Quantification of potentially toxic elements in food material by laser ablation-inductively coupled plasma-mass spectrometry (LA-ICP-MS) via pressed pellets

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ABSTRACT

Here, we validated a protocol for the elemental analysis of plant and food materials using laser ablation-inductively coupled plasma-mass spectrometry (LA-ICP-MS) and pressed pellets in compliance with the Green Chemistry principles, *i.e.* avoiding the use of hazardous reagents. The protocol included sample pre-treatment, preparation of pellets, and LA-ICP-MS optimisation for the food sample matrix using leaf certified reference materials. Sample homogenisation and particle size reduction (~10 μm) for samples with larger initial particle sizes proved crucial in improving signal stability and analytical results, whereas the raster mode was preferred over spot mode for greater accuracy. The validation of the technique was successful for determination of Mn, Ni, Cu, Zn, As, Se, Cd and Pb (z-score values ≤2). We propose LA-ICP-MS using pressed pellets as an alternative to ICP-MS in food analysis.

1. Introduction

All essential elements for human health (Ca, Cu, Fe, K, Mg, Mn, Mo, Zn, etc.) have a significant role in biochemical and physiological functions, but they can become highly toxic and cause health problems when over-abundant (Nagajyoti, Lee, & Sreekanth, 2010). Non-essential elements (*e.g.* As, Cd, Pb) might be toxic for humans, even at low concentrations (Nordberg, Fowler, & Nordberg, 2014). Acute or chronic poisoning by metals can cause malfunction of the vital organs and, after extended exposure, death (*e.g.* see review in Song & Li, 2015). Thus, monitoring the concentrations of such metal(loid)s, particularly in foods, is important; foods are a major source of metal ingestion for humans and animals (Nordberg et al., 2014). Environmental pollution, due to the contamination of agricultural land (*e.g.* via irrigation water, Mapanda, Mangwayana, Nyamangara, & Giller, 2005; Khan, Cao, Zheng, Huang, & Zhu, 2008) is another major reason for studying metals in plants and foods.

Institutes and environmental agencies worldwide, such as the U.S. Environmental Protection Agency (EPA) and European Environment Agency (EEA) under which the regional environmental agencies co-operate, are dedicated to establishing protocols for metal determinations in agricultural products. Inductively coupled plasma-mass spectrometry (ICP-MS) can address a broad range of analytical requirements and is a practical and, so far, the most suitable method for the types of analysis needed.

The application of methods based on 'Green Chemistry' has led to a need to develop acid-free analytical protocols for ICP-MS analysis. Laser ablation-inductively coupled plasma-mass spectrometry (LA-ICP-MS) is a promising analytical technique that also appears to be a powerful tool for direct solid analysis (Mokgalaka & Gardea-Torresdey, 2006). Thus, LA-ICP-MS is a time-effective and environmentally-friendly technique (Russo, Mao, Liu, Gonzalez, & Mao, 2002; Lee, Chang, & Jiang, 2003; Ito et al., 2009; Hanć, Piechalak, Tomaszewska, & Barałkiewicz, 2014) that also allows for the quantification of selected elements of interest simultaneously, thereby reducing operational costs. Likewise, laboratory operational costs are further reduced, as sample preparation is minimal, saving time, and far less complicated than conventional solution ICP-MS analysis (Russo et al., 2002; Arevalo, Bellucci, & McDonough, 2010). LA-ICP-MS avoids the risks of external contamination, minimizes the potential for analyte losses, requires only a small sample (Ito et al., 2009), and—due to the absence of a solution—polyatomic ion interferences are eliminated (Hu et al., 2008; Liu et al., 2008). Altogether, these benefits point to reliable and

