Zn. In detail, 0.5 g portions of the selected samples (WR0, WR3, and RR2) or the CRM (SRM 1568b) were weighed into special DigiTUBES and treated with 4.0 mL of concentrated HNO_3. Such sample mixtures were left overnight for pre-digestion (~7 h). Next, the DigiTUBES with contents were covered with PP ribbed watch glasses and placed into the digestion block. The following temperature program was applied: 90 °C for 30 min, 130 °C for 120 min, and cooling at room temperature (up to 10 min). This provided the WD of the material and the evaporation of the sample aliquots to about 1 mL or less. Afterward, 2 mL of concentrated H_2O_2 was added, and the DigiTUBES with the sample aliquots were still heated at 130 °C for the next 45 to 60 min until they were evaporated to near dryness. Finally, the resulting remnants were reconstituted with water to obtain 20.0 g solutions of the digested rice samples. Not to clog the concentric nebulizer, these sample solutions were filtered before the ICP OES measurements through the 0.45 μm Nylon syringe filters. In the same way, the blank sample solutions were prepared and analyzed to correct the final results. The latter ones were the mean values ($n = 3$) along with the standard deviations (SDs) as the precision measures.

2.3.2. Ultrasound-assisted extraction. Under the optimized conditions, the rice samples (0.5 g) were weighed into screwed 50 mL tubes, treated with 4.0 mL of concentrated HNO_3, and sonicated for 16 min in the ultrasonic bath, which was filled with water, having a temperature of 60 °C. This resulted in the complete solubilization of the samples and the extraction of the studied elements into the solution. Then, the sample aliquots were topped with water to obtain 20.0 g sample solutions. Before the measurements by ICP OES, the resultant sample solutions were filtered through 0.45 μm syringe filters. A schematic diagram of the new method based on the USAE sample preparation is given in Fig. 1S.† In the same way as the sample solutions, blank sample solutions were prepared (only HNO_3 was used, following the other steps of the procedure). The final, blank corrected results were the mean concentrations ($n = 3$) of the studied elements along with the SDs.

2.4. Multivariate optimization of the USAE procedure

The parameters of the USAE procedure that were considered in the Box–Behnken response surface design were: (i) the temperature of water filling the ultrasonic bath tank (A, in °C), the sonication time (B, in min), and the volume of a concentrated HNO_3 solution added per 0.5 g of a rice sample (C, in mL). These parameters were changed at 3 levels, *i.e.*, the lowest (−1), the middle (0) and the highest (+1), which were: 20, 40 and 60 °C for A, 10, 20 and 30 min for B, and 1.0, 2.5 and 4.0 mL for C. The matrix of the Box–Behnken response surface design included 15 randomized treatments, at which all 3 parameters A, B and C were set at 1 of these 3 levels. The standard order and the run order of these treatments in addition to the coded and the uncoded settings of the parameters A, B and C are given in Table 2S.† In addition, to evaluate the precision of the applied response surface design, 3 center points were entered, at which the middle settings of all parameters were used. All treatments were carried out in 1 block, and 3 independently made replicates were considered for each one.

Accordingly, the 0.5 g analytical samples of the test material WR0 were taken and treated with concentrated HNO_3 (1.0, 2.5, or 4.0 mL). Then, these sample mixtures were sonicated for 10, 20, or 30 min using the ultrasonic bath with water inside the tank, which was unheated (20 °C) or heated to 40 or 60 °C. The resulting sample mixtures or solutions (in the case of complete solubilization) were topped with water to prepare 20.0 g sample solutions. In the case of incomplete solubilization of the samples, the resulting mixtures were additionally centrifuged for 10 min at 11 000 rpm. The collected solutions or supernatants were subjected to the ICP OES analysis on the content of Al, Ba, Ca, Cu, Fe, K, Mg, Mn, Na, Sr and Zn *versus* the simple working standards solutions (no matching according to the HNO_3 concentration in the resulting sample solutions was considered). The corresponding procedural blank solutions were also prepared in 3 replicates for each treatment, analyzed, and considered in the final results.

The blank-corrected mean concentrations of the studied elements were the multiresponse of the Box–Behnken response surface design and were fitted with full quadratic functions that comprised the following terms: linear (A, B, C), square (A^2, B^2, C^2), and 2-way interactions (AB, AC, BC). A general form of the

regression model equation, elucidating the concentration of the studied elements *versus* the parameters of the USAE procedure, was as follows: $C_{element} = \beta_0 + \beta_1 A + \beta_2 B + \beta_3 C + \beta_{11} A^2 + \beta_{22} B^2 + \beta_{33} C^2 + \beta_{12} AB + \beta_{13} AC + \beta_{23} BC$, where β_0 is the intercept, while $\beta_1 - \beta_{33}$ – the coefficients of each term included in this equation. The mentioned intercept, the terms, and their coefficients were established by using the stepwise-selection-of-terms algorithm with α to enter and remove the term equal to 0.15, following the recommendations and tips of the software used, *i.e.*, Minitab 17. The analysis of variance (ANOVA) was used to test the statistical and practical significance of the established response surface regression models as well as their adequacy. The *p*-values for the regression models and the terms included in these models, as well as the *p*-values for the lack-of-fit test were considered in this case. In addition, the coefficients of determination (R^2, %) were also regarded. The statistically significant regression models, illustrating how the concentration of each element was changed *versus* the parameters *A*, *B* and *C* of the USAE procedure, were used to find the settings of these parameters that enabled achieving the concentrations of all studied elements that unbiasedly corresponded to their C_{REF}s as obtained by the WD procedure of the WR0 samples (the reference method).

