

Analytical, Nutritional and Clinical Methods

Elemental analysis of flour-based ready-oven foods by slurry sampling inductively coupled plasma optical emission spectrometry

Tomáš Černohorský^a, Anna Krejčová^{a,*}, Miloslav Pouzar^a, Lenka Vavrušová^b

^a Department of Environmental Protection, Faculty of Chemical Technology, University of Pardubice, nám. Čs. legií 565, CZ 532 10 Pardubice, Czech Republic

^b Department of Analytical Chemistry, Faculty of Chemical Technology, University of Pardubice, nám. Čs. legií 565, CZ 532 10 Pardubice, Czech Republic

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Abstract

A slurry sampling technique has been utilised for the determination of Na, K, Ca, Mg, S, P, Fe, Mn, Cu and Zn in wheat-flour and flour-based ready-oven foods using ICP-OES and a direct aqueous calibration technique. For 0.1% w/v suspension of flour in 0.1% w/v Triton X-100 and 6% v/v HNO₃, the procedural limits of detection (all in mg kg⁻¹) for Na, K, Mg, Ca, P, S, Fe, Zn, Mn and Cu were 7.51, 61.1, 0.645, 1.59, 5.25, 4.58, 1.50, 1.07, 0.867 and 1.58, respectively. The precision was expressed as the relative standard deviation (RSD) of 5–10% ($n = 10$) for 0.1% w/v suspension of wheat-flour. The accuracy was confirmed by the analysis of reference materials wheat-flour GBW 08503 and rice flour NIST 1568a.

The proposed method was applied to the analysis of two commercial samples of wheat-flour and four samples of flour-based ready-oven mixtures. The results have shown no significant differences when compared with those obtained after complete digestion of the samples analysed.

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1. Introduction

The accelerated rhythm of modern life and the increase of people living alone have determined changes in the preparation of food and in habits of consumption. In this consequence, the rapid progress of the ready-oven food technology and its products has to be mentioned. Dietary sources of essential elements important for correct physiological functions of human body are of permanent interest of food chemists. Reference daily intakes for 12 significant elements have been established: calcium (1000 mg), chloride (3400 mg), chromium (120 µg), copper (2 mg), iron (18 mg), iodine (150 µg), potassium (3500 mg), magnesium (400 mg), manganese (2 mg), molybdenum (75 µg), sodium

(2400 mg), phosphorus (1000 mg), selenium (70 µg) and zinc (15 mg) (Mindel, 2000). Wheat is one of cereals widely consumed in the human food all over the world. In the form of flour it is used for preparation of bread, cookies, pizzas, cakes and also ready-oven food. The knowledge of content of flour-based ready-oven food in the minerals is thus way important and a multi-element analysis method applicable to a variety of such kinds of foods and easy to use is significant from both a nutritional and a toxicological point of view.

Many techniques have been utilised for the elemental analysis of various matrices, including less common stripping voltammetry, X-ray fluorescence, neutron activation analysis, capillary zone electrophoresis or on the contrary wide extended flame atomic absorption spectrometry (F-AAS), graphite furnace spectrometry (GF-AAS), flame emission spectrometry and multi-element inductively

* Corresponding author. Tel.: +420 466 037 197; fax: +420 466 037 068.
E-mail address: anna.krejcov@upce.cz (A. Krejčová).