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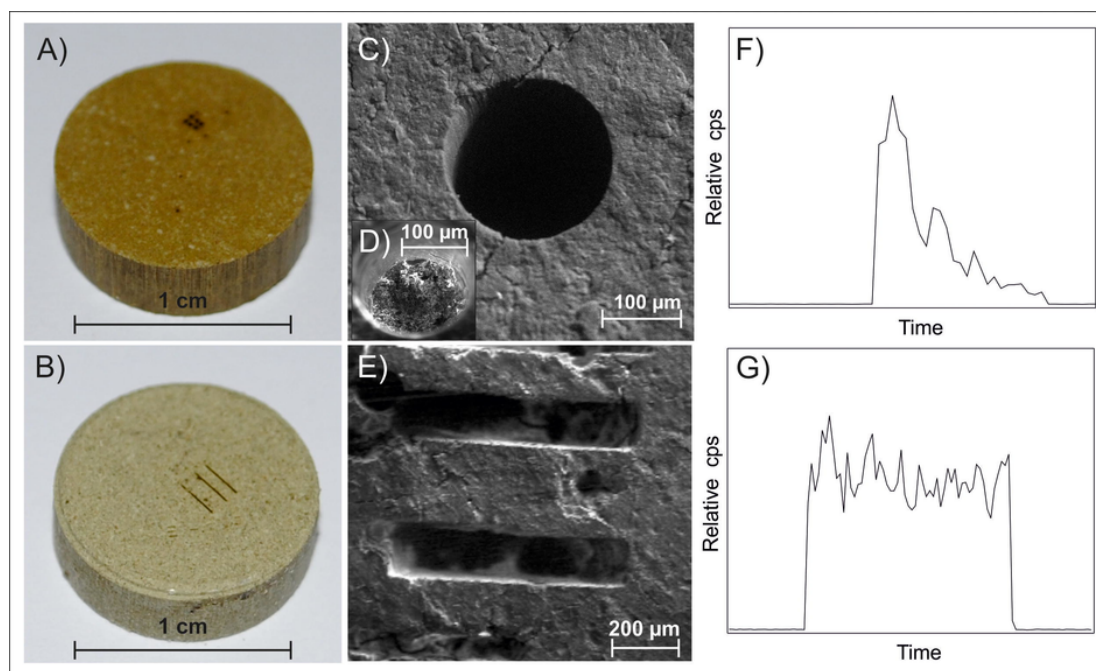
Fig. 1. A-B) Photographs of pressed pellets, C-E) Secondary electron images of laser craters in spot mode and raster mode, respectively, and F-G) Representative time resolved analysis (TRA) graphs of spot mode and raster mode, respectively.

Table 1
Laser Ablation parameters during the analyses for each CRM sample.

Sample	Spot mode				Raster mode			
	Fluence (J/cm^2)	Repetition rate (Hz)	Shot count	Spot size (μm)	Fluence (J/cm^2)	Speed (1μm/sec)	Repetiton rate (Hz)	Spot size (μm)
NIST1515_1	10	20	1200	110	10	1	40	180
NIST1515_2	10	20	1200	65	10	1	40	180
NIST1573a_1	5	10	1200	65	10	5	20	65
NIST1573a_2	5	10	1200	65	10	5	20	65
LGC-7162_1	10	20	1200	65	10	1	40	180
LGC-7162_2	10	20	1200	65	10	1	40	180

1 is for the original samples and 2 for the treated samples after milling.

safer analytical technique for food samples compared with ICP-MS methods.

LA-ICP-MS provides for precise analysis of trace and ultra-trace metal(loid)s in biological matrices (Becker, Matusch, & Wu, 2014). The aim was, therefore, to validate the use of LA-ICP-MS for the quantification of trace elements present in processed foods and plant materials. We describe the new analytical method and conditions for sample preparation and, secondly, analysis including matrix-matched standards and laser ablation parameters. Certified reference materials (CRMs) – commonly used for method validation – consisting of powdered leaves from apples, tomatoes and strawberries served as real-world samples.

2. Materials and methods

2.1. Reference materials

The number of certified elements is usually restricted in many food-related CRMs. After thorough evaluation, we chose three different CRMs that were the most suitable for development of the current analytical protocol: NIST1515 (apple leaves) and NIST1573a (tomato leaves), provided by the National Institute of Standards and Technology of the U.S. Department of Commerce (Gaithersburg, USA), and LGC-7162 (strawberry leaves) provided by LGC Standards (Middlesex,

UK), a division of the UK's designated National Measurement Institute. Particle distribution of the NIST materials was optimal for LA-ICP-MS analysis and, the fact that they have been used widely in previous studies, meant data from this study and those published previously were comparable. LGC-7162 with the largest particle size was used to test the impact of particle size reduction on analysis as well as for comparison with previous work. Leaf materials were preferred because metals tend to accumulate in them. In the selected CRMs, a variety of potentially toxic elements have been certified using various analytical techniques and methods of known accuracy, making them suitable for method validation. Among the techniques used for certification, dissolution ICP-MS prevailed, allowing direct comparison with LA-ICP-MS results.