Finally, the individual $d_{element}$ values for each element and the *D* value for all studied elements enabled us to find the global settings of the parameters *A*, *B* and *C* that provided the concentrations of these elements that did not statistically differ from the respective C_{REF}s. For a given combination of the parameters *A*, *B* and *C*, the $d_{element}$ value was calculated as follows:

$$d_{element} = \begin{cases} 0 \text{ if } C < C_L \text{ or } C > C_H \\ \dfrac{C - C_L}{C_{REF} - C_L} \text{ if } C_L < C < C_{REF} \text{ or } \dfrac{C_H - C}{C_H - C_{REF}} \text{ if } C_{REF} < C < C_H, \\ 1 \text{ if } C = C_{REF} \end{cases}$$

where the C_L and the C_H were the lowest and the highest, respectively, acceptable concentrations of a given element, arbitrarily selected based on the results of the Box–Behnken response surface design, while *C* was the concentration of this element modeled at given parameters. Subsequently, the *D* value, being the geometric mean of the $d_{element}$ values, was also calculated $\left(\sqrt[11]{C_{Al} C_{Ba} C_{Ca} C_{Cu} C_{Fe} C_K C_{Mg} C_{Mn} C_{Na} C_{Sr} C_{Zn}}\right)$ under these conditions and applied to confirm the usefulness of the given settings of the parameters to achieve the C_{REF}s for all elements.

3. Results and discussion

3.1. The reference method by wet digestion sample preparation along with ICP OES detection

To assess the trueness of the reference method selected in this work, the rice flour CRM, *i.e.*, SRM 1568b from NIST, with certified concentrations (C_{CRM}s) of Al, Ca, Cu, Fe, K, Mg, Mn and Zn was applied. The CRM samples were wet digested following the procedure described in Subsection 2.3.1, and the prepared sample solutions were analyzed by ICP OES. Using the *F*-test[23] as well as the *t*-test[23] (in the case when the calculated value of the *F*-test ($F_{calculated}$) was lower than the critical value of this test ($F_{critical}$)), or the *C*-test[23] (in the case when the $F_{calculated}$ was higher than the $F_{critical}$), the SD values and the mean concentrations of Al, Ca, Cu, Fe, K, Mg, Mn and Zn, as determined by the ICP OES method with the WD sample preparation in the digestion block, were compared with the C_{CRM}s. It was found that there were no statistically significant differences between the determined concentrations and the C_{CRM}s as the calculated values of the *t*-test ($t_{calculated}$) and the *C*-test ($C_{calculated}$) were lower than the respective critical values of both tests, *i.e.*, $t_{critical}$ and $C_{critical}$ (see Table 1). As such, the bias of the mean concentrations of Al, Ca, Cu, Fe, K, Mg, Mn and Zn determined in the CRM by using ICP OES along with the WD was statistically insignificant and changed from −2.5% for K to +5.9% for Ca. In the case of Ba, Na and Sr (with no certified concentrations), the CRM samples were spiked with single-element standard solutions of these elements to double the original concentration of these elements, as determined by the applied method. These concentrations were: 0.150 μg g^{-1} for Ba and Sr and 10.0 μg g^{-1} for Na. The results obtained for the unspiked and spiked samples enabled the recoveries of these elements to be evaluated, which were 99.3 ± 0.9% for Ba, 101 ± 2% for Na, and 100 ± 1% for Sr, and pointed out the bias in the range from −0.7% for Sr to +1.0% for Na. All these measures above proved that the proposed and applied ICP OES method, based on the WD sample preparation, provided true and precise results and, hence, could be applied to get the C_{REF}s in the analyzed rice samples, initially ground to a flour-like powder.

In addition, WD in a microwave-assisted closed-vessel system was carried out and accurate results were obtained in reference to the C_{CRM}s of Al, Ca, Cu, Fe, K, Mg, Mn and Zn (see Table 1 and the calculated values of the *t*- and *F*-tests applied for statistical comparison).

3.2. Development of the new alternative method based on the response surface design

Although the reference method, like other methods with the WD sample treatment, provided accurate results, it required a long time to treat the organic matrix (up to 220 min overall) at the elevated temperature (maximally 130 °C). To make the method "greener" it was decided to reduce the time of the sample treatment as well as its temperature by applying the

Table 1 The concentrations of Al, Ba, Ca, Cu, Fe, K, Mg, Mn, Na, Sr and Zn (in μg g^{-1}) determined in the certified reference material of rice flour/NIST SRM 1568b/by using wet digestion (WD) with concentrated HNO_3 and H_2O_2 (in a digestion block: 120 min, 130 °C, or a microwave-assisted system: 70 min, 190 °C) sample preparation procedure followed by the analysis of the resulting sample solutions by ICP OES and the developed ultrasound-assisted extraction (USAE) with concentrated HNO_3 (16 min, 60 °C) sample preparation procedure followed by the analysis of the resulting sample solutions by ICP OES. The statistically significant differences are italicized[a]

