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Analytical Methods

Ultrasound-assisted extraction for the determination of Cu, Mn, Ca, and Mg in alternative oilseed crops using flame atomic absorption spectrometry

Vanessa Cruz Dias Peronico, Jorge Luiz Raposo Jr. *

Federal University of Grande Dourados, School of Exact and Technology Science, PO Box 364, 79804-970 Dourados, MS, Brazil

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ABSTRACT

An ultrasound-assisted extraction procedure was evaluated for the multi-element determination of Cu, Mn, Ca, and Mg in alternative oilseed crops using flame atomic absorption spectrometry. The best results were obtained when 0.3 g of samples were used to extract the mineral content using 10 mL of a 1.40 mol L^{-1} HNO_3 solution for 10 min at 25 °C. The accuracy and precision of the analysis were evaluated using two oilseed reference materials, and the results were in agreement with reference values at 95% confidence level (paired *t*-test). The method was used to analyze five oilseed samples and the results were in agreement with those obtained using a closed-vessel microwave-assisted acid digestion system for sample preparation. The relative standard deviations were 0.52–6.13% for all of the standard and sample measurements, and the limits of detection were 666.7, 416.7, 333.4 μg g^{-1}, and 3.5 mg g^{-1} for Cu, Mn, Ca, and Mg, respectively.

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1. Introduction

Presently, various oilseeds are being investigated as viable alternatives for enhanced production of vegetable oils and/or biofuels from renewable vegetable sources (Liu et al., 2014; Nabi et al., 2015; Nigam & Singh, 2011). However, the production of biodiesel or vegetable oil from alternative sources requires dedicated attention, in particular to the nutritional content of the starting products. Foliar diagnosis and soil analysis provide an index of nutrient availability (Farago, 1994); however, the analysis of seeds could provide an indicative data of the mineral composition of the oil extract.

Highly sensitive analytical spectrometry techniques for the determination of the mineral content in environmental samples, include spectrophotometry (Kassem & Amin, 2013; Sabarudin, Oshima, & Motomizu, 2003; Szydlowska-Czerniak & Szlyk, 2003; Tarafder & Thakur, 2005), atomic emission spectrometry (Pohl, 2009; Rodríguez-Solana, Salgado, Domínguez, & Cortés, 2014), electrothermal atomic absorption spectrometry (ETAAS) (Bakkali, Martos, Souhail, & Ballesteros, 2009; Dancsak, Silva, Nóbrega, Jones, & Donati, 2014; López-García, Viñas, Romero-Romero, & Hernández-Córdoba, 2007), and inductively coupled plasma–optical emission spectrometry (ICP–OES) (Sandroni & Smith, 2002). Flame atomic absorption spectrometry (FAAS) is suitable for fast sequential multi-elemental analyses and has been widely used for the determination of macro- and micronutrients in agricultural samples (Gómez-Nieto, Gismera, Sevilla, & Procopio, 2015; Nunes et al., 2011; Oliveira, Gomes Neto, Nóbrega, & Jones, 2010; Stelmach, Pohl, & Szymczycha-Madeja, 2013). However, often the determination of these elements in oilseed samples using FAAS requires an acid digestion sample preparation (Naozuka, Vieira, Nascimento & Oliveira, 2011) to effectively reduce the oil content and convert the solid material into a compatible solution for the instrumentation. Moreover, because of advances in procedures based on the principles of green chemistry, an efficient, robust, and rapid sample pre-treatment using an ultrasound system (Lavilla, Vilas, & Bendicho, 2008; Nascentes, Korn, & Arruda, 2001; Neves et al., 2009; Ruiz-Jiménez, Luque-García, & Luque de Castro, 2003) has been routinely applied in laboratories as an alternative sample preparation procedure for challenging matrices that are usually recommended for atomic spectrometry (De La Calle, Cabaleiro, Lavilla, & Bendicho, 2009).

The physical effect produced by ultrasound systems (either bath or probe) includes cavitation, which consists of the nucleation, growth, and collapse of short-lived bubbles, which are formed in liquids/solutions that are exposed to low-frequency ultrasonic waves (<1 MHz) (Neves et al., 2009). During sample preparation, cavitations favor the extraction of chemical species from solid

* Corresponding author.
E-mail address: jorgejunior@ufgd.edu.br (J.L. Raposo Jr.).