2.2. Particle size distribution

Two different methods of milling were tested: Planetary Ball Mill, using a Deco-Mill (Grontal Soluciones Biotecnológicas, Granada, Spain), was applied for NIST1515 and Mixing Milling with a high power oscillating mill, using a MM400 Retsch (Retsch, Haan, Germany), was used for NIST 1573a and LGC7162. Both dry (dry sample powder) and colloidal wet (sample powder mixed with MiliQ water in a ratio of 4:1) grinding and different milling times (10–20 – 30–40 – 50–60 min) were tested. CRM samples as well as the

Table 2
Results obtained by LA-ICP-MS analysis for the three different CRMs analysed, including the certified values with the corresponding uncertainties and the mean measured concentrations with their standard deviations for the elements of interest (Mn, Ni, Cu, Zn, As, Se, Cd, Pb).

Element	Certified Value (mg/kg)	Spot Mode		Raster Mode	
		1515_1 (mg/kg)	1515_2 (mg/kg)	1515_1 (mg/kg)	1515_2 (mg/kg)
Mn	54 ± 3	53.8 ± 1.1	54.3 ± 0.9	53.9 ± 0.8	53.9 ± 0.4
Ni	0.91 ± 0.12	0.95 ± 0.09	0.92 ± 0.03	0.91 ± 0.01	0.92 ± 0.02
Cu	5.64 ± 0.24	5.65 ± 0.06	5.70 ± 0.26	5.61 ± 0.06	5.67 ± 0.04
Zn	12.5 ± 0.3	12.7 ± 0.4	12.5 ± 0.3	12.5 ± 0.4	12.6 ± 0.5
As	0.038 ± 0.007	0.039 ± 0.003	0.039 ± 0.01	0.037 ± 0.001	0.04 ± 0.07
Se	0.050 ± 0.009	0.055 ± 0.002	0.061 ± 0.02	0.054 ± 0.002	0.047 ± 0.01
Cd	0.013 ± 0.002	0.014 ± 0.003	1.51 ± 0.08	1.22 ± 0.64	1.54 ± 0.04
Pb	0.470 ± 0.024	0.470 ± 0.02	0.47 ± 0.01	0.470 ± 0.014	0.470 ± 0.01
		1573a_1 (mg/kg)	1573a_2 (mg/kg)	1573a_1 (mg/kg)	1573a_2 (mg/kg)
Mn	246 ± 8	251 ± 15	245 ± 2.4	245 ± 0.55	243 ± 1
Ni	1.59 ± 0.07	1.60 ± 0.1	1.60 ± 0.2	1.74 ± 0.22	1.58 ± 0.04
Cu	4.70 ± 0.14	4.87 ± 0.54	4.73 ± 0.18	4.70 ± 0.02	4.65 ± 0.01
Zn	30.9 ± 0.7	31.1 ± 1.9	30.8 ± 0.6	32.1 ± 2.4	30.5 ± 0.1
As	0.112 ± 0.004	0.112 ± 0.07	0.144 ± 0.06	0.114 ± 0.006	0.11 ± 0.009
Se	0.054 ± 0.003	0.037 ± 0.084	0.061 ± 0.038	0.02 ± 0.018	0.05 ± 0.13
Cd	1.52 ± 0.04	1.60 ± 0.49	1.54 ± 0.07	1.53 ± 0.07	1.50 ± 0.01
Pb[*]	0.58	0.63 ± 0.11	0.62 ± 0.11	0.59 ± 0.02	0.58 ± 0.007
		LGC7162_1 (mg/kg)	LGC7162_2 (mg/kg)	LGC7162_1 (mg/kg)	LGC7162_2 (mg/kg)
Mn	171 ± 10	179 ± 39	161 ± 6	183 ± 25	170 ± 2.7
Ni	2.6 ± 0.7	2.60 ± 0.3	2.70 ± 1.1	2.32 ± 0.2	2.59 ± 0.05
Cu[*]	10	12.5 ± 1.7	10.8 ± 6.5	15.4 ± 2.4	9.98 ± 0.25
Zn	24 ± 5	27.8 ± 6.7	17.9 ± 2	22.7 ± 3	24.0 ± 2.9
As	0.28 ± 0.07	0.28 ± 0.02	0.22 ± 0.4	0.14 ± 0.38	0.30 ± 0.04
Se[*]	0.04	6.00 ± 6.5	1.00 ± 12	0.021 ± 0.015	0.04 ± 0.003
Cd	0.17 ± 0.04	0.16 ± 0.03	0.07 ± 0.1	0.17 ± 0.14	0.17 ± 0.01
Pb	1.8 ± 0.4	2.37 ± 0.8	3.32 ± 0.2	1.11 ± 0.3	1.79 ± 0.03