	Al	Ba	Ca	Cu	Fe	K	Mg	Mn	Na	Sr	Zn
Certified concentrations = C_{CRM}											
Mean, $n = 3$	4.21		118	2.35	7.42	1282	559	19.2			19.42
SD	0.17		2	0.08	0.22	6	5	0.9			0.13
Concentrations determined using WD											
Mean, $n = 3$	4.27	0.151	125	2.40	7.36	1250	546	19.5	10.2	0.141	19.6
SD	0.12	0.011	4	0.07	0.32	30	9	0.4	0.4	0.008	0.2
Concentrations determined using microwave-assisted WD											
Mean, $n = 3$	4.11	0.153	116	2.39	7.43	1269	531	19.3	10.6	0.140	18.5
SD	0.09	0.003	6	0.03	0.21	11	18	0.3	0.3	0.001	0.6
Concentrations determined using USAE											
Mean, $n = 3$	4.29	0.156	126	2.47	7.66	1260	544	19.3	10.8	0.139	19.3
SD	0.09	0.005	5	0.04	0.19	20	11	0.5	0.4	0.002	0.5
Comparison of the concentrations obtained with WD and the certified concentrations											
$F_{calculated}$	2.01		6.66	1.31	2.12	*29.75*	3.24	5.06			2.37
$F_{critical}$	19.00		19.00	19.00	19.00	19.00	19.00	19.00			19.00
$t_{calculated}$	+0.499		+2.665	+0.815	−0.268	−1.376[b]	−2.187	+0.528			+1.307
$t_{critical}$	2.776		2.776	2.776	2.776	4.303[c]	2.776	2.776			2.776
Comparison of the concentrations obtained with microwave-assisted WD and the certified concentrations											
$F_{calculated}$	3.57		9.00	7.11	1.10	3.36	12.96	9.00			*21.30*
$F_{critical}$	19.00		19.00	19.00	19.00	19.00	19.00	19.00			19.00
$t_{calculated}$	−0.900		−0.548	+0.811	+0.057	−1.797	−2.596	+0.183			−2.119
$t_{critical}$	2.776		2.776	2.776	2.776	2.776	2.776	2.776			4.303[c]
Comparison of the concentrations obtained with USAE and the certified concentrations											
$F_{calculated}$	3.57		10.41	4.00	1.34	13.22	4.84	3.24			14.79
$F_{critical}$	19.00		19.00	19.00	19.00	19.00	19.00	19.00			19.00
$t_{calculated}$	+0.720		+2.515	+2.324	+1.430	−1.837	−2.150	+0.168			−0.402
$t_{calculated}$	2.776		2.776	2.776	2.776	2.776	2.776	2.776			
Comparison of the concentrations obtained with USAE and concentrations obtained with WD											
$F_{calculated}$	1.78	4.84	1.56	3.06	2.84	2.25	1.49	1.56	1.00	14.91	6.25
$F_{critical}$	19.00	19.00	19.00	19.00	19.00	19.00	19.00	19.00	19.00	19.00	19.00
$t_{calculated}$	+0.231	+0.717	+0.297	+1.504	+1.396	+0.480	−0.244	−0.541	+1.837	−0.866	−0.965
$t_{critical}$	2.776	2.776	2.776	2.776	2.776	2.776	2.776	2.776	2.776	2.776	2.776
Comparison of the concentrations obtained with USAE and concentrations obtained with microwave-assisted WD											
$F_{calculated}$	1.00	2.78	1.44	1.78	1.22	3.31	2.68	2.78	1.78	4.00	1.44
$F_{critical}$	19.00	19.00	19.00	19.00	19.00	19.00	19.00	19.00	19.00	19.00	19.00
$t_{calculated}$	+2.449	+0.891	+2.218	+2.771	+1.407	0.683	+1.067	0.000	−0.693	−0.775	+1.774
$t_{critical}$	2.776	2.776	2.776	2.776	2.776	2.776	2.776	2.776	2.776	2.776	2.776

[a] C_{CRM}: the certified concentration given in the attest. SD: the standard deviation. $F_{critical}$: the critical value of the F-test at $\alpha = 0.05$, *i.e.*, $F_{critical}$ ($df_1 = 2$, $df_2 = 2$) = 19.00. $t_{critical}$: the critical value of the t-test at $\alpha = 0.05$, *i.e.*, $t_{critical}$ ($df = 4$) = 2.776. [b] Since the $F_{calculated}$ value was higher than the $F_{critical}$ value, the C-test was applied. [c] The critical value ($C_{critical}$) of the C test was calculated.

USAE procedure at the sample preparation step. Unfortunately, the initial experiments, when the temperature of the ultrasonic bath tank was set to 20, 40 and 60 °C, the sonication time was set to 10, 20 and 30 min, while the volume of the HNO_3 solutions was set to 1.0, 2.5 and 4.0 mL (see the description in Section 2.4), proved that it was not possible to replace concentrated HNO_3 with its less concentrated solutions. When 1.0, 2.5 and 4.0 mol L^{-1} HNO_3 solutions were used, it was not possible to completely or partially solubilize the rice samples and quantitatively extract some of the elements. As such, the recoveries of Al, Cu, Fe and Zn, the elements possibly being strongly bound to the rice matrix, were very low.