coupled plasma-emission spectrometry (ICP-OES) and inductively coupled plasma-mass spectrometry (ICP-MS) (Taylor, Branch, Day, Patriarca, & White, 2006). Sample preparation remains the major limiting step in analytical capacity. Dry ashing may take 2–3 days to prepare an analyzable solution. Conventional acid digestions are faster (3–4 h) than dry ashing but need a permanent operator attention. Microwave digestion is usually performed with nitric acid in a closed high-pressure vessel (at temperature above the boiling point of nitric acid) and is generally complete within 1 h (Dolan, Nortrup, Bolger, & Capar, 2003). Alternatively, a variety of analytical methods have been performed involving the direct analysis of solid or slurried samples. These methods bring clearly some advantages: simplification of sample pre-treatment, reduced risk of sample contamination, minimization of analyte losses during pre-treatment operations or due to incomplete release of the analyte from the solid matrix, and no hazardous or corrosive reagents are required. The slurry nebulisation involves the direct aspiration of suspended sample directly into an AAS or ICP-OES. Several attributes of slurries have been acknowledged as critical for the stability, homogeneity, transport and nebulisation efficiency – mainly the particle size, the slurry concentration and the use of dispersants (Ebdon, Foulkes, & Sutton, 1997).

ICP-OES and/or ICP-MS is widespread in multi-element analysis of micro- and macronutrient and toxic elements in food. In connection with size exclusion chromatography, ICP-OES and ICP-MS speciation analysis of Na, Mg, P, K, Ca, Mn, Fe, Co, Ni, Cu, Zn, Se and Mo species in samples of defatted soybean flour and extract of soybean flour were performed (Fingerová & Koplík, 1999). Liquid chromatography connected with ICP-MS was used for the speciation analysis of elements (P, Mn, Fe, Co, Ni, Cu, Zn, Mo) in semi coarse maize flour and wholemeal rye flour (Koplík et al., 2006). Dolan et al. (2003) have reported determination of As, Cd, Hg and Pb in dietary supplements product and NIST standard reference materials using microwave digestion and high-resolution ICP-MS. Black rice flour reference materials were analysed (Cr, Fe, Cd and Pb) after microwave digestion by isotope dilution ICP-MS (Park & Suh, 1997).

F-AAS and ICP-OES were used for evaluation of wheat-flour confectionery products (hard biscuits) as a source of Zn and Cu (Šebečić & Verdina-Dragojević, 2004). Analysis of trace elements in wheat samples from Serbian was carried out after decomposition using F-AAS (Fe and Zn) and GF-AAS (Pb, As, Cd, Cu and Mn) (Škrbić, Đurišić-Mladenović, & Cvejanov, 2005).

The elemental analysis of slurries was used for determination of Cd, Pb, Cu, Mn and Zn in biological and environmental samples (wheat-flour, spinach, etc.) by F-AAS (Jacob & Berndt, 2002) or for elemental analysis of biological samples (1% w/v in 1% aqueous Triton X-100) (Mochizuki, Sakashita, Iwata, Ishibashid, & Gunji, 1991). In connection with ICP-OES, the slurry technique was applied for analysis of milk powders (1% slurries with

addition of Triton X-100; the internal standard Lu) (McKinstry, Indyk, & Kim, 1999), powdered coffee and milk (Riberio, Moretto, Arruda, & Cadore, 2003), multi-vitamins preparations (0.1–0.2% w/v in 6% v/v HNO₃, with quantification incorporating standard slurries or the standard addition method) (Krejčová, Kahoun, Černohorský, & Pouzar, 2006) or biological reference materials (concentrations up to 1% w/v, particles < 20 μm, prepared in 10% HNO₃ containing 0.01% Triton X-100, the standard additions method) (Matusiewicz & Golik, 2004).

The best means of a slurry analysis is probably achieved using GF-AAS because the whole introduced sample is atomised. In F-AAS and ICP-OES, the residence time of particles in the flame or the plasma is very short and the sample evaporation–excitation–atomisation may be incomplete. On the other hand, for a monitoring of a group of many elements as in our case, GF-AAS is a too slow method.

González, Gallego, and Valcárcel (1998) applied the direct slurry sampling to the determination of Ni, Cr and Co in wheat-flour by GF-AAS (3% w/v slurry in 15% HNO₃ for the determination of Ni and 5% HNO₃ and 10% H₂O₂ were necessary for the determination of Co and Cr). Araujo, Macedo, dos Santos, and Ferreira (2006) have used slurry/F-AAS for the determination of manganese in wheat-flour as well as and recommended a sample concentration 1% w/v in 2.0 mol L⁻¹ nitric acid solution and a sonication time of 15 min.

