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## ORIGINAL ARTICLE

# Rapid method of element determination in rye crispbread by ICP OES

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## KEYWORDS

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**Abstract** In this work, various sample preparation procedures, i.e., microwave-assisted acid digestion in a mixture of HNO<sub>3</sub> and H<sub>2</sub>O<sub>2</sub> solutions, solubilisation in *aqua regia* or tetramethyl ammonium hydroxide and extraction in diluted HNO<sub>3</sub> or in HCl, for the determination of the total content of Ba, Ca, Cd, Cr, Cu, Fe, Mg, Mn, Ni, P, Pb, Sr and Zn in rye crispbread using inductively coupled plasma optical emission spectrometry were compared. Analytical characteristic was evaluated by comparing the accuracy and precision of the results and limits of detection of elements. Among these five procedures solubilisation in *aqua regia* provides the best results, i.e., limits of detection of elements within 0.12–31.4 ng mL<sup>-1</sup>, precision of 0.4–5% and accuracy better than 5%. Additionally, a good agreement between the measured and certified values of the NIST 1567a was found for all elements. The proposed procedure is simple, reduces sample handling and minimises time and reagent consumption. Thus, it can be alternatively used instead of microwave-assisted acid digestion for routine analysis. Six different rye crispbreads were analysed with this procedure.

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## 1. Introduction

Bread is an essential food in human nutrition. It is the most important product of grain in our diet and the main component at the base of the pyramid proper nutrition. Bread is made of 80% of all cereals produced and is an important source of energy and building block. The unique role of bread

in human nutrition results from three basic factors such as high share of starch, presence of nutrients, i.e., carbohydrates, fats with a high content of unsaturated fatty acids, proteins and presence of numerous flavouring substances. In addition, bread is a great source of vitamins (group B and E), minerals, antioxidants and contains tolerable dietary fibres which are essential in our diet (Van Dokkum et al., 1989). Moreover, the elemental composition of this food product is reflected by the type of flour used for making bread, and different substances added during its production, e.g., water, salt, yeast (Chaoui et al., 2006; Dewettinck et al., 2008).

In recent years growing interest in the consumption of crispbread has been observed. This type of bread has three times less calories compared to white bread produced from wheat flour and can be stored for several months due to low

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content of water. The knowledge about mineral contents of crispbread is of great importance, since the popularity of these food products is increasing rapidly. Therefore, determination of total concentrations of elements in crispbread enables one to assess its nutritive quality and also helps to judge its possible ill-effects that may be caused to human health. Assessment of total concentrations of elements in different bread samples is primarily performed using spectrochemical methods such as flame atomic absorption spectrometry (FAAS) (Al-Mussali and Al-Gahri, 2009; Demirözü et al., 2003; Hussein and Bruggeman, 1997; Khaniki, 2005; Winiarska-Mieczan and Kwiecień, 2011), electrothermal atomic absorption spectrometry (ET AAS) (Demirözü et al., 2003; Gawalko et al., 1997; Jalbani et al., 2007), inductively coupled plasma optical emission spectrometry (ICP OES) (Gülfe, 2012; Isserliyska et al., 2001) or inductively coupled plasma mass spectrometry (ICP MS) (Khouzam et al., 2011, 2012; Nardi et al., 2009). Unfortunately, samples of crispbread for atomic spectrometry measurements have to be in the form of aqueous solutions, and therefore initially prepared, i.e., brought into solution form by appropriate digestion and/or dissolution treatments. Typically, decomposition of the matrix of bread samples is carried out by a conventional hot-plate or microwave-assisted heating of bread samples with oxidising reagents, including  $\text{HNO}_3$ ,  $\text{HNO}_3 + \text{H}_2\text{O}_2$ ,  $\text{HNO}_3 + \text{HClO}_4$  (Al-Mussali and Al-Gahri, 2009; Isserliyska et al., 2001; Jalbani et al., 2007; Khouzam et al., 2011, 2012; Nardi et al., 2009). Except for the mentioned wet acid digestion procedures, dry-ashing procedures are also used at the stage of the sample preparation of bread before its spectrochemical analysis (Demirözü et al., 2003; Winiarska-Mieczan and Kwiecień, 2011). Unfortunately, although effective, the total wet or dry digestion is time-consuming, requires the use of large amounts of concentrated reagents and can lead to loss of analytes and/or contamination of samples. Hence, it is worth examining whether simpler alternative approaches to sample preparation, considerably diminishing the time of sample treatment and eliminating all inconveniences of the digestion step, would find application in this type of analysis.