To find out the working conditions of the USAE procedure, the effect of the selected parameters of this sample preparation

procedure, *i.e.*, *A*, *B* and *C*, on the concentrations of Al, Ba, Ca, Cu, Fe, K, Mg, Mn, Na, Sr and Zn determined in rice (the WR0 material was used) was studied using the Box–Behnken response surface design (see the description in Section 2.4). When all planned experiments were carried out and the resulting sample solutions were analyzed by ICP OES, the created data matrix, *i.e.*, the concentrations of the studied elements obtained under different conditions according to the treatments within the Box–Behnken design, was statistically analyzed. At first, it was checked for each element if the SD value of the determined concentrations between the treatments, carried out under different conditions, was higher than the SD values of the concentrations determined for 3 parallel samples prepared at a given treatment. This condition was met for all studied elements; therefore, it was concluded that the multi-response (=the concentrations of the studied elements) of the Box–Behnken response surface design was influenced by the changes in the parameters selected to develop the USAE sample preparation procedure. In addition, the relative standard deviations (RSDs), evaluated for the concentrations of the elements determined after running the center points treatment, showed that the selected response surface design functioned quite well. The mentioned RSD values were as follows: 6.0% for Al, 3.0% for Ca, 0.7% for Ba, K, Mn and Sr, 1.1% for Cu, 1.7% for Fe, 1.9% for Mg, 4.4% for Na and 1.3% for Zn.

The equations of the established response surface regression models for all studied elements are given in Table 3S.† The *p*-values of the models were lower than the $\alpha = 0.15$ level of the stepwise-selection-of-terms algorithm that was used to establish the linear, square, and 2-way interaction terms in the regression equations (*p*-values were changed from 0.000 for Al and K to 0.061 for Ca). Next to this, it was found that the *p*-values of the lack-of-fit test were higher than $\alpha = 0.15$ and varied from 0.166 for Ba to 0.889 for Al, which proved the statistical significance of the regression models. In the case of Mg, the *p*-value of the regression model established for this element, equal to 0.387, was higher than the mentioned α level. This might indicate that the model for this element is statistically insignificant. However, the *p*-value of the lack-of-fit test was really high, *i.e.*, 0.448, which did not allow this model to be rejected either. Additionally, considering the R^2 values that were changed in the following ranges: 100–80% for Al, K, Na and Zn, 79–60% for Ba, Fe and Mn, and <60% for Ca, Cu, Mg and Sr, it was concluded that the response surface regression models given in Table 3S† reasonably well fitted the collected data. As such, they properly described the variance of the concentrations of the studied elements *versus* the examined parameters *A*, *B* and *C* of the USAE procedure and, hence, could be used for the development of this procedure based on the optimization of the multi-response with the aid of the individual $d_{element}$s and the *D* approach.

Analyzing the terms included in the equations of the response surface regression models, it was noted that the parameter *C* (the volume of concentrated HNO_3 added to the 0.5 g rice sample) was statistically significant for all studied elements and presented as linear terms (for Al, Ba, Fe, K, Mn, Na, Sr and Zn), square terms (Al, Cu, K, Na, Sr and Zn), and 2-way interaction terms (Al, Ba, Ca, Fe and Na). The exception was Mg, for which the only statistically significant term was the interaction between the parameters *A* and *B*.

Finally, it was also verified how the residuals between the measured concentrations of the studied elements and the predicted concentrations of these elements based on the response surface regression models behaved. No serious deviations in the normal probability plots were observed for all studied elements. In addition, no trends were confirmed to exist in the scatter plots of the normalized residuals *versus* the run order. The residuals accompanying the established response surface regression models for the concentrations of the studied elements were uncorrelated and followed the normal distribution.

3.3. Selection of the optimal conditions of the USAE procedure

To find the settings of the parameters *A*, *B* and *C* of the USAE procedure that, following the ICP OES analysis of the resulting sample solutions, would enable obtaining the concentrations of the studied elements equal to their C_{REF}s (as determined by using the reference method), the equations of the response surface regression models were used. The settings of the parameters *A*, *B* and *C* for the individual elements are collected in Table 4S† along with the individual $d_{element}$ values, which were changing from 0.87 to 1.00 (for Cu, Fe, K, Mg, Mn, Na, Sr and Zn). To find out a single set of settings for the parameters *A*, *B* and *C* that would provide the concentrations of all studied elements that would statistically correspond to the C_{REF}s, the *D* value was considered. Fig. 2S† shows how the *D* is changed when the parameters *A*, *B* and *C* are changed as well. Accordingly, knowing the C_{REF}s in the WRF0 material, the individual $d_{element}$ values were calculated and the *D* was retrieved. The best results (see Fig. 2S†), characterized by the highest *D* value of 0.72, were achieved when the following settings of the parameters were used: $A = 60$ °C (the highest studied), $B = 16$ min (in the middle of the studied range, *i.e.*, 10–30 min), and $C = 4.0$ mL (the highest studied). The concentrations of the elements fitted under these conditions were found not to statistically differ from the respective C_{REF}s, as was proved by the statistical comparison of the fitted concentrations of the elements with the respective C_{REF}s (see the $t_{calculated}$ and the $C_{calculated}$ values in Table 2). Since for all elements, the $t_{calculated}$ and $C_{calculated}$ values were lower than the respective $t_{critical}$ and $C_{critical}$ values, it was evident that the global settings selected for the USAE procedure were very promising and gave a potential opportunity to develop the much simpler sample preparation procedure (only 16 min of the treatment of the rice samples at 60 °C as compared to the 120-min treatment of the samples at 130 °C for the WD) before the multielement ICP OES analysis of rice samples.