This paper reports the development of an easy and convenient sample preparation for determination of Na, K, Ca, Mg, S, P, Fe, Mn, Cu and Zn in wheat-flour-based ready-oven mixtures followed by a slurry nebulization of slurried samples into ICP-OES using direct calibration with aqueous standards, with slurry standards or using standard addition method.

2. Materials and methods

2.1. Equipment

The measurements were carried out with the sequential, radially viewed ICP atomic emission spectrometer INTEGRA XL 2 (GBC, Dandenong Australia, <<http://www.gbcs.com>>), equipped with the ceramic V-groove nebulizer and the glass cyclonic spray chamber (both Glass expansion, Australia, <<http://www.geicp.com>>). Samples were crushed in an agate mortar and then grinded in the jet-mill (Sturtevant Inc, USA, <<http://www.sturtevantinc.com/>>). Particle size distribution of fine-powdered samples was determined by examining a suspension using Mastersizer 2000 (Malvern Instruments Ltd., United Kingdom, <<http://www.malvern.co.uk/>>). Homogenization of slurries was performed using an ultrasonic bath Power-sonic UCC 1 (Verkon, s.r.o., Czech Republic, <<http://www.verkon.cz/>>). Demineralised water was taken from the Milli-Q Plus water-purification system (Millipore, Bedford, USA, <<http://www.millipore.com/>>). The samples

were decomposed in the microwave decomposition apparatus BM 1 S/2 (Plazmatronika, Poznan, Poland, <<http://www.plazmatronika.pl/>>). Other equipment used included a magnetic stirrer and calibrated volumetric glassware.

2.2. Reagents and samples

The single component standards of Na, Mg, Ca, P and S (each one with the content of $10000 \pm 30 \mu\text{g mL}^{-1}$, CPI International, USA) and K, Fe, Mn, Ni, V and Zn ($1000 \pm 3 \mu\text{g mL}^{-1}$, CPI International, USA, <<http://www.cpiinternational.com>>) were used. For the slurry preparation and decomposition, Triton X-100 (Merck; <<http://www.merck.cz/>>), Spolostan 4 (Avas, spol.s.r.o., <<http://www.avas-concrete.com>>), sodium hexametaphosphate (Fosfa, a.s., <<http://www.fosfa.cz>>) and analytical grade (65% w/v) HNO_3 (Lachema, Czech Republic) were used.

Two brands of wheat-flour and four brands of ready-oven powdered mixtures were purchased in a supermarket. The samples, listed in Table 1, and the standard reference materials wheat-flour GBW 08503 and rice flour NIST 1568a were used for validation of the proposed methodology.

2.3. Standards preparation

Aqueous standards: Three multi-element standards were prepared: (i) containing K, P, S (100 mg L^{-1}), Ca, Mg (50 mg L^{-1}), Na, Zn, Fe (10 mg L^{-1}), Cu, Mn (2 mg L^{-1}), (ii) the standard (i) diluted two times and (iii) the standard (i) 10 times diluted. All these solutions were stabilised with 6 mL 65% w/v $\text{HNO}_3/100 \text{ mL}$ of solution, as well as the corresponding blank.

Standard slurries: (i) 0.1 and (ii) 0.2 g of the reference material wheat-flour GBW 08503 and 0.05 g Triton X-100 were accurately weighed into a 50 mL volumetric flask, 3 mL of HNO_3 and 15–25 mL of water was added and treated in an ultrasonic bath for 15 min. After cooling to room temperature, the standard slurries were completed to volume with water homogenized by sonication. The

water standard blank containing 6 mL $\text{HNO}_3/100 \text{ mL}$ was used.

