Analytical Methods

The cryogenic grinding as the important homogenization step in analysis of inconsistent food samples

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Abstract

Some homogenisation approaches have been investigated to make easier and overcome troublesome preparation of inconsistent food samples. Contents of Na, Ca, Mg, P, Fe, Mn and Zn in muesli, seed and instant food samples were determined by inductively coupled plasma optical emission spectrometry after their grinding with an agate mortar, a kitchen coffee grinder and a cryogenic mill.

The efficiency of a grinding step was evaluated using RSDs and homogeneity factors (H-factor). For cryogenically grinded samples, RSDs were detected about 4% and H-factors on 10, what is acceptable for the analytical purpose. The results for grinding with an agate mortar as well as a coffee grinder were quite unsatisfactory (RSDs in tens percent). Differences between RSDs and H-factors for the procedures tested were detected to be statistically significant. Different element contents were observed in differently treated samples which is probably a result of an unevenly element distribution in inhomogeneous components forming sample.
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1. Introduction

Due to an increased interest in the quality control of food as well as finding of biological roles of nutrients and their function in chronic diseases, nutritional assessment of food intakes are of permanent interest to food chemists and in consequence to analytical chemists. The elemental analysis is a routine matter for convenient analytical techniques as flame or electrothermal atomic absorption spectrometry (F–AAS, ET–AAS), inductively plasma coupled optical emission and mass spectrometry (ICP–OES, ICP–MS).

In the trace elemental analysis of food, analysts usually meet an incredibly wide range of samples with various matrices composition and degrees of homogeneity. A sample homogenization plays a very important role and is a limiting factor in a correctness and reproducibility of results obtained. Homogeneity of sample can be estimated by calculating the homogeneity factor according to: $H = RSD \cdot m^{1/2}$, where H = homogeneity factor, RSD = relative standard deviation and m = sample mass. Homogeneity factors below 10, determined in small sample masses, are considered sufficient for the homogeneity of the materials (Nomura, Silva, Nogueira, & Oliveira, 2005).

A precise solid sample preparation (drying, homogenization followed by a sub-sampling, mineralisation or dissolution and filling-up to a fixed volume) is the most important and the most critical part of an analysis because it is responsible for the largest and often hidden sources of errors. Some of preparation steps may be sources of contaminations. A mechanical sample homogenization can cause a metal contamination from grinding equipment. Volatile elements can be lost owing to heat generation as well (Hoenig, 2001).

A choice of a grinding technique depends on properties of a sample matrix, especially on its hardness, fibre and fat contents. The optimum size of a grind relies on end-use of a sample. Most of difficulties experienced in a conventional

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grinding are overcome by grinding using liquid nitrogen. The cryogenic grinding is a process carried out at low temperature with frozen samples, which allows a good sample homogenisation, and yields more accurate results. Liquid nitrogen at $-196\ °C$ provides refrigeration required for pre-cooling samples and for maintaining a desired low temperature by absorbing a heat generated during grinding operation. According to the main features, the cryogenic grinding technique is characterised by protection of hot-labile components, a short grinding time per sample and an easy, rapid cleanup of an equipment. Main advantages of cryo-grinding are extreme fine grinding due to brittleness and fine grinding of difficult materials, more uniform dispersal of flavour, reduced visual speckling, increased throughput, reduced grinding power consumption and lower cost of powder (Cubadda, Raggi, & Marconi, 2005; Manohar & Sridhar, 2001).

An understanding of a mechanism of wear is another point for the choice of grinding method. The mechanism of ball wear has been systematically investigated since the early 1970s (Gundewar, Natarajan, Nayak, & Satyanarayana, 1990; Tkáčová, Števulová, Lipka, & Šepelák, 1995). According to recent studies, a ball wear in dry grinding is entirely caused due to abrasion and erosion. Wet grinding provides a complex, aggressive, abrasive and corrosive environment that causes a 7- to 20-fold increase in a ball wear. Water and other liquids with high relative permittivity contribute further to a corrosive wear (Gundewar et al., 1990). Tkáčová et al. (1995) investigated the influence of the energy supply conditions and the nature of grinding environment on the Fe contamination of vibration ground quartz. In an attempt to explain the mechanism of wear, changes in the state of iron in a grinding product were studied.