[*] Values that have not been certified, but were given in the corresponding certificates as indicative values; 1 is for the original and 2 for the treated samples.

acquired ground materials were analysed for particle size distribution using a Mastersizer HYDRO 2000MU (MALVERN Instruments; Iesmat S.A., Madrid, Spain), while data were processed with the relevant software. All the wet samples were centrifuged to separate the solid from the liquid prior to analysis. For this purpose, an Eppendorf Centrifuge 5804 (Andaluza de Instrumentación SL, Seville, Spain) was used for 7 min at 3000 rpm. The solid material was freeze-dried overnight until completely dry in order to prepare pressed pellets for analysis.

2.3. Preparation of pressed pellets

Pressed pellets were prepared for the original CRMs and materials after milling (0.5 g sample mixed with 10% binding material, Fig. 1A and E), using an SRT1 roller mixer (Stuart Scientific, Staffordshire, UK). Methylcellulose (HPMC), an inert non-ionic viscoelastic polymer that does not complex with ionic species, was used as the binder. HPMC was analysed prior to sample preparation to ensure it did not contain any traces of the elements of interest. Each sample powder was pressed into a pellet (12 mm diameter, 3 mm thickness) using a Specac Atlas 15 T hydraulic manual press (Specac Ltd., Orpington, UK) at 5 t pressure for 3 min. The awls used were designed to shape the pellet to the standard size of the laser sample holder. Punches used for the process had completely flat surfaces and were made of teflon (Polytetrafluoroethylene-PTFE) rather than metal to avoid contamination. The pellets were stored at room temperature until the analysis.

2.4. LA-CP-MS analysis

The equipment used for LA-ICP-MS analyses was a Photon Machine excimer 193 nm laser coupled to an Agilent 8800 QQQ ICP-MS (Andaluza de Instrumentación SL, Seville, Spain). Samples were introduced into the ablation chamber using a modified sample holder, which carried up to 15 samples simultaneously. Helium carrier gas flow was supplied through the ablation cell. The wavelength of the beam (193 nm)

minimized the effect of deep hole fractionation, either in high or low energy pulses, as well as other matrix effects, making ablation of some materials more efficient. In this study, using reaction cells by collision to remove elemental interferences was rejected as an option, because testing showed the results to be equally good with or without it.

Different analyses were conducted on the CRMs to test the efficiency of the LA-ICP-MS technique. Two different samples for each CRM were analysed; the original and the milled material, using both raster and spot modes. To avoid bias, the samples must be completely dry, and the laser energy level must be adjusted carefully prior to analysis. The system was set up and tuned using NIST612 (synthetic glass) as the external standard with a calibrating range of low (7), medium (133), and high (208) atomic masses. ^{44}Ca was used for internal calibration in all analyses, as it represents a major mass in all the samples. All parameters—carrier flow, sample depth, lenses tuning, spot diameter, repetition rate, *etc.*—were adjusted for each set of samples with the aim of achieving the best possible sensitivity and stability. The operating conditions for laser ablation are summarised in Table 1.