Standard additions: 0.1 g of the reference material wheat-flour GBW 08503 and 0.05 g of Triton X-100 were accurately weighed into a 50 mL volumetric flask, and (i) 25, (ii) 10 and (iii) 5 mL of the most concentrated aqueous standard and the appropriate amount of HNO_3 was added (in total 6 mL $\text{HNO}_3/100 \text{ mL}$ of slurry) and treated in ultrasonic bath for 15 min. After cooling to a room temperature, the standard slurries were completed to volume with water and homogenized in the ultrasonic bath. The water standard blank containing 6 mL $\text{HNO}_3/100 \text{ mL}$ was used.

2.4. Sample preparation

Prior to analysis, samples were homogenized and decomposed. For the ICP-OES determination, both digests and slurries were prepared.

Microwave digestion: Approximately 0.3–0.5 g of a powder sample or a reference material was accurately weighed into an acid washed PTFE digestion tube. 6 mL of concentrated nitric acid (65% w/v) was added, and the tube was heated in a microwave oven at the power setting of 80% for 10 min and at 100% for 10 min. The maximum total output of the microwave generator was 700 W (minimum pressure = $24 \times 10^5 \text{ Pa}$, maximum pressure = $25 \times 10^5 \text{ Pa}$). The digest was transferred into a 100 mL acid washed volumetric flask, filled up with demineralised water and stored in polypropylene flasks. Two water blanks were run with each batch of samples which consist of six parallel decompositions.

The slurry preparation: About 0.1 g of powdered sample and 0.05 g of Triton X-100 was accurately weighed into an acid washed 50 mL volumetric flask, 6 mL of HNO_3 and 15–25 mL of water was added and treated in the ultrasonic bath for 15 min. After cooling to room temperature, the standard slurries were completed to volume with water and homogenized in the ultrasonic bath.

2.5. The ICP-OES method

Measurement conditions were optimised based on signal-to-background ratio of the least concentrated elements

Table 1
Powdered samples used in the study

Sample	Producer
Smooth flour	Ramill a.s., Praha, Czech Republic, < http://www.odkolek.cz/odkolek/ramill >
Wholemeal flour	Ramill a.s., Praha, Czech Republic, < http://www.odkolek.cz/odkolek/ramill >
Milky rice classic	Dr. Oetker s.r.o., Kladno, Czech Republic, < http://www.oetker.cz/ >
Dumplings	Amylon s.r.o., Havlíčkův Brod, Czech Republic, < http://www.amylon.cz >
Ginger bread	Labeta s.r.o., Pardubice, Czech Republic, < http://www.labeta.cz >
Pancake	Labeta s.r.o., Pardubice, Czech Republic, < http://www.labeta.cz >

Table 2
The optimised operating conditions for ICP-OES analysis with slurry sample introduction

Parameter	Value
RF power	1100 W
View height	8 mm
Gas	Argon 99.999%
Plasma gas	0.6 L min^{-1}
Auxilliary gas	10 L min^{-1}
Nebulizer gas	0.65 L min^{-1}
Sample aspiration rate	1.5 mL min^{-1}
Read	On-peak, 3 s
Background correction	Fixed point
Number of replicates	10

Table 3
Analytical characteristics of the method proposed

Parameter	λ (nm)	LOD (mg kg ⁻¹)	RSD (%)	Parameter	λ (nm)	LOD (mg kg ⁻¹)	RSD (%)
Na	588.995	7.51	7.22	S	180.781	4.58	7.31
K	769.896	61.1	8.13	Fe	259.940	1.50	8.23
Mg	285.213	0.645	5.12	Zn	213.856	1.07	7.69
Ca	393.366	1.59	4.89	Mn	257.610	0.867	8.63
P	178.284	5.25	5.89	Cu	324.754	1.58	8.78

(Cu, Mn). For aspirated solutions and slurries, the same measurement conditions (listed in Table 2) were used. The emission lines are listed in Table 3. Net analyte emission was based on taking the difference of measured emission intensity on the top of the peak and background near the peak. In case of the spectral line 178.284 nm of phosphorus, possible interference of Fe can occur. The concentration of 10 mg L⁻¹ Fe measured on that phosphorus lines did not produce any detectable phosphorus concentration readout. A higher iron concentration in digests and slurries was not expected.