A new high-capacity device for cryogenic grinding was developed by Singh and Goswami (1999), and its performance was evaluated for grinding spices without losses of volatile oils and flavouring components. Engelsen and Wibetoe (2002) used cryogenic grinding for spruce seeds to solve the problem of agglomerating during grinding at room temperature. Mierzwa, Sun, Chung, and Yang (1998) applied cryogenic grinding to the sample preparation of tealeaves in slurry sampling GFAAS. Samples were ground for 20 min in a mix mill employing an additional liquid nitrogen cooling system that improved the efficiency of grinding. Santos et al. (2002) used cryogenic grinding for sample preparation for determination of Cd and Pb in food slurries. The grinding procedure without a pre-cooling step (a grinding time of 2 min) did not produce a fine powder, mainly for fresh samples, thus, a pre-cooling time was considered strictly necessary. Santos, Barbosa, de Souza, and Krug (2003) applied cryogenic grinding also for sample preparation for determination of Cu, Mn and Pb in human teeth. Teeth samples were ground in a cryogenic mill in two steps: pre-cooling (5 min) and cryogenic grinding (2 min) in liquid nitrogen. After grinding, 90% of sample particles were lower than 150 μm. In the work presented by Nomura et al., a rapid cryogenic grinding procedure to reduce particle sizes of breakfast cereal samples has been proposed (Nomura et al., 2005). Gouveia, Lopes, Fatibello-Filho, Nogueira, and Nóbrega (2002) recommended cryogenic homogenization before elemental analysis of ready-to-eat breakfast cereal as well. Booth, Reilly, and Farmakalidis (1996) analyzed samples of breakfast cereals ad raw ingredients and proved losses of all minerals during the processing of whole food cereal grains to the final product.

The present work evaluates the usability of the cryogenic grinding as a rapid and powerful mean for a treatment of demanding food samples that are not able to be grinded using alternative methods. This study has the main objectives to demonstrate the general advantage of grinding of such complicated food samples under cryogenic condition and its irreplaceableness in a sample preparation process.

2. Materials and methods

2.1. Equipment

Samples were crushed in an agate mortar and then grinded using the Freezer/Mill 6750 with Model 6751 grinding vials (Spex, Certi-Prep Group, USA) containing a liquid nitrogen bath (4–5 L). The cylindrical grinding vial assembly consisted of two stainless steel end plugs, a polycarbonate central body, and a steel impactor. As well as samples were broken in a common kitchen coffee grinder (ETA, Czech Republic) commonly used as the first step in a comminution procedure. The measurements were carried out with the sequential, radially viewed ICP atomic emission spectrometer INTEGRA XL 2 and ICP oa-TOF mass spectrometer Optimass 8000 (both GBC Scientific Equipment Pty Ltd., Australia), ICP–OES was equipped with the ceramic V-groove nebulizer and the glass cyclonic spray chamber, ICP-MS with the concentric nebulizer Micro Mist coupled to a 70 mL thermostated (15 °C) cyclonic spray chamber (all Glass expansion Pty. Ltd., Australia). Microwave system Speedwave^{TM} MWS-3$^+$ with high-pressure PFA vessels DAC 100 and the maximum total output of the microwave generator is 1450 W (Berghof, Germany) was used for control digestions procedure. The demineralised water was taken from the Milli-Q Plus water-purification system (Millipore, Bedford, USA). Other equipment used included calibrated volumetric glassware. The calculations and statistical evaluation were carried out using commercial software ADSTAT 1.25 (Trilobyte Statistical Software Ltd., Pardubice, Czech Republic).

2.2. Reagents

The single component standards of Mg, Ca and P (each one with the content of $10,000 \pm 30\ \mu g\ mL^{-1}$, CPI International, USA) and Na, Fe, Mn, Zn, Be ($1000 \pm 2\ \mu g\ mL^{-1}$, Analytika Co. Ltd., Czech Republic) were used. For the decomposition, analytical grade 65% w/v HNO_3 and 30% w/v H_2O_2 (both Lach-Ner, Czech Republic) was used.

2.3. Samples

Two brands of muesli breakfast cereals, linseeds, pumpkin seeds and two brands of instant soups (chicken and goulash) were made by local Czech producers. They were purchased at supermarket and stored at −4 °C before analysis.

The first muesli sample was a very inhomogeneous mixture of wholemeal leaflets, coconut, hazelnuts, almonds and sultanas with big pieces. The second muesli sample contained oat flakes, hazelnuts and almonds. Pumpkin seeds were oval with a dark-green coat and a longer length about 1.5 cm. Brown oval linseeds had a longer length about 3 mm. Instant soups mutually differ only in flavour and they usually contain basic ingredients as follow: dried vegetable, meal, egg and spices, noodles, root vegetable, potato stark, wheat flour, milk proteins, vegetable fat, salt, aromatic ingredients, etc. As producers declare, the NaCl content in dry matter of instant soup varies from 3% to 14% w/w and a total dried matter is about 98%.