To confirm the correctness of the response surface regression models and the established set of settings of the parameters *A*, *B* and *C* for all studied elements, an independent validation experiment was carried out, in which the WR0 samples were prepared using the USAE procedure and run

Table 2 The concentrations of Al, Ba, Ca, Cu, Fe, K, Mg, Mn, Na, Sr and Zn (in μg g^{-1}) obtained by using the wet digestion (WD, with concentrated HNO_3 and H_2O_2, 120 min, 130 °C) sample preparation procedure followed by the analysis of the resulting samples solutions by ICP OES (target values), the established response surface regression models for all elements at the optimal parameters settings, *i.e.*, $A = 60$ °C, $B = 16$ min, and $C = 4.0$ mL, providing the highest possible overall desirability (fitted values), and using the ultrasound-assisted extraction (USAE, with 4.0 mL of concentrated HNO_3, 16 min, 60 °C) sample preparation procedure followed by the analysis of the resulting sample solutions by ICP OES (model validation values). In all experiments, the WR0 material was used. The statistically significant differences are italicized[a]

	Al	Ba	Ca	Cu	Fe	K	Mg	Mn	Na	Sr	Zn
Target values = C_{REF}											
Mean, $n = 3$	0.498	0.451	48.5	2.04	1.35	543	184	9.09	4.80	0.190	14.8
SD	0.038	0.020	3.3	0.14	0.14	28	5	0.10	0.35	0.006	0.3
Fitted values											
Mean, $n = 15$	0.433	0.449	45.3	2.03	1.31	558	180	8.91	4.85	0.192	14.4
SD	0.159	0.019	3.9	0.58	0.35	15	8	0.19	1.47	0.004	0.4
D	0.869	0.949	0.490	0.946	0.938	0.558	0.588	0.528	0.932	0.596	0.754
Model validation values											
Mean, $n = 3$	0.425	0.457	42.6	2.17	1.55	570	186	9.04	4.50	0.195	14.5
SD	0.035	0.008	1.3	0.06	0.17	6	2	0.08	0.25	0.004	0.2
Comparison of fitted values and target values											
$F_{calculated}$	12.51	1.55	1.00	12.26	4.46	*4.88*	1.83	2.58	12.60	3.15	1.27
$F_{critical}$	19.42	3.74	19.42	19.42	19.42	3.74	19.42	19.42	19.42	3.74	19.42
$t_{calculated}$	−0.688	−0.165	−1.321	−0.029	−0.191	+0.743[b]	−0.823	−1.571	+0.057	+0.735	+1.626
$t_{critical}$	2.121	2.121	2.121	2.121	2.121	4.218[c]	2.121	2.121	2.121	2.121	2.121
Comparison of model validation values and fitted values											
$F_{calculated}$	14.74	4.03	6.43	*66.75*	3.03	1.98	11.43	4.03	*24.70*	1.40	2.86
$F_{critical}$	19.42	19.42	19.42	19.42	19.42	19.42	19.42	19.42	19.422	3.74	19.42
$t_{calculated}$	+0.111	−0.920	−0.732	−0.534[b]	−1.492	+1.151	−1.652	−1.495	+0.812[b]	−1.553	−0.544
$t_{critical}$	2.121	2.121	2.121	2.295[c]	2.121	2.121	2.121	2.121	2.508[c]	2.121	2.121
Comparison of model validation values and target values											
$F_{calculated}$	1.18	6.25	6.44	5.44	1.47	9.68	6.25	1.56	1.96	2.25	2.25
$F_{critical}$	19.00	19.00	19.00	19.00	19.00	19.00	19.00	19.00	19.00	19.00	19.00
$t_{calculated}$	−2.447	+0.071	−1.747	+0.577	+0.738	+2.236	+1.493	−0.242	−0.792	+0.102	−0.865
$t_{critical}$	2.776	2.776	2.776	2.776	2.776	2.776	2.776	2.776	2.776	2.776	2.776

[a] C_{REF}: the concentration obtained by using the reference method. SD: the standard deviation. $F_{critical}$: the critical values of the *F*-test at $\alpha = 0.05$, *i.e.*, $F_{critical}$ ($df_1 = 14$, $df_2 = 2$) = 19.42, $F_{critical}$ ($df_1 = 2$, $df_2 = 14$) = 3.74, and $F_{critical}$ ($df_1 = 2$, $df_2 = 2$) = 19.00. $t_{critical}$: the critical values of the *t*-test at $\alpha = 0.05$, *i.e.*, $t_{critical}$ ($df = 16$) = 2.121, and $t_{critical}$ ($df = 4$) = 2.776. [b] Since the $F_{calculated}$ value was higher than the $F_{critical}$ value, the *C*-test was applied. [c] The critical value ($C_{critical}$) of the *C* test was calculated.

using the established optimal parameters, *i.e.*, $A = 60$ °C, $B = 16$ min and $C = 4.0$ mL. The prepared sample solutions were then analyzed by ICP OES *versus* the simple standard solutions, while the determined concentrations of Al, Ba, Ca, Cu, Fe, K, Mg, Mn, Na, Sr and Zn were statistically compared with the fitted concentrations and the C_{REF}s. The results of these two comparisons are given in Table 2. As can be seen, the determined concentrations of the studied elements achieved in the validation experiments did not differ from the fitted concentrations, as predicted using the response surface regression models, and from the C_{REF}s, as obtained by using the reference method. In both cases, the $t_{calculated}$ and $C_{calculated}$ values were lower than the respective critical values of these tests. This confirmed that the developed, based on the response surface design along with the optimization by the individual $d_{elelement}$s and *D* values approach, sample preparation procedure gave accurate (true and precise) results of the multielement analysis of rice by ICP OES. This new analytical method could be used for the faster (~14-fold) and cheaper (lower electricity consumption) multielement analysis of rice as compared to the method with WD using a hot plate or a digestion block. Considering the microwave-assisted WD procedure, the new USAE sample preparation procedure could also be attractive because it does not require any sophisticated and expensive device such as a microwave oven. It is also easier to use it because dispensable digestion tubes are available, saving the time of analysis and high purity reagents necessary to eventually clean them. In contrast, microwave-assisted WD requires digestion vessels to be especially pre-cleaned using an appropriate temperature/digestion program.