In case of digests, aqueous standards were used. For slurries, aqueous standards, standard slurries and standard addition were used. During sample aspiration, slurries were agitated with a magnetic stirrer. After aspiration of each suspension, a 6% v/v nitric acid was flushed through the nebuliser-torch system to remove any residual sample. Including the washing time between slurries, the total time for analysis was approximately 5 min.

3. Results and discussion

3.1. Measurement conditions setting

The most concentrated aqueous standard was used in this study. Step by step, single operating parameters were changed to obtain a maximum net signal-to-background intensity ratio (SBR) of the least concentrated element Cu and Mn. The nebuliser argon gas flow rate, sample aspiration rate, plasma power and viewing height were optimised. The plasma gas flow and auxiliary gas flow rates were not optimised, but were selected based upon previous experience to ensure plasma stability. Apart from Cu and Mn, the other elements were presented in higher concentrations and it was possible to use compromise-working conditions. To investigate the effect of a presence of solid particles in plasma, the axial intensity profiles of analysed elements for solutions and standard suspensions of the reference material wheat-flour GBW 08503 were measured. It was found that the maximum of intensity for slurries tends to shift to higher observation heights. The highest SBR of Cu was reached with the viewing height 7 mm above coil and the forward power 1000 W for solutions and 8 mm and 1100 W for slurries. Because the sample weight used for preparation as well as element concentration, was higher in case of solution, only unified conditions – the best for Cu in slurries – were used for both solutions and slurries in further analysis.

The influence of sample aspiration rate on the signal intensity was followed. For the pumping rate greater than some 2 mL min⁻¹, the signal intensity did not increase, slurry nebulisation got worse apparently and a mass drained from the chamber increased. Therefore, a slurry and solution sample aspiration rate of 1.5 mL min⁻¹ was adopted.

3.2. Slurry composition

In order to achieve a good dispersion of powdered samples, various nitric and hydrochloric acid concentration and presence of additional substances were tested. The effect of both acids was very similar: from their low concentration, they improved wetting and dispersion of multivitamin powder. Finally in this study, HNO₃ was used in resultant concentration 6% v/v, because it was also employed as the mineralising agent for microwave digestion. Due to its oxidising properties and facilitation of element extraction, nitric acid is suitable for slurry preparation.

In case of particles smaller than 10 μ m, the presence of nitric acid only did not seem to be sufficient to achieve a good consistency of slurries. Tested Triton X-100 (0.01–0.5%) improved and shortened a process of slurry preparation in order to avoid a formation of sample agglomerates, which occurred especially for flours in the presence of acid only. A gradual solid phase deposition on spray chamber inner surface was also reduced. A visible sample deposition occurs after about two hours of continuous slurry aspiration. After aspiration of each slurry, 6% v/v HNO₃ was used for flushing through the nebuliser – spray chamber-torch system to remove such residuals. This results in a significant decrease of solid residue in the introduction system and no changes of the emission signal are observed during a long run. The addition of Spolostan 4 and/or sodium hexametaphosphate also improved the slurry consistency, but it impedes the determination of sulphur or phosphorus, respectively.

The concentration of the slurry is an important factor to consider before the analysis. For slurries less than 0.5% the signal intensity increased linearly with concentration. This was not the case for slurry concentrations greater than 0.8% approximately, where the mass drained from the chamber was probably increased. Routine analyses were consequently conducted with slurry concentrations of 0.1–0.2% that are sufficient for the determination of main, minor and trace elements in the kind of samples investigated.