The main goal of this work was to compare various sample preparation procedures and develop a rapid, precise and accurate method for the multi-elemental analysis of rye crispbreads by ICP OES. To the best knowledge, the present work reports for the first time results of the analysis of such products referred to their mineral composition (macro-, micro- and trace-elements) as well as the comparison of several alternative sample preparation procedures of rye crispbread samples, i.e., solubilisation in *aqua regia*, tetramethyl ammonium hydroxide (TMAH), extraction in  $\text{HNO}_3$  or  $\text{HCl}$ , prior to their analysis by ICP OES on the content of 13 elements, i.e., Ba, Ca, Cd, Cr, Cu, Fe, Mg, Mn, Ni, P, Pb, Sr and Zn. The selected procedure was applied for the analysis of six different rye crispbreads.

## 2. Experimental

### 2.1. Samples

Six rye crispbreads (*Chaber*, *Finn Crisp*, *Granex*, *Rymut*, *Ryvita* and *Wasa*) were purchased in a local market (Wroclaw, Poland). Prior to analysis, the rye crispbreads were mixed

and ground in an agate mortar. The particle size of ground samples was within 200–500  $\mu\text{m}$ . Samples were stored in polyethylene containers.

### 2.2. Reagents

All chemicals were of analytical grade. Concentrated  $\text{HNO}_3$  (Merck, Darmstadt, Germany) and  $\text{HCl}$  (POCh, Gliwice, Poland) solutions, in addition to a 30% (m/v)  $\text{H}_2\text{O}_2$  solution (POCh) and tetramethyl ammonium hydroxide (TMAH) (Sigma–Aldrich, Germany) were used for sample preparation. Working standard solutions were prepared by dilutions of a multi-element (1000  $\mu\text{g mL}^{-1}$ ) ICP standard (Merck). De-ionised water (18.2  $\text{M}\Omega\text{ cm}$ ) was obtained from an EASYpure™ water purification system (Barnstead, Thermolyne Corporation, USA). Glassware and plastic bottles were cleaned with a 10% (v/v)  $\text{HNO}_3$  solution and rinsed several times with de-ionised water.

### 2.3. Apparatus

A radial inductively coupled plasma sequential spectrometer JY38S (Jobin Yvon, France) was used to measure total concentrations of Ba, Ca, Cd, Cr, Cu, Fe, Mg, Mn, Ni, P, Pb, Sr, Zn in all samples and blank solutions. Operating parameters were as follows: 1000 W of RF power, Ar (99.9999%) flow rates: 13  $\text{L min}^{-1}$  of a plasma gas, 0.2  $\text{L min}^{-1}$  of a sheath-gas and 0.25  $\text{L min}^{-1}$  of a carrier-gas. Solutions were introduced into the plasma torch using a Burgener (MiraMist) nebuliser and a cyclonic type spray chamber at a flow rate of 0.75  $\text{mL min}^{-1}$ . Analytical lines of Ba II 233.527 nm, Ca I 317.933 nm, Cd II 228.802 nm, Cr II 267.716 nm, Cu I 324.754 nm, Fe II 259.940 nm, Mg I 285.213 nm, Mn II 259.373 nm, Ni II 221.647 nm, P I 214.914 nm, Pb II 220.353 nm, Sr II 407.771 nm and Zn I 213.856 nm were measured.

A Milestone (Italy) high-pressure microwave digestion system (MLS-1200 MEGA), equipped with a rotor MDR 300/10, was used for the microwave-assisted sample decomposition. An Elpin (Poland) thermostatic water bath shaker (type 357) and a Polsonic (Poland) ultrasonic cleaning bath with controlled heating and exposition time (frequency: 40 kHz and power:  $2 \times 400$  W) were used for experiments in which samples of rye crispbread were treated with *aqua regia* and TMAH solutions. A MPW-350 centrifuge (MPW Med. Instruments, Poland) was used to accelerate the separation of liquid phases from solid particles.

### 2.4. Sample preparation procedures

The following sample preparation procedures were tested:

*Microwave-assisted digestion (P1)*: 0.5-g rye crispbread samples were weighed into Teflon digestion vessels, and 6 mL of a concentrated  $\text{HNO}_3$  solution with 1 mL of a 30%, (v/v)  $\text{H}_2\text{O}_2$  solution was added. Samples were subjected to microwave heating with a maximum power of 600 W for 43 min (step 1: 250 W, 4 min; step 2: 0 W, 5 min; step 3: 250 W, 6 min; step 4: 400 W, 5 min; step 5: 0 W, 5 min; step 6: 600 W, 4 min; step 7: 0 W, 5 min; step 8: 600 W, 4 min and step 9: 0 W, 5 min). After cooling, colourless sample solutions were quantitatively transferred into 25-mL volumetric flasks and made up to the volume with de-ionised water.