Six different short rasters of 1 min were conducted for each analysis, including 1 min blank analysis prior to every raster; the total duration of analysis was 12 min. During the blank period, the laser beam ablated only He, which also functioned as an instrumental blank. The same parameters (duration and number of spots) were applied in the spot mode. Number of shots per analysis and repetition rates were adjusted to achieve the same ablation time in both raster and spot modes. Similarly, the fluence parameter was reduced when repetition rate decreased. Spot size selection was made considering the degree of heterogeneity for each sample, which increased with particle size. Parameters for laser ablation, including total energy set-point and gas flow rates, were constant for all analyses. The total energy produced by the laser was 7 mJ. He flow rate was 0.8 l/min and 0.2 l/min, respectively, for carrier and auxiliary He gas flow.
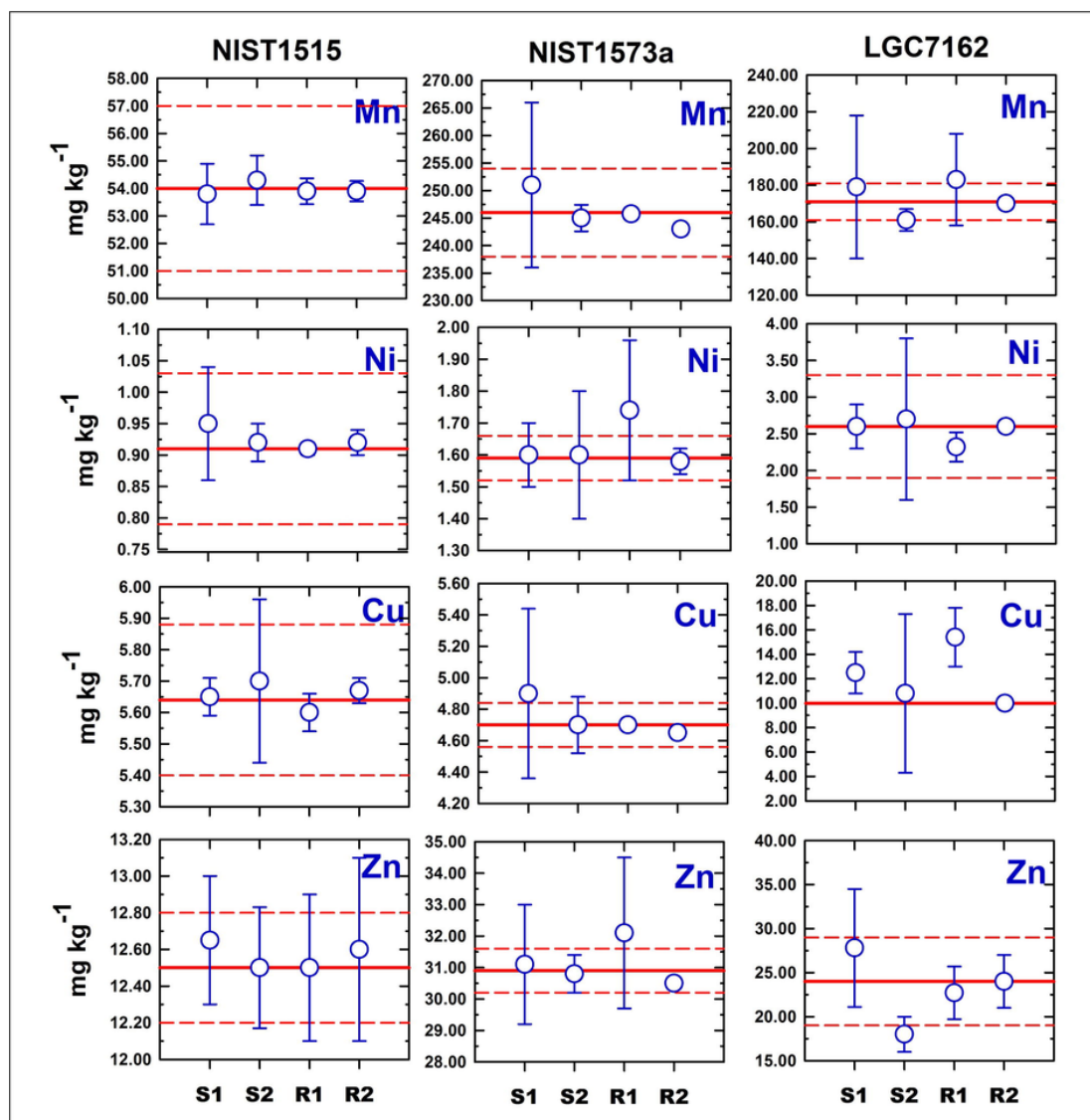
Fig. 2. Measured mean concentrations of Mn, Ni, Cu and Zn including their Standard Deviation compared to the certified values. S stands for spot mode and R for raster, while 1 is for the original samples and 2 for the milled ones.

In the raster mode, a second experiment entailed changing the number and duration of rasters, so as to compare the efficiency of different analyses. Accordingly, only 1 large raster of 10 min was performed after 2 min blank analysis, giving a total duration of 12 min. In spot mode, a spot size of 65 μm was used in all analyses, except for one (NIST1515_1) where 180 μm was applied to compare the effect on the results (Fig. 1B, C & F). These spot size options were likewise applied in raster mode.

Parameters for ICP-MS data acquisition were common for all analyses: RF (1500 W), sample depth (4 mm), carrier flow gas (Ar; 0.8 l/min), ionic lenses (Octapole Bias −18 V, Octapole Reflect 120 V, Energy Discrimination 5 V) and integration time for all measured masses (0.1 ms). The elements of interest included Mn, Ni, Cu, Zn, As, Se, Cd and Pb. Based on the work of Longerich, Jackson, and Günther (1996), the limit of detection (LOD) for each element was calculated using © Iolite software, provided with the ICP-MS apparatus, using the instrumental blank standard deviation. The values (mg/kg) for each element were: 0.14 for Mn, 0.035 for Ni, 0.009 for Cu, 0.13 for Zn, 0.007 for As, 0.01 for Se, 0.054 for Cd, and 0.001 for Pb. The contribution of the chemical blank (binding material-HPMC) was zero, so it was not considered in calculating the LODs.