2.4. Standards preparation

Multi-element standards (Na, Mg, Ca and P) for muesli and seed samples were prepared containing four levels of concentration: (i) Na 10, Mg 50, Ca 20 and P 100 mg L^{-1}, (ii) the same elements five times, (iii) 10-fold and (iv) twenty times diluted as (i). Standards for Fe, Zn and Mn were: (i) Fe 10, Zn 2 and Mn 0.5 mg L^{-1}, (ii) the same elements five times, (iii) 10-fold and (iv) twenty times diluted as (i). Calibration standards were prepared with 10 mL 65% w/v HNO_3/100 mL of solution which was used for the microwave decomposition in that volume. The water standard blank contained 10 mL 65% w/v HNO_3/100 mL of solution as well.

Single and multi-element standards were prepared for analysis of instant soups containing as well as four levels of concentration. (1) single Na 500–100–50–5 mg L^{-1}, (2) multi-element (i) Ca, Mg, P 5 and Cr, Cu, Fe, Mn, Ni, Pb, Zn 0.1 mg L^{1}, (ii) the same elements with half concentrations as (i), (iii) the same elements five time diluted as (i), (iv) the same elements 10-fold diluted as (i). Due to the presence of high amount of NaCl in samples analysed, the internal standard Be 0.1 mg L^{-1} was used. Calibration standards were prepared with 14 mL 65% w/v HNO_3/100 mL of solution. The water standard blank contained 14 mL 65% w/v HNO_3/100 mL of solution and Be 0.1 mg L^{-1}.

2.5. Sample preparation

Prior to analysis, samples were homogenised in more ways. The first one was crushing in an agate mortar (one sample about 20 min). The second one was grinding in a kitchen coffee grinder, the third a cryogenic grinding. For muesli, all procedures were used. Instant soups and seeds were treated only with an agate mortar and under cryo-genic conditions. For cryogenic grinding, about 4 g of a sample was used. The precooling time was 15 min. The programme consisted of 3 grinding cycles; each grinding cycle time was 2 min as well as cooling time between grinding steps, the total time of the cryogenic procedure was 25 min. The impactor frequency used was 10 Hz. Owing to the heating to a room temperature after grinding, seed oil flowed out and samples were not homogenous. Immediately after grinding, seed samples were weighted into a special digestion vessel. For grinding in a coffee grinder, about 10 g of a muesli sample was taken. The duration of grinding was 1 min, then samples were sieved (the sieve 1 mesh) and a rest from a sieve repeatedly processed in a grinder.

An amount 0.2 g of a muesli and/or seed sample was accurately weighed into an acid washed TPFA digestion tube and 7 mL of nitric acid (65% w/v). The tube was heated in a microwave oven at the power setting of 70% and 160 °C for 15 min, at 80% and 180 °C for 5 min and at 90% and 200 °C for 5 min. The maximum total output of the microwave generator was 1450 W and maximum pressure in a digestion tube 100 bar. The digest was transferred into a 50-mL acid washed volumetric flask and the flask was filled up with demineralised water and stored in polypropylene container. In case of instant soups, approximately 0.5 g of sample was accurately taken and 7 mL of nitric acid (65% w/v) and 2 mL H_2O_2 (30% w/v) was added. The tube was heated in a microwave oven at the power setting of 50% and 150 °C for 10 min, at 70% and 220 °C for 20 min. A digest was transferred into a 50-mL acid washed volumetric flask and an internal standard were added and the flask was filled up with demineralised water and stored in a polypropylene container. Each sample was decomposed in ten replicates. Two water blanks were run with each batch of samples.