For slurries analysis, a very significant parameter is the particles size that can decrease the recovery. Improved recoveries are likely to be the result of a more efficient evaporation of smaller particles in the plasma. Less homogenous samples dumplings and milk rice were crushed with an agate mortar. For this way of sample preparation, it was found that a median particle size of 100 μm resulted. Those pre-crushed samples and all samples remained were then grinded in the jet-mill for one hour. Particle size distribution of fine-powdered samples was determined by examining a suspension using Mastersizer 2000. For all samples, the mean diameter of particle was about 7–9 μm . After prolonged periods of grinding above 2 h, an agglomeration of small particles appeared, so grinding time of 1 h was adopted. For food materials, a more suitable grinding under cryogenic condition can be used; it is less time-consuming and also ensures particle sizes inferior to 10 μm in less than 10 min.

In order to evaporate, ionize and excite and atomise solid matrices efficiently, Ebdon et al. (1997) recommended in their review a slurry particle size less than 20 μm . Larger particles do not reach the plasma and are responsible for the loss of signal. Furthermore, a slurry nebulisation into plasma requires that both the analyte transport efficiency through the sample introduction system and the atomisation efficiency of particles in the plasma are identical with those observed for solutions. Although nitric acid used in suspense preparation facilitates element extraction and some chemical forms are easily solvable, a significant part of analysed elements is bond on solid particles and is not dissolved. So that we did not feel sure if the simple aqueous calibration is suitable for such analysis, both the calibration with standards suspension and the standard addition method were employed.

Mermet used the Mg II 280.270 nm/Mg I 285.213 nm intensity ratio to express the analytical performance response of the plasma to changes in operating conditions

and chemical composition (Mermet, 1991). The Mg II 280.270 nm/Mg I 285.213 nm intensity ratio is used as a practical tool for assessing the energy transfer between the plasma and the injected species and it can also evaluate matrix composition effect. This factor calculated for Mg in the most concentrated aqueous multi-elemental standard was 16.12, for 0.05% w/v suspension of the reference material wheat-flour GBW 08503 16.12, for 0.2% suspension 16.14, and for 2% suspension 16.15. Theoretically, the ratio can be affected by the presence of easily ionized elements in a sample, e.g. Na, K, Ca and Mg. In 0.1% w/v slurry of the GBW 08503 used for routine analysis, contents of Ca and Mg less than 1 mg L^{-1} and K less than 2 mg L^{-1} are presented approximately. This amount does not induce a matrix interference (Krejčová, Černohorský, & Čurdová, 2001). It has been shown by Ebdon et al. (1997) that transport effects are the most important interference effects in slurry nebulizations.

3.3. Analytical characteristics and validation of the process

For the slurry analysis, all limits of detection given by ICP-OES software were calculated as the concentration equivalent to three times standard deviation of the background counts ($3\sigma_{\text{slurry}}$, in $\mu\text{g mL}^{-1}$). For all elements, the standard suspension with the concentration of the reference material wheat-flour GBW 08503 0.2% w/v was used. The procedural limits of detection (LOD, in mg g^{-1}) were worked out as $\text{LOD} = f_{\text{dilution}} * 3\sigma_{\text{slurry}}$. The dilution factor f_{dilution} takes into account the dilution of sample during the preparation step. In this case, the dilution factor is 500. The $3\sigma_{\text{slurry}}$ was determined by 10 repetitive standard suspension measurements. Mainly in the case of Mg and Ca, it was necessary to reduce the photo-multiplier voltage to let down their signal intensities, affecting than the real ICP-OES detection ability for these elements. This is summarised in Table 3. Expressed as the relative standard

Table 4

The analysis of the reference material wheat-flour GBW 08503 – the results of analysis after total microwave digestion and slurry procedures compared with content certified