3. Results and discussion

3.1. Particle size distribution and sample homogenisation

One significant difficulty encountered in LA-ICP-MS analysis is the heterogeneity of samples, and it should be stressed that biological samples can be particularly problematic when applying LA-ICP-MS, owing to different conditions within one same sample and the various parameters of the apparatus while measuring (Evans, Pisonero, Smith, & Taylor, 2014). To achieve the optimal performance, representative but homogeneous samples of a specific fineness are needed (Russo et al., 2002; Hanć et al., 2014). Thus, homogenisation of the samples prior to analysis is very important; various methods have been described for this purpose, *i.e.* grinding (Becker & Dietze, 1999; Punshon, Jackson, Bertsch, & Burger, 2004; Mokgalaka & Gardea-Torresdey, 2006; Ito et al., 2009). For samples with a large particle size, the formation of craters during ablation leads to irregularities and particles are not ablated evenly. Particle size reduction improves ablation, provides greater signal stability, improves spatial resolution and allows homogeneity using different laser beam diameters to be documented more
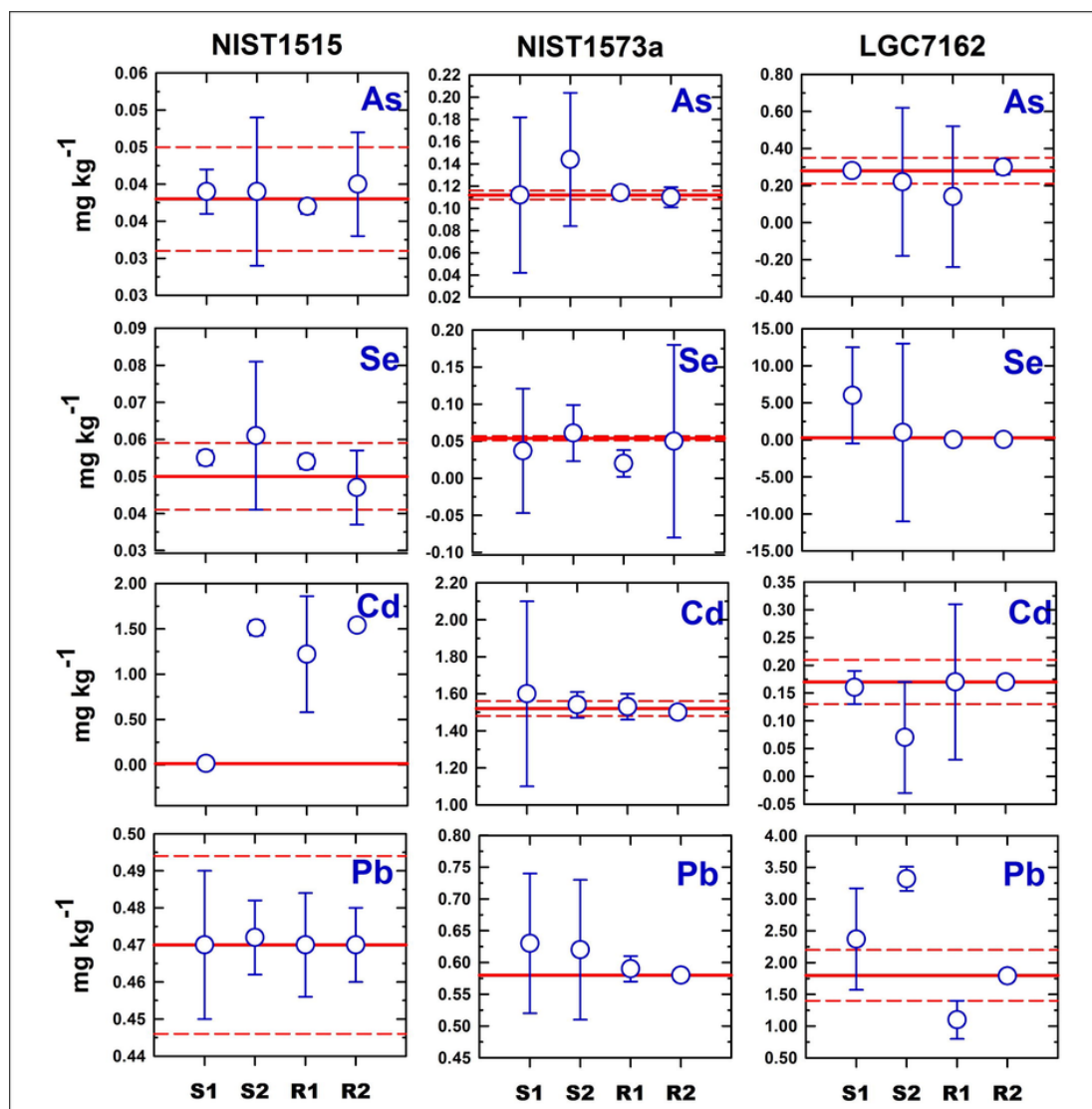
Fig. 3. Measured mean concentrations of As, Se, Cd and Pb including their Standard Deviation compared to the certified values. S stands for spot mode and R for raster, while 1 is for the original samples and 2 for the milled ones.