*Solubilisation in aqua regia (P2)*: 0.25-g rye crispbread samples were weighed into 30-mL polypropylene (PP) centrifuge tubes and 2 mL of *aqua regia* was added. Tubes were stoppered and resulting mixtures were sonicated in an ultrasonic bath for 15 min. Then, they were made up to 25 mL with de-ionised water and finally, the resulting sample solutions were centrifuged for 10 min at 14,006g. Supernatants were taken for determination of elements by ICP OES.

*Solubilisation in TMAH (P3)*: 0.25-g rye crispbread samples were weighed into 30-mL PP centrifuge tubes and 1.0 mL of a 25% (v/v) TMAH aqueous solution was added. Tubes were stoppered and resulting mixtures were sonicated in an ultrasonic bath for 30 min. Then 1 mL of concentrated  $\text{HNO}_3$  was added and tubes were shaken in water bath at 70 °C for 10 min. Afterwards, the solutions were cooled, made up to 25 mL with de-ionised water and then centrifuged for 10 min at 14,006g. Supernatants were taken for determination of elements by ICP OES.

*Extraction in  $\text{HNO}_3$  (P4)*: 0.25-g rye crispbread samples were weighted into 30-mL PP centrifuge tubes and 5 mL of a 3.0 mol  $\text{L}^{-1}$  (m/v)  $\text{HNO}_3$  solution was added. Tubes were stoppered and resulting mixtures were sonicated in an ultrasonic bath at 50 °C for 30 min. Then, mixtures were cooled, made up to 25 mL with de-ionised water and finally centrifuged for 10 min at 14,006g to remove any solid particles. Supernatants were taken for determination of elements by ICP OES.

*Extraction in HCl (P5)*: 0.25-g rye crispbread samples were weighted into 30-mL PP centrifuge tubes and 5 mL of a 3.0 mol  $\text{L}^{-1}$  (m/v) HCl solution was added. Tubes were stoppered and resulting mixtures were sonicated in an ultrasonic bath at 50 °C for 30 min, cooled, made up to 25 mL with de-ionised water and finally centrifuged for 10 min at 14,006g to remove any solid particles. Supernatants were taken for determination of elements by ICP OES.

The above procedures (P1–P5) were also applied for decomposition of the certified reference material (NIST 1567a-Wheat Flour). *Wasa* was used for comparison of different sample preparation procedures. For each sample preparation procedure tested (P1–P5), three parallel sample solutions were prepared in addition to respective blank solutions that were used to correct final results. Then, the chosen sample preparation procedure was applied to prepare other rye crispbread products before their analysis on the total concentration of 13 elements by ICP OES against the external calibration with simple working standard solutions. The sample of each rye crispbread brand was analysed in triplicate ( $n = 3$ ). Until analysis, sample solutions were kept at 4 °C.

### 2.5. Statistical methods

Statistical analysis of the obtained results was performed according to *t*-test at the 95% significance level. The degree of relationship between concentrations of elements in analysed rye crispbreads was evaluated by calculating Pearson's correlation coefficients (*r*) (Ellison et al., 2009).

## 3. Results and discussion

Analytical characteristics of the examined sample preparation procedures prior to element measurements by ICP OES were investigated. Accuracy was evaluated by comparing total concentrations

of elements in a certified reference material (NIST 1567a) obtained using different sample preparation procedures. Additionally, the recovery study was carried out. Precision of the procedure was determined as the relative standard deviation (RSD) for three independently prepared samples. Limits of detection (LODs) were calculated in the standard way (criterion  $3\sigma$ ) from the expression  $LOD = 3\sigma/a$ , where *a* is a slope related to sensitivity and  $\sigma$  means the standard deviation of the blank samples for 10 independent measurements.

### 3.1. Comparison of sample preparation procedures

#### 3.1.1. Accuracy

Accuracy was verified by comparing total concentrations of elements in a certified reference material (NIST 1567a). Accordingly the CRM was subjected to all sample preparation procedures. The comparison of the element determination in the CRM obtained by different sample preparation procedures was made using *t*-test at the 95% significance level of 4.303.