Finally, the new USAE sample preparation procedure along with the ICP OES measurements was also applied to the analysis of the CRM. In this case, the determined concentrations of the studied elements obtained using the new alternative method were compared with the C_{CRM}s included in the certificate (see Table 1). According to the $t_{calculated}$ values, the new method

provided true results; the bias between the determined concentrations and the C_{CRM}s was in the range from −2.7% for Mg to +6.8% for Ca. Similarly, as before, in the case of Ba, Sr and Na, the CRM samples were spiked with known amounts of their single-element standards solutions and subjected to the newly developed method with USAE sample preparation. The determined recoveries of these elements were as follows: 101 ± 1% for Ba, 98.2 ± 1.3% for Sr, and 100 ± 1% for Na; hence, the bias ranged from −1.8% to +1.0%. Finally, when comparing the concentrations of the studied elements in the CRM determined with the new method with the C_{REF}s obtained using the reference method (with the open-vessel as well as the microwave-assisted closed-vessel WD for the sample preparation), the differences between them were also statistically insignificant (see Table 1); the differences in the concentrations of the elements spanned the range from −1.5% for Zn to +5.9% for Na in the case of the WD with the digestion block and from −4.6% for Zn to +1.7 for Cu in the case of the WD with the microwave-assisted closed-vessel system.

Both comparisons made and the obtained statistical measures univocally confirmed that the newly developed ICP OES based method with the alternative to the WD sample preparation by USAE was reliable and could be routinely used for the analysis of rice. As compared to the USAE procedure reported for the determination of Cd, As, Pb and Se by GFAAS,[22] the method proposed in the present contribution was much faster, *i.e.*, 16 min *versus* 120 min, and used lower temperature of water in a tank of the ultrasonic bath, *i.e.*, 60 °C *versus* 80 °C. In addition, the resulting sample solutions were acidic, which is more convenient for the ICP OES measurements using glass/quartz concentric nebulizers mounted on Scott-type or cyclonic spray chambers. This certainly favorably distinguishes the newly proposed sample preparation procedure in the present work from the studies in which USAE was actually used but the rice samples prior to the ICP OES analyses were treated with an alkaline (pH = 8) pancreatin solution (the determination of As, Cd, Mn and Zn)[17] or alkaline (pH > 10) EDTA solution (the determination of P, K, Mg, Ca, Zn, Mn, Cu and Mo).[16]

3.4. Analytical application

The newly developed analytical method was applied for the analysis of several different rice samples, *i.e.*, WR, BR, JR, PBR and RR. In addition, two additional rice samples, *i.e.*, WR3 and RR2, were additionally wet digested in a digestion block, following the ICP OES analysis for trueness verification. The results of this analysis and the statistical comparison are given in Table 3.

As can be seen, no statistically significant differences were found between the determined concentrations of all elements in WR3 and RR2 and the respective C_{REF}s. This proved the good trueness of the results obtained with the new method; the bias of the determined concentrations of the studied elements in reference to their C_{REF}s was changed from −7.9% for Fe to +7.7% for Ba in the case of WR3 and from −2.5% for Al to +3.1% for Ba in the case of RR2. The precision of the results, expressed as the RSD, was also acceptable and changed in the following ranges: 0.9–14.3% for Al, 0.8–5.6% for Ba, 0.9–4.8% for Ca, 0.7–4.9% for Cu, 0.6–7.0% for Fe, 0.8–3.0% for K, 1.1–3.7% for Mg, 0.8–4.5% for Mn, 1.4–5.7% for Na and 0.6–8.7% for Sr and 1.0–4.0% for Zn.

The limits of detection (LODs) of the studied elements, assessed for rice (the mass of the samples and the final mass of the sample solutions were considered), and based on the $3SD_{blank}$ criterion, where SD_{blank} is the SD for the repeatedly prepared and measured procedural blank sample solutions ($n = 5$), were as follows: 76 ng g^{-1} for Al, 10 ng g^{-1} for Ba, 1.8 μg g^{-1} for Ca, 28 ng g^{-1} for Cu, 200 ng g^{-1} for Fe, 2.7 μg g^{-1} for K, 64 ng g^{-1} for Mg, 4.0 ng g^{-1} for Mn, 1.7 μg g^{-1} for Na, 10 ng g^{-1} for Sr, and 120 ng g^{-1} for Zn. These LODs were 1.8–1.9-fold (Al, Ba, Ca, and Zn), 2.1-fold (Fe and Sr), 2.6-fold (Cu), 3.4-fold (Mg), and 4.0-fold (Mn) better than those assessed for the reference method, mostly because the SD_{blank} values obtained for the latter method were higher as a result of higher fluctuations of the background for these elements. Concurrently, the values of the LODs of K and Na obtained with the new method were 30 and 20% higher than the respective LODs of these elements achievable with the reference method. Comparing the LODs obtained with the sample preparation procedure proposed here with those reported by Oliveira *et al.* (2012),[16] who used the USAE treatment of rice samples with an alkaline EDTA solution, except for Ca, Fe and Zn, they were better from 2 times (for Cu, Mg and Mn) to 11 (for Al) and even 18 times (for K).