efficiently. Large laser spot sizes (> 50 µm) provide better sensitivity, as long as particle size and the distribution permit efficient ablation and transport in the He flow towards the ICP-MS plasma torch. Particle size effects must be minimized by using pressed pellets, formed with flat punches, otherwise the laser is not focused on all the particles encountered by the beam.

In view of these issues, different milling techniques (Section 2.2) were tested. Wet milling gave better results, supporting the time-saving character of the protocol. Milling gave different results, depending on the original grain size. NIST1515 (apple leaves) and NIST1573a (tomato leaves), with original sizes between 8 and 13 µm, did not improve significantly. This can be explained by the inherent characteristics of the materials, since the particles are flat and the initial grain sizes were already small, hampering any additional gain. In contrast, LGC7162 (strawberry leaves, approx. 90–180 µm), achieved almost a 90% particle-size reduction after milling. However, an increase in homogeneity was evident in all materials, regardless of the original particle size, providing better conditions for analyses. In this sense, this study points to alternatives to overcome issues with sample homogenisation among natural materials that are heterogeneous.

3.2. Evaluation of the analytical protocol

After testing different laser ablation modes and spot sizes, we decided to use spot and short raster modes, and no important differences were observed in terms of the efficiency of either method with the spot sizes tested. The results were interpreted based on the divergence of concentrations from the certified (published) values as well as on the standard deviation (SD) of values. Nickel, As, Se, Cd and Pb were chosen as elements of interest because they are cumulative poisons posing a risk for human health even at low doses (Chowdhury & Chandra, 1986) and food and beverages are a major exposure route to these elements for humans (Duruibe, Ogwuegbu, & Egwurugwu, 2007; Nordberg et al., 2014). Additional essential elements, including Mn, Cu and Zn, were chosen due to their abundance in nature, and their potential to accumulate in foods with serious implications for human well-being in the event of over-exposure (Nordberg et al., 2014). The resulting mean concentration and SD for the elements of interest are presented in Table 2 and Figs. 2 and 3. All certified values including the uncertainties are also provided. The results are given for both milling techniques: NIST1515 treated with wet planetary milling, and
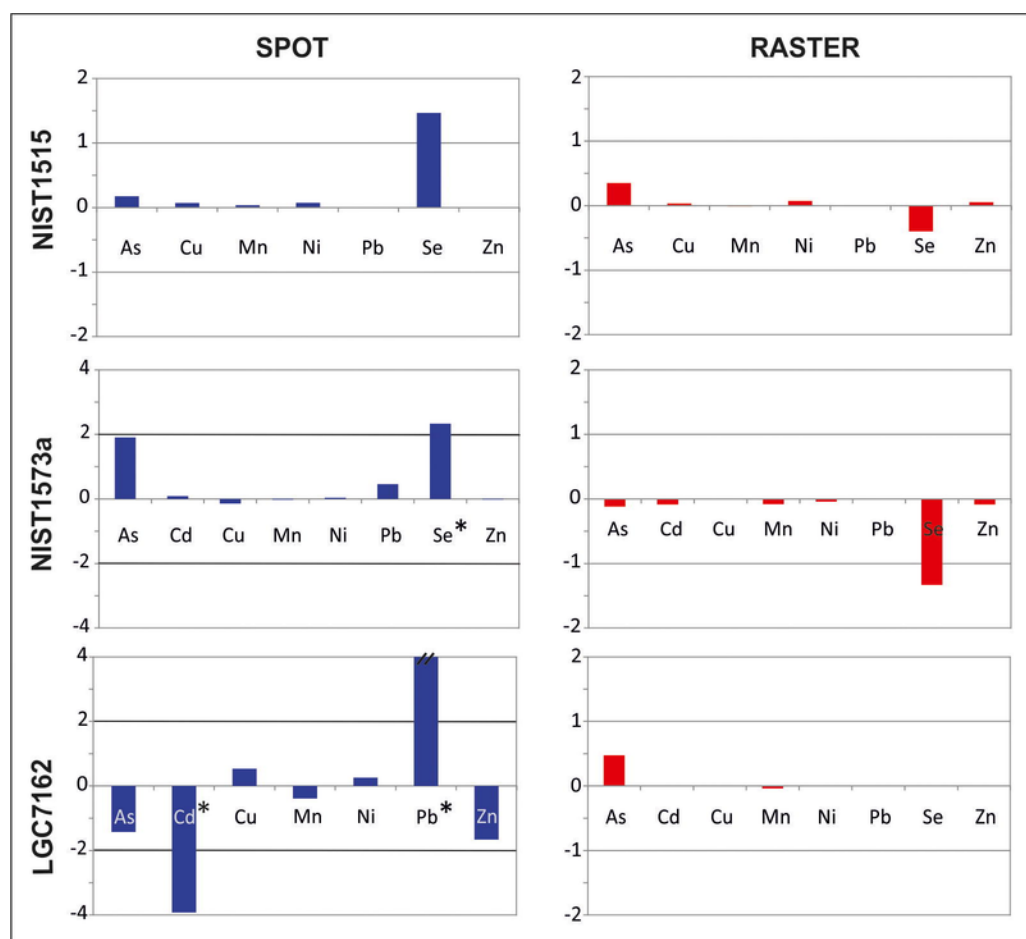
Fig. 4. Z-scores for the milled CRMs in spot mode and raster mode. The results are presented for elements with acceptable z-scores (≤2), except for the elements slightly out of acceptable values, marked with * in spot mode (Se = 2.3 for NIST1573a; Cd = 3.9 and Pb = 5.6 for LGC7162), which presented improved z-scores in raster mode.