As it can be seen in Table 1, for all the examined elements a good agreement between obtained data after using microwave-assisted digestion (P1) and solubilisation in *aqua regia* (P2) and the certified values was observed. In the case of solubilisation in TMAH (P3) for elements such as Cd, Cu, Mg, Mn and Zn also values comparable to certified ones were received. For these elements differences in concentrations (measured and certified) were found to be within the limits of standard deviation uncertainty. Furthermore, the lack of differences between the compared values of the *t*-test ( $t_{calculated} < t_{critical}$ ) suggests that microwave-assisted acid digestion (P1) and solubilisation in *aqua regia* (P2) provide comparable results, although procedure 2 is much faster, easier and enables accurate determination of concentrations of studied elements. For the two remaining methods (P4 and P5) a lowering of the content of the majority of elements can be observed. Differences between concentrations of elements determined in sample solutions obtained after application procedures P4 and P5 are statistically significant, i.e., values of the calculated parameter *t* are higher at the critical value. Only in the case of Cu after application extraction in  $\text{HNO}_3$  (P4) statistically insignificant difference was obtained.

Additionally, the accuracy of all tested sample preparation procedures was also evaluated by the recovery test. For this purpose, samples of *Wasa* rye crispbread were spiked with known amounts of examined elements at two concentrations (0.5 and 1.0  $\mu\text{g mL}^{-1}$ ) and prepared with all tested procedures. It was established, that independently of the spiked levels, recoveries of all elements are in the range of 97.0–106% (P1), 99.1–103% (P2), 95.7–110% (P3), 76.6–117% (P4) and 74.7–114% (P5). As it can be seen, the results achieved for the two procedures, i.e., microwave-assisted acid digestion (P1) and solubilisation in *aqua regia* (P2) lead to practically quantitative recovery of all elements studied. Also, for these procedures, slopes of curves from standard additions and external calibrations were comparable, hence, it can be concluded that matrix effects are not observed in practice. The recovery results obtained for solubilisation in TMAH (P3), similarly to the previous results obtained for the CRM, provide quantitative recoveries only for some elements, i.e., Cd, Cr, Cu, Mg, Mn, Pb and Zn. Recoveries for extraction in  $\text{HNO}_3$  (P4) or in HCl (P5) indicate that they are not suitable for direct multi-element analysis by ICP-OES.

**Table 1** Concentrations (in  $\mu\text{g g}^{-1}$ ,  $n = 3$ ) of elements determined by ICP OES in a certified reference material (White Flour) prepared using different sample preparation procedures: microwave-assisted digestion in  $\text{HNO}_3$  with  $\text{H}_2\text{O}_2$  (P1), solubilisation in *aqua regia* (P2) and TMAH (P3), extraction in  $\text{HNO}_3$  (P4) and HCl (P5).

	Certified value		Experimental value					$t_{\text{calculated}}^{\text{c}}$				
	P1	P2	P1	P2	P3	P4	P5	P1	P2	P3	P4	P5
Ca	191 ± 4	188 ± 3	193 ± 3	111 ± 11	373 ± 36	< LOD <sup>b</sup>	65.1 ± 6.9	1.732	1.155	8.756	12.60	31.60
Cd	0.026 ± 0.002	0.024 ± 0.001	0.029 ± 0.003	0.041 ± 0.008	0.041 ± 0.003	0.041 ± 0.008	0.092 ± 0.021	3.464	1.732	3.248	–	5.444
Cu	2.10 ± 0.20	2.11 ± 0.06	2.10 ± 0.05	2.37 ± 0.11	2.37 ± 0.11	2.37 ± 0.11	1.49 ± 0.10	0.289	0.000	4.251	3.233	10.56
Fe	14.1 ± 0.5	14.2 ± 0.4	14.0 ± 0.3	12.7 ± 0.4	12.7 ± 0.4	12.7 ± 0.4	6.54 ± 0.42	0.433	0.577	6.062	18.71	31.18
Mg	400 ± 20	393 ± 14	396 ± 9	409 ± 13	409 ± 13	409 ± 13	235 ± 13	0.866	0.770	1.199	11.82	21.98
Mn	9.40 ± 0.90	9.50 ± 0.29	9.40 ± 0.44	9.74 ± 0.54	9.74 ± 0.54	9.74 ± 0.54	6.40 ± 0.44	0.597	0.000	1.091	5.484	11.81
P	1340 ± 60	1336 ± 32	1350 ± 15	1540 ± 55	1540 ± 55	1540 ± 55	850 ± 56	0.216	–	6.300	–	–
Pb	0.020 <sup>a</sup>	3.36 ± 0.14	3.32 ± 0.16	3.61 ± 0.20	3.61 ± 0.20	3.61 ± 0.20	< LOD <sup>b</sup>	–	–	–	–	–
Zn	11.6 ± 0.4	11.5 ± 0.2	11.5 ± 0.4	11.9 ± 0.7	11.9 ± 0.7	11.9 ± 0.7	7.77 ± 0.36	0.866	0.433	0.742	11.57	18.43

<sup>a</sup> Information value.