	Certified (mg kg^{-1})	MW ^a (mg kg^{-1})	S/AS ^b (mg kg^{-1})	S/SS ^b (mg kg^{-1})	S/SA ^b (mg kg^{-1})
Na	10	11.3 ± 0.71	10.6 ± 0.836	9.2 ± 0.90	11.3 ± 0.79
K	1980 ± 280	1890 ± 156	1823 ± 137	2120 ± 134	1706 ± 137
Ca	441 ± 44	453 ± 23	480 ± 27	483 ± 32	459 ± 27
Mg	551 ± 42	526 ± 27	578 ± 32	582 ± 25	530 ± 29
P	23900	22 100 ± 1326	23001 ± 1452	24020 ± 1498	22280 ± 1217
S		1537 ± 128	1520 ± 115	1610 ± 112	1550 ± 119
Fe	39.8 ± 5.2	37.2 ± 3.1	36.7 ± 3.5	40.8 ± 2.9	37.6 ± 2.9
Zn	22.7 ± 4.0	19.6 ± 1.6	21.0 ± 1.8	22.8 ± 1.7	22.0 ± 1.8
Mn	19.6 ± 2.0	21.2 ± 1.9	19.1 ± 1.9	18.7 ± 1.8	20.0 ± 2.1
Cu	4.40 ± 0.62	3.81 ± 0.35	3.62 ± 0.37	3.78 ± 0.33	3.92 ± 0.35

MW – Analysis of digested samples.

S/AS – Slurry analysis, aqueous standards were used.

S/SS – Slurry analysis, standard suspensions were used.

S/SA – Slurry analysis, standard additions were used.

^a Mean ± SD of six replicates.

^b Mean ± SD of five replicates.

Table 5
Elemental analysis of the reference material rice flour NIST 1568a, samples of wheat-flour and wheat based ready-oven mixtures – comparison of the result of the ICP-OES after microwave digestion and slurry technique using aqueous calibration standards

Sample	Method	Element (mg kg ⁻¹)									
		Na	K	Mg	Ca	P	S	Fe	Zn	Mn	Cu
NIST 1568a	Declared	6.6 ± 0.8	1280 ± 80	560 ± 20	118 ± 6	1530 ± 80	1200 ± 20	7.4 ± 0.9	19.4 ± 0.5	20 ± 1.6	2.4 ± 0.6
	MW	7.31 ± 0.72	1330 ± 105	542 ± 48	110 ± 9.6	1459 ± 71	1267 ± 61	8.51 ± 0.52	20.6 ± 1.3	18.1 ± 0.88	2.09 ± 0.11
	S/AS	7.57 ± 0.62	1120 ± 93	593 ± 36	129 ± 7.6	1596 ± 103	1310 ± 70	7.08 ± 0.39	18.8 ± 1.2	21.2 ± 1.4	1.99 ± 0.091
Smooth flour	MW	<LOD	2370 ± 163	493 ± 36	406 ± 20	11320 ± 326	826 ± 69	35.6 ± 2.7	17.6 ± 1.2	12.3 ± 0.98	<LOD
	S/AS	<LOD	2118 ± 174	427 ± 28	432 ± 18	12987 ± 402	799 ± 61	32.3 ± 2.8	15.8 ± 1.4	14.3 ± 0.63	<LOD
Wholemeal flour	MW	<LOD	1869 ± 102	543 ± 30	401 ± 27	12228 ± 471	713 ± 58	29.8 ± 2.7	15.1 ± 1.3	10.8 ± 0.58	<LOD
	S/AS	<LOD	1701 ± 111	526 ± 29	423 ± 30	11963 ± 432	703 ± 57	28.5 ± 2.5	14.2 ± 1.2	10.3 ± 0.68	<LOD
Milky rice classic	MW	314 ± 29	91.0 ± 8.6	310 ± 14	295 ± 15	326 ± 18	392 ± 27	41.5 ± 3.2	3.88 ± 0.28	1.70 ± 0.18	<LOD
	S/AS	333 ± 30	85.9 ± 7.2	297 ± 12	313 ± 16	298 ± 19	375 ± 32	42.8 ± 2.9	4.15 ± 0.31	1.99 ± 0.14	<LOD
Dumplings	MW	296 ± 19	3422 ± 261	225 ± 12	220 ± 12	901 ± 75	1276 ± 99	17.4 ± 0.95	7.48 ± 0.56	4.08 ± 0.26	<LOD
	S/AS	312 ± 25	3526 ± 305	208 ± 16	203 ± 12	953 ± 56	1133 ± 97	18.7 ± 0.87	7.91 ± 0.59	3.87 ± 0.27	<LOD
Ginger bread	MW	341 ± 26	<LOD	193 ± 13	196 ± 9.2	773 ± 53	962 ± 73	<LOD	5.46 ± 0.72	2.90 ± 0.13	<LOD
	S/AS	326 ± 31	<LOD	187 ± 14	207 ± 13	763 ± 38	950 ± 86	<LOD	5.69 ± 0.44	3.12 ± 0.26	<LOD
Pancake	MW	383 ± 19	2168 ± 149	467 ± 23	470 ± 26	4218 ± 256	1237 ± 96	14.8 ± 1.0	18.7 ± 1.1	10.8 ± 0.89	<LOD
	S/AS	372 ± 24	2220 ± 187	487 ± 16	456 ± 21	4008 ± 213	1187 ± 89	14.3 ± 0.96	18.0 ± 1.0	11.2 ± 0.83	<LOD