2.6. The ICP–OES method

The measurement conditions were optimised based on the signal-to-background ratio of the least concentration expected (Mn), but it was also necessary to modify them in order to set the plasma stable due to high salt concentration for analysis of instant soups. The measurement conditions and emission lines are listed in the Tables 1 and 2. The

Table 1
The operating conditions for ICP–OES analysis

Parameter	Instant soup	Muesli, seed
RF power	1150 W	1100 W
View height	5 mm	6 mm
Gas	Ar 99.999%	Ar 99.999%
Plasma gas	0.7 L min^{-1}	0.65 L min^{-1}
Auxilliary gas	12 L min^{-1}	11 L min^{-1}
Nebulizer gas	0.65 L min^{-1}	0.5 L min^{-1}
Sample aspiration rate	2 mL min^{-1}	2 mL min^{-1}
Read	On-peak, 3 s	On-peak, 3 s
Background correction	Fixed point	Fixed point
Number of replicates	3	3

Table 2
The analytical characteristics of ICP–OES method

	λ (nm)	Instant soups		Muesli, seeds	
		LOD (mg kg^{-1})	RSD (%)	LOD (mg kg^{-1})	RSD (%)
Na	588.995	1.58	4.4	3.01	4.1
Ca	422.673	0.318	4.2	0.635	4.2
Mg	285.213	0.129	2.2	0.301	4.6
P	178.284	1.05	2.6	2.31	4.1
Fe	259.940	0.301	4.4	0.682	3.9
Mn	257.610	0.173	4.2	0.405	4.3
Zn	213.856	0.214	2.8	0.511	3.5

LOD, limit of detection; RSD, relative standard deviation.

analyte emission was based on taking the difference of measured emission intensity on the top of the peak and background near the peak. Including the washing time between samples, the total time for analysis was approximately 5 min.

3. Results and discussion

3.1. Analytical characteristics of the process

All limits of detection given by ICP–OES software were calculated as the concentration equivalent to three times standard deviation of the background counts (3σ, µg L^{-1}). The procedural limits of detection (LOD, in mg g^{-1}) were worked out as LOD $= f_{\text{dilution}} \times 3\sigma$. The dilution factor f_{dilution} takes into account the dilution of sample during the preparation step. They are summarised in the Table 2. The 3σ were determined by ten repetitive measurements of the lowest concentration calibration standard. In case of analysis of instant soups, the lowest concentration calibration standard with the presence of Na was used. The concentration of Na was based on the highest content of Na in samples analysed. For Mg and Ca, it was necessary to reduce the photo-multiplier voltage to let down their signal intensities and the real ICP–OES detection ability for Mg and Ca is far better. The RSD values were obtained for ten repetitive measurements of two chosen, cryogenically treated, samples (muesli I and chicken instant soup).

3.2. Grinding process

In the form available on a market, all types of samples discussed have specific features that unable their direct digestion. Muesli and instant soup samples are characterized by a wide inhomogeneity because they consist of relatively big, hard and fat pieces of incredibly manifold raw materials. One problem associated with a high fat content in muesli samples is agglomeration of a sample and even an increase of particles especially if a ball mill is used that was tested in this study as well. The ball mill was definitely unsuitable for seed and soups because oil flew out of seeds during grinding process or a ball skipped only on noodles and root vegetable from a instant soup without any effect. During processing of instant soups and seeds in the kitchen

coffee grinder, fat components stuck on its knife as well as seeds got stick on it and made grinding impossible. Grinding of muesli samples was without visible problems. Apparently in all three cases, an agate mortar produced insufficiently homogenous grinds but better than a ball mill.

3.3. Analysis of samples

Together with the direct analysis of samples, the standard additions were carried out in order to check real concentrations of elements analysed and to evaluate a matrix effect of table salt soups or other matrix components. From the results given in the Tables 3 and 4, it is clear that the determination using acid standard provides good results in case of muesli and seed samples as well as the internal standardisation for instant soups. Related to the standard addition results, recoveries found were 94–104% for both calibration procedures.

Results of analysis of samples treated in several ways show significant differences between element amounts mainly in case of instant soups and muesli samples. Different element contents observed in differently pulverized samples are probably a result of an unevenly element distribution in inhomogeneous components forming sample.

Differences between relative standard deviations as well as homogeneity factors were detected. Used as an indicator of efficiency for single grinding processing, significance of differences between RSDs for was proved statistically using Hotelling T^2 statistics and Bonferroni intervals.

In the Fig. 1, ranges of the H-factor for samples analysed are displayed. Clearly for all three samples, cryogenic grinding procedure results in a find grind with the comparable H-factor about 10 that is suitable for analytical purposes. After treatment with the agate mortar, the homogeneity depends on sample composition, its hardness and a fat content. As well as the coffee grinder, both do not produce a sample homogenous enough.