<sup>b</sup> Below the limit of detection.

<sup>c</sup> Critical value of  $t$ -test ( $t_{\text{critical}}$ ): 4.303 ( $p = 0.05$ ,  $n = 3$ ).

### 3.1.2. Limits of detection

Limits of detection (LODs) of elements for the five tested sample preparation procedures are listed in Table 2. As can be seen, the LODs for most of the elements (e.g. Ba, Cd, Fe, Mn, P, Pb and Zn) using solubilisation in *aqua regia* (P2) are approximately similar to those obtained for microwave-assisted acid digestion (P1). In the case of Ca, Cr, Cu, Ni and Sr LOD values are lower for procedure 2 (P2) compared to those for procedure 1 (P1), with the exception of Mg whose LOD value is higher for solubilisation in *aqua regia* (P2). Microwave-assisted digestion (P1), solubilisation in TMAH (P3) and extraction in  $\text{HNO}_3$  (P4) or in HCl (P5) show comparable LOD value for elements such as Ca, Cd, Cu, Sr (P3), Ba, Ca, Cd, Cu, Ni, P, Pb (P4) and Ba, Sr (P5). Detection limits for Fe, Mg, Mn, Zn (P3, P4, P5), Ba, P, Pb (P3), Cr, Sr (P4) and Ca, Cd, Cu, Ni, P (P5) are higher to those determined using microwave-assisted digestion (P1). In general, the detectability of procedure 2 (solubilisation in *aqua regia*) is considered satisfactory for alternative methods of analysis of rye crispbreads.

### 3.1.3. Precision

Total concentrations of elements (arithmetic mean with RSD values) determined by ICP OES in *Wasa* rye crispbread samples prepared using different sample preparation procedures are shown in Table 3. As it can be seen, the precision of concentrations of all elements obtained after the use of microwave-assisted acid digestion (P1) and solubilisation in *aqua regia* (P2) was comparable. RSD values vary from 0.6% to 5.6% and from 0.4% to 5.0% for procedures 1 and 2, respectively. The only exception is Ni (procedure 1) for which a much higher RSD value was observed. In the case of solubilisation in TMAH (P3), RSD values were below 5% for 5 out of 13 elements determined, i.e., Ba, Cu, Fe, Mg and Zn. For elements such as Fe, Mn, Zn (P4) and Ba, Fe, Mn, Zn (P5) a high precision (RSD < 5%) was obtained. Finally, the precision of the determination of elements using solubilisation in TMAH (P3), extraction in  $\text{HNO}_3$  (P4) or  $\text{H}_2\text{O}$  (P5) procedures is much lower than that achieved by the usage of *aqua regia* based procedure (P2). Accordingly, RSD values up to 15%, 13% and 20% for P3, P4 and P5 procedures were found, respectively. It was found that the results observed for CRM, in reference to precision followed the same regularities as observed for bread.

Additionally, concentrations of the elements obtained after application of different sample preparation procedures were compared to those resulting from microwave-assisted acid digestion (P1) using  $t$ -test at the 95% level of significance. Differences between results obtained using reference procedure (P1) and those achieved using the second procedure (P2) are statistically insignificant. In this case, the values of the calculated parameter  $t$  are lower than the critical value of this test which is equal to 4.303. Procedure 3 can be used alternatively instead of procedure 1, however only for selected elements, i.e., Cd, Cr, Cu, Mg, Mn, Pb and Zn. For these elements differences between their concentrations determined in sample solutions resulting from the microwave-assisted acid digestion (P1) and the solubilisation in TMAH (P3) are also statistically insignificant. For the two remaining procedures (P4 and P5), a significant decrease in the content of most elements can be observed. These sample preparation procedures were found to be not suitable for proper determination of the studied



elements and could lead to analytical errors during analysis. These results are confirmed with those obtained for the certified reference materials analysed by various sample preparation procedures.