MW – ICP OES after microwave digestion, three replicates.

S/AS – Slurry analysis with aqueous calibration standards, three replicates.

deviation, the precision of the method proposed was also based on repeated analysis (10 replicates) of the 0.2% w/v suspension of the reference material wheat-flour GBW 08503.

The validation of the procedure was based on analysis of the reference material wheat-flour GBW 08503, as well. Compared with certified values, results obtained for microwave digests, and slurries analysed using aqueous standards, standards slurries and standard additions are summarised in Table 4, together with corresponding precision. All results obtained were subjected to one-way analysis of variance (ANOVA) to ascertain (at 95% confidence level) the homogeneity across the analytical procedures. The ANOVA results proved that there was not significant variation between single analytical procedures employed.

3.4. Analysis of real samples

The analysis of actual elements levels in wheat-flours and wheat-based mixtures were carried out using the ICP-OES slurry analysis with the calibration based on aqueous calibration standards. Compared with the analysis after digestion, the results are presented in Table 5. Cu was not detected in any samples. Na was not found in both flour samples, in another samples analysed there was about 300 mg kg⁻¹. With the exception of the sample of Ginger bread, Fe was up to 40 mg kg⁻¹. The content of K varied from 80 to 2300, Mg 190–550, Ca 200–700, P 300–12300, S 700–1300, Mn 1.7–15 and Zn 4–19, all in mg kg⁻¹. The ANOVA procedure proved that there was not a statistically significant difference between both analytical procedures compared.

4. Conclusion

A slurry sampling ICP-OES technique has been utilised for multi-element analysis of Na, K, Ca, Mg, P, S, Fe, Mn, Zn and Cu in wheat-flours, wheat-based mixtures and reference materials. In general, determined concentrations in slurried samples are similar to those obtained for corresponding samples in solution. Moreover, this methodology allowed finding certified values in appropriate reference materials.

Results obtained for the routine slurry ICP-OES analysis of multivitamin preparation show possible work simplification in a preparation step especially with a fast cryogenic grinding. Method based on digestion using acids can result in incomplete dissolution of the sample, evaporative losses of the more volatile elements and contamination problems. Dissolution is also time-consuming and the sample preparation time often exceeds the analysis time. The proposed analytical method offers an interesting perspective for other similar materials for their direct determination based on slurry sample preparation. It is also an attractive alternative for laboratories not equipped with any digestion technique.

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