3.4. Contamination from a grinding process

The study of contamination effects during cryogenic grinding was carried out and is discussed in full length separately (Pouzar, Krejčová, Černohorský & Pešková,

Table 3
The results for analysis of the muesli samples

		Muesli I				Muesli II			
		STD cryo	Cryo	CG	Mortar	STD cryo	Cryo	CG	Mortar
Na	c	56.1	53.8	77.3	63.3	2020	1950	1880	1720
	RSD	4.1	3.1	130	64	3.9	4.6	5.3	17
	H	9.2	6.9	280	140	8.8	10	12	37
Ca	c	396	373	616	446	408	398	562	416
	RSD	4.2	5.6	81	60	4.6	3.5	85	79
	H	9.3	13	180	135	10.3	7.9	190	180
Mg	c	727	751	707	836	853	864	812	731
	RSD	4.6	4.4	9.8	26	3.9	4.0	17	63
	H	10	9.8	22	57	8.7	8.9	39	140
P	c	2820	2760	2540	2700	2620	2720	2700	2500
	RSD	4.1	4.0	3.2	15	4.0	3.8	3.9	28
	H	9.2	9.0	7.1	34	9.0	8.4	8.7	62
Fe	c	123	119	157	103	199	204	185	217
	RSD	3.9	4.1	63	70	4.0	4.0	57	64
	H	8.7	9.2	140	160	9.0	9.0	130	140
Mn	c	27.6	29.5	24.9	25.8	28.9	30.1	24.6	20.0
	RSD	4.3	5.0	7.9	20	4.2	3.7	11	35
	H	9.7	11	18	45	9.3	8.2	25	78
Zn	c	14.4	15.4	7.8	13.6	24.0	24.8	20.7	29.3
	RSD	3.5	3.0	22	28	4.8	3.3	17	43
	H	7.8	6.6	49	62	11	7.3	38	95

c, the concentration in mg kg^{-1}; RSD, the relative standard deviation in %; H, the homogeneity factor in g^{-2}; STD cryo, the standard addition method applied for cryogenically treated samples.

Table 4
The results for analysis of the seed and instant soup samples

		Linseed			Pumpkin			Chicken soup			Goulash soup		
		STD cryo	Cryo	Mortar	STD cryo	Cryo	Mortar	STD cryo	Cryo	Mortar	STD cryo	Cryo	Mortar
Na	c	325	334	319	59.1	56.0	66.4	76.6	78.4	72.5	64.9	65.1	62.2
	RSD	3.6	3.9	13	4.2	4.5	120	4.4	4.6	13	4.0	3.1	19
	H	8.0	8.8	28	9.4	10	273	9.7	10	29	8.9	6.9	42
Ca	c	2450	2340	2380	614	632	594	823	790	764	626	650	642
	RSD	4.6	3.8	5.7	3.7	4.3	73	4.2	4.0	16	4.1	4.2	15
	H	10	8.4	13	8.2	9.5	162	9.3	8.9	35	9.1	9.3	34
Mg	c	3831	3792	3733	6299	6163	6223	526	557	542	624	601	576
	RSD	4.1	3.7	4.4	3.4	3.0	4.9	2.2	3.1	12	3.1	3.4	9.6
	H	9.1	8.4	9.9	7.6	6.8	11	4.8	7.0	26	7.0	7.6	21
P	c	6700	6770	6720	13300	13300	13600	1820	1863	1520	1940	2008	1966
	RSD	4.0	3.4	4.1	3.8	3.5	4.7	2.6	3.1	17	4.0	4.0	5.9
	H	9.0	7.7	9.3	8.4	7.9	10.6	5.7	7.0	38	9.0	8.9	13
Fe	c	167	162	188	<LOD	<LOD	<LOD	19.1	18.9	18.7	59.6	60.4	56.8
	RSD	4.0	3.2	4.2				4.9	4.2	16	4.6	3.6	28
	H	8.9	7.1	9.3				11	9.3	36	10	8.0	63
Mn	c	23.6	24.1	20.6	51.4	52.0	50.0	8.22	7.81	8.36	9.19	9.61	10.2
	RSD	4.2	4.3	5.4	4.2	2.7	5.2	4.2	4.0	8.7	3.9	3.8	23
	H	9.8	9.6	12	9.4	6.0	12	9.5	9.0	19	8.7	8.4	51
Zn	c	63.6	63.8	62.1	97.0	95.6	94.1	13.9	13.2	14.6	20.7	20.1	19.9
	RSD	3.6	3.1	4.3	3.6	3.3	3.9	2.8	3.6	10	4.3	4.4	9.3
	H	8.1	7.0	9.6	8.0	7.3	8.8	6.3	7.9	23	9.6	9.8	21

c, the concentration in mg kg^{-1}; RSD, the relative standard deviation in %; H, the homogeneity factor in g^{-2}; STD cryo, the standard addition method applied for cryogenically treated samples.