### 3.2. Application to the analysis of rye crispbread products

Considering the analytical characteristic of sample preparation procedures (in terms of accuracy, limit of detection and precision), solubilisation in *aqua regia* (P2) was found to be the most suitable prior to multi-element analysis of rye crispbread products by ICP OES. This procedure was demonstrated to be a much faster, straightforward and more precise alternative to wet digestion procedures. Concentrations of 13 elements (in  $\mu\text{g g}^{-1}$ ) were determined in six different rye crispbread prepared with the aid of solubilisation in *aqua regia* (P2) and results of this analysis are presented in Table 4. They are mean values for three replicates ( $n = 3$ ) with RSDs.

In all cases, the precision is good and varies from 0.4% (for Sr in *Wasa*) to 5.0% (for Ni also in *Wasa*). In general, the highest concentrations of elements were found in *Finn Crisp* (Cr, Cu, Fe, Mg) and *Wasa* (Ba, P, Pb, Zn). In contrast, the lowest contents of elements were found in *Ryvita* (Ba, Cr, Mg, Mn, Zn) and *Chaber* (Ca, Ni, P, Sr). Concentration of Cd in *Finn Crisp* and *Ryvita* is below its LOD.

As it can be seen, Ca, Mg and P are the major mineral constituents of rye crispbreads. Concentrations of macro-elements increased in the order: Ca < Mg < P. The level of Mg is about two times higher than that of Ca, except for *Granex* for which a different relation is noticed (Ca > Mg). The highest content of these elements were detected in *Granex* (Ca), *Finn Crisp* (Mg) and *Wasa* (P), and the lowest concentrations were found in *Chaber* (Ca and P) and *Ryvita* (Mg). The concentration of P is 4 times higher than that of Mg and is from 3 (*Granex*) up to 8 times higher (*Chaber*, *Finn Crisp*) than that of Ca. The results measured for Ca are in accordance with those published by Zhao et al. (2013), who determined that the Ca contents of wheat grains ranged from 359 to 638  $\mu\text{g g}^{-1}$ . Concentrations of Mg are higher than those obtained by Nardi

et al. (2009), but significantly lower than those determined by Zhao et al. (2013).

Concentrations of the trace essential elements (i.e. Cu, Fe, Mn, and Zn) can be arranged as follows: Cu < Zn < Mn < Fe in *Rymut* and *Ryvita*, Cu < Mn < Fe < Zn in *Granex* and *Wasa*, Cu < Fe < Zn < Mn in *Chaber* and Cu < Mn < Zn < Fe in the case of *Finn Crisp*. The content of Cu is significantly reduced (3.12–4.28  $\mu\text{g g}^{-1}$ ) and is about 1 order of magnitude lower than those of Fe (27.4–39.5  $\mu\text{g g}^{-1}$ ), Mn (21.7–36.8  $\mu\text{g g}^{-1}$ ) and Zn (21.1–39.8  $\mu\text{g g}^{-1}$ ).

Results for Cu presented in this study are generally comparable to those determined in Lebanese bread (Khouzam et al., 2012) and cereals (Tokalioğlu and Gürbüz, 2010). Nardi et al. (2009) reported a lower Cu value for bread (1.9  $\mu\text{g g}^{-1}$ ) and wheat samples (0.92  $\mu\text{g g}^{-1}$ ), but Demirözü et al. (2003) obtained mean concentrations of this element in bakeries which are much higher (22.1  $\mu\text{g g}^{-1}$ ). Contents of Fe in rye crispbreads are very similar to those obtained by Khouzam et al. (2012), but higher than those reported by Demirözü et al. (2003) and Khouzam et al. (2011). Tokalioğlu and Gürbüz (2010) established that the concentrations of Fe in Turkish cereals were within 7.48–34.3  $\mu\text{g g}^{-1}$ . Khouzam et al. (2012) reported the range of Mn and Zn concentrations in Lebanese bread as 7.5–58.7 and 8.2–40.9  $\mu\text{g g}^{-1}$ , respectively.