Considering all rice samples analyzed in this work it was observed that the highest variance in the mean concentrations of the studied elements, expressed as the coefficient of variance (CV), was established for Al (the CV of 140%), Ba (the CV of 158%), Ca (the CV of 149%), Fe (the CV of 92%) and Mg (the CV of 86%). The lowest variance of the mean concentrations of the studied elements in the studied rice samples was noted for Cu (the CV of 24%) and Zn (the CV of 34%). The average concentrations of the studied elements, *i.e.*, 0.625 μg g^{-1} for Al, 0.586 μg g^{-1} for Ba, 85.4 μg g^{-1} for Ca, 2.28 μg g^{-1} for Cu, 2.68 μg g^{-1} for Fe, 1180 μg g^{-1} for K, 277 μg g^{-1} for Mg, 11.8 μg g^{-1} for Mn, 10.2 μg g^{-1} for Na, 0.264 μg g^{-1} for Sr and 13.8 μg g^{-1} for Zn, corresponded to the concentrations of these elements reported by other authors.[2,15–17] Nevertheless, it was noted that the concentrations of Ba, Ca, Fe, Mg, Mn, Sr and Zn determined in RR were much higher than the mean concentrations of these elements in other types of rice.

The two-side one-way analysis of variance (ANOVA) for the independent groups was applied to check if the concentrations of the elements could be used for the classification/discrimination of the rice samples. The 95% significance level ($\alpha = 0.05$) was considered in this analysis. Since the variance within five groups of rice, *i.e.*, WR, BR, JR, PBR and RR, was unequal, the ANOVA with Welch correction was selected. Next, the *post hoc* least-significant difference (LSD) Fisher test was used to look for differences between all possible pairs of the rice groups due to the mean concentration of the studied elements. This comparison gave the possibility of finding 10 such differences for each element. The results of this comparison are given in Table 5S.† It was established that the concentration of Fe provided 6 pairs of rice differing from each other, while the

Table 3 The concentrations of Al, Ba, Ca, Cu, Fe, K, Mg, Mn, Na, Sr, and Zn (in μg g^{-1}) determined in different rice samples, *i.e.*, white rice (WR), basmati rice (BR), jasmine rice (JR), parboiled rice (PBR), and red rice (RR), by using the developed ultrasound-assisted extraction (USAE) with concentrated HNO_3 (16 min, 60 °C) sample preparation procedure followed by the analysis of the resulting sample solutions by ICP OES. For comparison purposes, the selected rice samples were subjected to the wet digestion (WD) with concentrated HNO_3 and H_2O_2 (120 min, 130 °C) sample preparation procedure followed by the analysis of the resulting sample solutions by ICP OES. The statistically significant differences are italicized[a]

	Al	Ba	Ca	Cu	Fe	K	Mg	Mn	Na	Sr	Zn
WR1											
Mean, $n = 3$	3.52	0.334	500	1.47	2.97	1620	375	11.5	14.8	0.436	8.02
%RSD	3.3	0.9	1.9	1.8	7.0	1.2	2.3	3.2	1.4	1.1	1.0
WR2											
Mean, $n = 3$	0.254	0.238	33.5	2.84	0.738	875	109	8.31	3.62	0.119	13.6
%RSD	10.6	1.7	2.1	4.1	3.4	1.5	2.5	2.8	5.6	0.8	1.4
WR3											
Mean, $n = 3$	0.381	0.126	40.5	2.15	1.29	712	174	8.25	5.21	0.159	16.7
%RSD	13.9	1.1	3.4	1.9	4.9	0.9	1.7	0.8	1.5	1.1	2.3
WR3 subjected to WD											
Mean, $n = 3$	0.361	0.117	39.2	2.09	1.40	688	174	8.50	4.92	0.161	16.1
%RSD	10.2	6.8	3.3	2.9	8.6	2.6	2.3	2.4	4.7	3.7	1.9
$F_{calculated}$	2.05	*64.00*	1.16	2.25	4.00	6.61	1.78	11.11	8.27	9.00	1.78
$F_{critical}$	19.00	19.00	19.00	19.00	19.00	19.00	19.00	19.00	19.00	19.00	19.00
$t_{calculated}$	+0.536	+1.579[b]	+1.179	+1.441	−1.420	+2.152	0.000	−2.055	+2.063	−0.548	+2.078
$t_{critical}$	2.776	4.303[c]	2.776	2.776	2.776	2.776	2.776	2.776	2.776	2.776	2.776
WR4											
Mean, $n = 3$	0.316	0.084	44.4	1.62	1.30	596	111	9.35	5.39	0.238	15.5
%RSD	14.0	1.0	4.5	3.5	3.9	1.4	1.5	1.9	1.6	1.0	1.3
WR5											
Mean, $n = 3$	0.425	0.457	42.6	2.17	1.55	574	190	9.12	4.50	0.197	14.5
%RSD	8.2	1.7	3.0	1.8	5.2	1.0	1.1	0.9	5.7	1.7	1.6
BR1											
Mean, $n = 3$	0.535	0.083	51.1	2.58	2.28	771	148	7.80	17.7	0.303	18.0
%RSD	13.2	1.3	3.4	2.4	2.6	2.3	3.3	1.5	4.6	3.6	1.1
BR2											
Mean, $n = 3$	0.491	0.093	57.9	2.23	1.74	760	129	8.01	26.9	0.364	12.0
%RSD	1.0	1.1	4.8	3.1	4.0	3.0	3.1	1.7	1.5	3.8	1.7
JR1											
Mean, $n = 3$	0.317	0.335	38.7	1.75	0.907	581	96.4	9.65	8.43	0.156	12.5
%RSD	14.3	0.8	1.8	2.9	2.0	0.9	2.6	2.3	1.9	1.3	2.7
JR2											
Mean, $n = 3$	0.276	0.342	40.5	1.62	1.57	557	136	9.21	8.28	0.137	13.8
%RSD	1.1	5.6	3.5	4.9	0.6	1.8	3.7	1.4	3.0	1.5	2.9
PBR1											
Mean, $n = 3$	0.316	0.092	52.7	2.52	3.35	1970	424	15.6	5.32	0.136	10.1
%RSD	2.5	2.2	4.7	3.6	2.7	1.0	1.9	4.5	3.8	2.2	4.0
PBR2											
Mean, $n = 3$	0.344	0.132	11.2	2.73	1.21	1620	180	1.97	6.81	0.092	3.99
%RSD	1.2	0.8	0.9	4.4	2.5	1.2	2.8	3.6	4.7	8.7	1.0
RR1											
Mean, $n = 3$	0.560	2.64	93.6	3.01	8.17	2350	756	23.9	14.2	0.526	19.9
%RSD	0.9	2.3	1.3	0.7	2.6	2.1	1.2	1.7	2.1	0.6	1.5
RR2											
Mean, $n = 3$	0.395	2.66	103	3.01	7.79	2400	769	31.1	11.0	0.571	20.6
%RSD	5.1	0.8	1.0	4.7	1.8	0.8	1.3	1.3	2.7	1.4	1.5