Spectrochimica Acta, in the edition processing). The sample of pure cellulose (provided by Department wood, pulp and paper, University of Pardubice, Czech Republic) was grinded under various conditions (in a new, pure grinding vessel, after metal containing electro-waste samples, etc.).

The microwave digestion followed by the o-TOF–ICP–MS (o-TOF–ICP–MS spectrometer Optimass 8000, GBC, Australia) determination of selected elements was performed. In the process of cryogenic grinding, two sources of the sample contamination were detected – con-
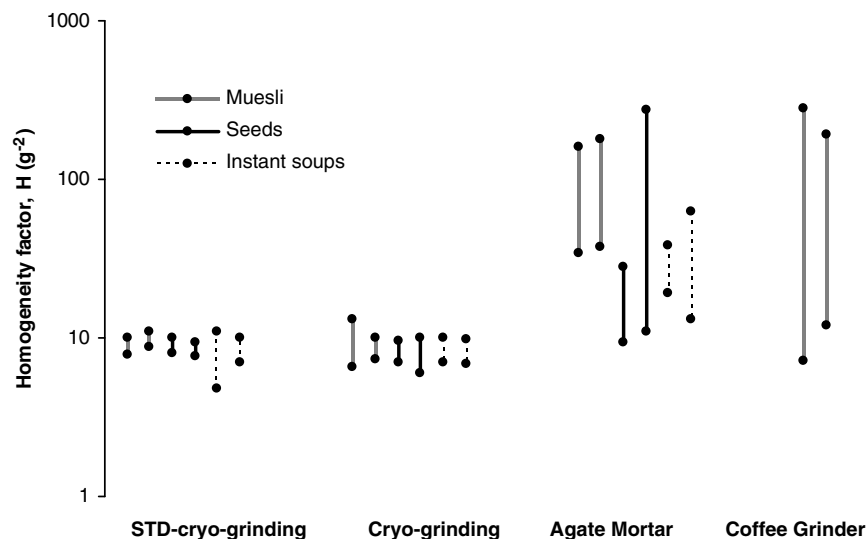
Fig. 1. The limit values of the homogeneity factors for all elements analysed in muesli, seed and instant soup samples. (STD cryo – the standard addition method applied for cryogenically treated samples).

tamination through wearing of metal parts of a grinding set and cross-contamination caused by previously ground sample (electro-waste). The significant contamination by Fe on the level of hundreds $\mu g\,g^{-1}$ from metal parts of a grinding vessel was observed. In comparison with the ICP–OES limits of detection for our food samples, the wearing Fe contamination is negligible. As well as a detectable cross-contamination, e.g. a higher content of Cu, by previous ground electro-waste sample was detected due to an incompletely washed sample adsorbed on the polycarbonate part of a grinding vessel.

4. Conclusion

Some homogenisation approaches have been investigated in this work to improve the efficiency of the preparation of very inhomogeneous food samples as muesli, seed and instant soup samples. Results of analysis of samples treated in more ways show significant differences between element amounts mainly in case of instant soups and muesli samples. Different element concentrations detected in differently crushed samples are supposedly a result of an unevenly element distribution in inhomogeneous components forming sample. Except the cryogenic grinding, the results show poor characteristic expressed as the RSDs and the homogeneity factor for grinding with an agate mortar as well as a coffee grinder; using of a ball mill was impossible at all. For cryogenically treated samples, RSDs were about 4% what means H-factors on 10. Differences between relative standard deviations as well as homogeneity factors were detected to be statistically significant (Hotelling T^2 statistics and Bonferroni intervals).

From the experiments carried out it is evident, that common laboratory grinding equipments visibly fails during a homogenisation of inhomogenous samples (agglomeration, flowing of oil, sticking on a knife, moving of a ball only on

a sample surface). During the grinding process, the Fe contamination probably connected with wearing of metal parts of a grinding vessel was observed in hundreds $\mu g\,g^{-1}$ that is seems to be irremovable but in the case of ICP–OES analysis negligible. On the other hand, the cross-contamination from proceeding sample (e.g. Cu from electro-waste samples) can be avoided easily using a new polycarbonate part of a grinding vessel.

The work approved the usability of the grinding under cryogenic condition as a rapid and powerful pre-treatment step with a low risk of contamination for complex samples that are not able to be grinded using alternative methods and demonstrated the general advantage for such complicated materials hardly decomposed without powderisation.

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