Concentrations of non-essential elements, i.e., Ba and Sr, are relatively low (1.38–2.67  $\mu\text{g g}^{-1}$  and 1.05–2.80  $\mu\text{g g}^{-1}$ , respectively). The contents of Sr were slightly higher than those obtained by Nardi et al. (2009) for bread and wheat samples, but significantly lower than those reported by Zhao et al. (2013) for wheat grains. In the case of Pb, its concentrations are high and vary between 1.10 and 4.27  $\mu\text{g g}^{-1}$ . The level of Pb in rye crispbreads is generally significantly higher than that published in the relevant literature (Cuadrado et al., 2000; Demirözü et al., 2003; Khouzam et al., 2011, 2012; Zhao et al., 2013). Considering the Commission regulation (EC, 2006), the maximum permissible level of Pb is 0.20  $\mu\text{g g}^{-1}$  for cereals and pulses. Concentrations of Cr and Ni are very low and within the following ranges 0.220–0.959  $\mu\text{g g}^{-1}$  (Cr) and 0.214–0.489  $\mu\text{g g}^{-1}$  (Ni). Zhao et al. (2013) determined much higher Cr contents in wheat (3.38–6.49  $\mu\text{g g}^{-1}$ ). Contents of Ni found in this work are consistent with the findings of Khouzam et al. (2012). Cd was determined in *Chaber*, *Granex*, *Rymut* and *Wasa* rye crispbread. The obtained results for Cd are higher than those previously reported by Demirözü et al. (2003) and Cuadrado et al. (2000), but in quite a good agreement with those observed by Zhao et al. (2013).

Differences in the analysed sample could have several reasons such as source of cereals, geographic area, nature of soil in the place of constituent cultivation and different production processing.

The degree of relationship between concentrations of elements in analysed rye crispbreads was evaluated by calculating Pearson's correlation coefficients ( $r$ ). It was found that there is a very highly positive correlation ( $r > 0.9$ ) between concentrations of Ca–Sr and Cr–Cu. A highly positive correlation ( $r = 0.7$ – $0.9$ ) was observed for concentrations of the following pairs of elements: Ba–Cd, Ba–Pb, Ba–Zn, Cd–Mg, Cr–Mg, Cr–P, Cr–Zn, Cu–Mg, Cu–P, Mg–P and a negative correlation only for one pair: Mn–Ni. For other couples of elements, positive or negative correlations were shown and they are moderate ( $r \pm 0.4$  to  $\pm 0.7$ ), low ( $r \pm 0.2$  to  $\pm 0.4$ ) or almost negligible ( $r$  0 to  $\pm 0.2$ ).

**Table 2** Limits of detection (in  $\text{ng mL}^{-1}$ ) of elements by ICP OES with different sample preparation procedures: microwave-assisted digestion in  $\text{HNO}_3$  with  $\text{H}_2\text{O}_2$  (P1), solubilisation in *aqua regia* (P2) and TMAH (P3), extraction in  $\text{HNO}_3$  (P4) and HCl (P5).

	P1	P2	P3	P4	P5
Ba	1.35	1.20	1.68	1.38	1.39
Ca	9.65	6.80	11.1	11.7	17.0
Cd	1.43	1.26	1.48	1.50	2.03
Cr	1.72	0.87	1.46	1.95	1.38
Cu	1.36	0.97	1.16	1.23	1.66
Fe	1.36	1.35	3.49	2.69	3.08
Mg	1.70	2.01	2.67	3.32	2.38
Mn	0.28	0.22	0.46	0.38	0.54
Ni	4.34	2.82	3.26	4.15	6.34
P	129	126	183	143	150
Pb	31.1	31.4	55.3	36.9	36.7
Sr	0.16	0.12	0.20	0.26	0.15
Zn	0.79	0.69	1.09	1.26	1.06

**Table 3** Concentrations (in  $\mu\text{g g}^{-1}$ ) of elements determined by ICP OES in *Wasa* rye crispbread prepared using different sample preparation procedures: microwave-assisted digestion in  $\text{HNO}_3$  with  $\text{H}_2\text{O}_2$  (P1), solubilisation in *aqua regia* (P2) and TMAH (P3), extraction in  $\text{HNO}_3$  (P4) and HCl (P5).