Table 3 (*Contd.*)

	Al	Ba	Ca	Cu	Fe	K	Mg	Mn	Na	Sr	Zn
RR2 subjected to WD											
Mean, $n = 3$	0.405	2.58	104	3.08	7.68	2440	760	31.4	11.2	0.566	20.4
%RSD	9.1	2.8	2.1	5.8	4.7	2.0	3.2	1.9	5.4	4.1	3.9
$F_{calculated}$	2.72	12.96	6.25	1.65	3.59	6.25	5.76	2.25	4.00	7.62	7.11
$F_{critical}$	19.00	19.00	19.00	19.00	19.00	19.00	19.00	19.00	19.00	19.00	19.00
$t_{calculated}$	−0.449	+1.854	−0.775	−0.532	+0.493	−1.285	+0.600	−0.721	−0.516	+0.350	+0.405
$t_{critical}$	2.776	2.776	2.776	2.776	2.776	2.776	2.776	2.776	2.776	2.776	2.776
Max. mean	3.52	2.66	500	3.01	8.17	2400	769	31.1	26.9	0.571	20.6
Min. mean	0.254	0.083	11.2	1.47	0.738	557	96.4	1.97	3.62	0.092	3.99
Average	0.625	0.586	85.4	2.28	2.68	1180	277	11.8	10.2	0.264	13.8
%CV	140	158	149	24	92	60	86	65	66	61	34
Max. %RSD	14.3	5.6	4.8	4.9	7.0	3.0	3.7	4.5	5.7	8.7	4.0
Min. %RSD	0.9	0.8	0.9	0.7	0.6	0.8	1.1	0.8	1.4	0.6	1.0

[a] RSD: the relative standard deviation. $F_{critical}$: the critical value of the *F*-test at $\alpha = 0.05$, *i.e.*, $F_{critical}\,(df_1 = 2, df_2 = 2) = 19.00$. $t_{critical}$: the critical value of the *t*-test at $\alpha = 0.05$, *i.e.*, $t_{critical}\,(df = 4) = 2.776$. [b] Since the $F_{calculated}$ value was higher than the $F_{critical}$ value, the *C*-test was applied. [c] The critical value ($C_{critical}$) of the *C*-test was calculated.

concentrations of Ba and Sr were responsible for 5 such pairs. In addition, RR was established to be the most distinguishable due to the concentration of the studied elements out of all types of rice compared. In this case, 26 differences between RR and other types of rice were found due to the content of the selected elements, *i.e.*, Ba, Fe, K, Mg, Mn, Na, Sr and Zn.

4. Conclusions

This work provides a new analytical method suitable for the multielement analysis of rice by ICP OES. The Box–Behnken response surface design of experiments was carried out, and the obtained multiresponse was optimized by means of desirability functions and the overall desirability. This enabled the development of an alternative to the WD sample pretreatment procedure, being part of this method. The proposed USAE of the rice samples before the ICP OES analysis of their prepared sample solutions is fast and very simple. It does not require any advanced decomposition/mineralization equipment except for an ultrasonic bath and allows disposable tubes/containers to be used. As such, it is much cheaper to operate and more suitable for routine analysis of rice samples. The validated ICP OES method with the sample preparation by the USAE procedure, with the trueness being ±8% as the relative error, and the precision changing within 1–14% as the RSD, was applied for the convenient determination of Al, Ba, Ca, Cu, Fe, K, Mg, Mn, Na, Sr and Zn in different rice samples (white, basmati, jasmine, parboiled and red).

Author contributions

P. Pohl: conceptualization, methodology, formal analysis, writing – original draft, writing – review and editing. K. Greda: experimental design, formal analysis, writing – review and editing. M. Welna: investigation, validation, writing – review and editing. P. Jamroz: formal analysis, writing – review and editing. A. Dzimitrowicz: visualization, writing – review and editing. A. Szymczycha-Madeja: investigation, validation, writing – review and editing.

Conflicts of interest

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

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