NIST1573a and LGC7162 treated with the wet mixer milling. Z-scores were calculated for validation of the results. To this end, the fit-on-purpose target standard deviation was set at 15% of the certified value. Z-scores for milled samples are presented in Fig. 4, showing elements with satisfactory results (scores ≤2). In the Supplementary Material, each metal is described independently, since – on occasions – they behaved differently, depending on the mode of analysis and the material.

Overall, concentrations of the target elements were in good agreement with reference values (Table 2) in all three CRM, reflecting the efficiency of the new protocol. However, Cd and Se showed some abnormal peaks, both before and after sample treatment. Fractionation effects and heterogeneity of the samples could explain these, which need to be considered in future analyses. Optimum homogeneity of the samples, therefore, must be achieved prior to analysis to avoid differences in element concentrations when the laser crosses samples with different particle sizes, resulting in spurious peaks. Milling of the samples is recommended for this purpose, meaning fractionation effect should be decreased as much as possible. Raster mode was preferred over spot, because the signal showed greater stability along the raster line, uninfluenced by fractionation. For external standard purposes, NIST1573a was better in both modes, with respect to stability and sensitivity.

4. Conclusions

We developed a protocol in compliance with green chemistry for the analysis of foods, using LA-ICP-MS with pressed pellets, for deter-mination of a variety of elements (Mn, Ni, Cu, Zn, As, Se, Cd, Pb). The results underline the efficiency of the protocol with respect to the elements of interest, suggesting that it would be an alternative to the more conventional ICP-MS technique. Particle size reduction and homogenisation of the sample by milling ensured that signal interferences could be avoided, and more precise results obtained. Raster mode is recommended over spot mode during ablation, as it provided greater accuracy for a wider variety of samples and elements (Fig. 4). Nevertheless, both modes should be tested to determine which is best for each material and element under analysis. Future studies might focus on optimising the LA-ICP-MS technique for different kinds of foods/food parts.

Another challenging aspect of LA-ICP-MS is the use of an appropriate matrix, as a standard, which is vital for optimal results, due to a scarcity of suitable materials. Based on the current study, NIST1573a (tomato leaves) is a pertinent matrix for similar foods, although not suitable for all trace elements.

Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at https://doi.org/10.1016/j.foodchem.2018.08.118.

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