	P1	P2	P3	P4	P5
Ba	2.65 (3.4)	2.67 (2.3)	3.22 (3.8)	2.10 (5.5)	1.57 (3.9)
Ca	715 (2.5)	720 (2.4)	922 (6.2)	177 (6.1)	44.6 (11)
Cd	0.149 (3.5)	0.151 (3.1)	0.181 (12)	0.155 (13)	0.105 (14)
Cr	0.790 (4.0)	0.797 (2.1)	0.798 (15)	0.498 (13)	0.640 (20)
Cu	3.92 (4.2)	3.90 (3.8)	3.94 (4.5)	4.29 (7.2)	2.79 (8.3)
Fe	27.4 (0.80)	27.4 (0.60)	29.6 (1.1)	22.2 (2.3)	20.8 (3.2)
Mg	1006 (1.8)	1013 (2.0)	1060 (4.1)	820(7.6)	797 (7.9)
Mn	24.4 (0.60)	24.2 (0.50)	24.1 (0.60)	22.0 (2.9)	21.4 (3.1)
Ni	0.483 (11)	0.489 (5.0)	1.23 (12)	< LOD <sup>a</sup>	< LOD <sup>a</sup>
P	4535 (2.1)	4560 (1.8)	3950 (5.4)	3865 (5.5)	3680 (6.1)
Pb	4.30 (5.6)	4.27 (4.6)	4.35 (6.2)	< LOD <sup>a</sup>	< LOD <sup>a</sup>
Sr	2.84 (3.0)	2.80 (0.40)	4.19 (6.0)	2.24 (5.3)	2.13 (5.2)
Zn	40.0 (2.4)	39.8 (1.8)	41.6 (2.3)	35.6 (3.0)	34.4 (2.7)
Digestion quality	Clear, colourless solution without undissolved residues	Clear, colourless solution with a small amount of undissolved residues	Greenish solution with a large amount of undissolved residues	Yellow solution with undissolved residues	Yellow solution with undissolved residues

Average values ( $n = 3$ ) with relative standard of deviation (RSD) in brackets.

<sup>a</sup> Below the limit of detection.

**Table 4** Concentrations of elements in analysed rye crispbreads.

	Concentration, $\mu\text{g g}^{-1}$					
	Chaber	Finn Crisp	Granex	Rymut	Ryvita	Wasa
Ba	1.90 (1.7)	1.74 (1.3)	1.58 (2.5)	2.16 (1.9)	1.38 (3.3)	2.67 (2.3)
Ca	371 (2.2)	520 (2.8)	1065 (4.1)	580 (1.9)	555 (1.8)	720 (2.4)
Cd	0.110 (3.6)	< LOD <sup>a</sup>	0.036 (4.8)	0.166 (4.4)	< LOD <sup>a</sup>	0.151 (3.1)
Cr	0.314 (3.5)	0.959 (2.4)	0.257 (3.5)	0.365 (2.4)	0.220 (2.9)	0.797 (2.1)
Cu	3.43 (1.4)	4.28 (3.0)	3.12 (1.2)	3.37 (3.7)	3.31 (4.0)	3.90 (3.8)
Fe	29.1 (2.6)	39.5 (2.1)	31.1 (2.8)	37.9 (2.9)	28.9 (1.6)	27.4 (0.6)
Mg	877 (1.3)	1055 (1.0)	895 (1.6)	1035 (2.8)	859 (3.4)	1013 (2.0)
Mn	36.8 (2.9)	32.2 (3.7)	29.2 (1.6)	35.7 (1.1)	21.7 (1.3)	24.2 (0.5)
Ni	0.214 (1.2)	0.368 (2.1)	0.367 (2.4)	0.379 (2.1)	0.521 (3.2)	0.489 (5.0)
P	2934 (1.4)	4210 (1.6)	3180 (1.5)	3705 (1.7)	3570 (2.6)	4560 (1.8)
Pb	1.70 (1.9)	1.18 (3.3)	1.77 (4.1)	1.10 (3.6)	1.26 (3.9)	4.27 (4.6)
Sr	1.05 (1.5)	1.89 (1.7)	4.23 (1.5)	1.29 (1.6)	1.48 (1.5)	2.80 (0.4)
Zn	29.8 (2.3)	34.9 (3.0)	31.5 (2.5)	30.1 (2.2)	21.1 (3.6)	39.8 (1.8)

Average values ( $n = 3$ ) with relative standard of deviations (RSDs) in brackets.

<sup>a</sup> Below the limit of detection.

#### 4. Conclusion

This work demonstrates for the first time the comparison of various sample preparation procedures (conventional and alternative) and their applicability for the determination of total concentrations of 13 elements by ICP OES in crispbreads. The sample preparation procedures developed based on partial decomposition in *aqua regia* are easy, time-saving, give good results, reproducible, dependable, reliable for determination of total concentrations of Ba, Ca, Cd, Cr, Cu, Fe, Mg, Mn, Ni, P, Pb, Sr and Zn. Additionally, the results with the proposed procedure were comparable to those obtained using the usual method of sample preparation by digestion in the

mixture of concentrated  $\text{HNO}_3/\text{H}_2\text{O}_2$ , and therefore can be recommended as an alternative approach to conventional sample treatment. Differences in these values evaluated using *t*-test at a confidence level of 95% were not statistically different. Moreover, this simple sample handling can be successfully used for routine analysis to perform the process of quality control of rye crispbread by ICP OES.

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