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materials through dissolution or complete mineralization (Aleixo et al., 2004; Capelo, Maduro, & Vilhena, 2005; Nascentes et al., 2001; Ruiz-Jiménez et al., 2003) performed at ambient temperature into dilute acid solutions (Aleixo et al., 2004; Domínguez-González, Moreda-Piñeiro, Bermejo-Barrera, & Bermejo-Barrera, 2005; Krishna & Arunachalam, 2004). Therefore, the use of ultrasound-assisted extraction into dilute acid solutions for the determination of macro- and micronutrients in agro-industrial samples avoids the use of concentrated acid solutions for sample digestion.

Herein, this work describe the development of a simple and robust sample preparation procedure that uses an ultrasound-assisted extraction system for the fast-sequential multi-element determination of Cu, Mn, Ca, and Mg in alternative oilseeds crops using FAAS to circumvent conventional sample pretreatment procedures based on acid digestion.

2. Experimental

2.1. Instrumentation and apparatus

An Agilent 240FS flame atomic absorption spectrometer (Agilent Technologies®, Santa Clara, CA, USA) equipped with a deuterium background corrector and monoelement hollow cathode lamps (Agilent Technologies®, Santa Clara, CA, USA) was used throughout this work. High purity acetylene (99.7% White Martins, Dourados, Brazil) was used as fuel, and an air–acetylene flame was used for atomization of Cu, Mn, Ca, and Mg. The optimum acetylene and air flow rates were 2.0 and 13.0 L min^{-1}, respectively, for Cu, Mn, and Mg and 2.2 and 13.4 L min^{-1}, respectively, for Ca. All measurements were performed under optimum conditions using five replicates. A 515 Orion (Fanem®, Brazil) forced air oven and a TE-361 (Tecnal®, Brazil) stainless steel mill were used to dry and powder the oilseed samples, respectively. A Unique USC-14004 (Unique®, Brazil) ultrasonic bath, operating at 40 kHz, was used to leach the elements from the oilseed samples. An Excelsa™ 206 BL (Fanem®, Brazil) centrifuge was used to separate the solid and liquid phases. A Multiwave 3000 microwave oven (Anton Paar®, Graz, Austria) was used as a comparative sample preparation procedure, which employed acid digestion of the samples.

2.2. Reagents and analytical solutions

High purity deionized water obtained from a Milli-Q Plus reverse osmosis system (resistivity 18.2 MΩ cm, Millipore, Bedford, MA, USA) was used to prepare all of the solutions. Nitric acid [65% (v/v), Sigma–Aldrich®, St. Louis, MO, USA] was used for the microwave-assisted acid digestion and to prepare all of the solutions. Hydrochloric acid [37% (v/v), Sigma–Aldrich®, St. Louis, MO, USA] was used to optimize the acid extraction solution. A 5% (m/v) La solution was prepared by dissolving 58.6 g of La_2O_3 (99.9% purity, Sigma–Aldrich®, St. Louis, MO, USA) in 250 mL of concentrated hydrochloric acid, followed by dilution to 1000 mL using deionized water. An aliquot of this solution was added in reference, blank, and sample solution in order to contain 1.0% (m/v) La to avoid the interference caused by phosphate, silicate or aluminum anions on the determination of Ca and Mg in air–acetylene flame.

Different dilute nitric acid solutions (0.14, 1.40, and 2.80 mol L^{-1}) were prepared for the evaluation of the effect of the acid concentration of the extraction solvent on the ultrasonic assisted extraction.

Multi-element analytical solutions containing 0.05–5.00 mg L^{-1} of Cu, 0.10–4.00 mg L^{-1} of Mn, 0.50–4.00 mg L^{-1} of Ca, and 0.30–4.00 mg L^{-1} of Mg were prepared using appropriate dilutions of 1000 mg L^{-1} single-element standard stock solutions (SpecSol®, SRM-682, USA) in 1.0% (v/v) nitric acid and 1.0% (m/v) La solution.

All of the solutions were stored in high-density polypropylene bottles (Nalgene®, Rochester, NY, USA). Plastic bottles and glassware were cleaned by soaking in 10% (v/v) HNO_3 for at least 24 h followed by thorough rinsing with deionized water before use.

2.3. Sampling and sample preparation

Samples from the alternative oilseeds crops *Crambe abyssinica Hochst*, *Guizotia abyssinica*, *Brassica napus var. oleífera*, *Carthamus tinctorius L.*, and *Raphanus sativus L. var. oleiferus Metzg* were collected during the 2012 harvest period from the Experimental Farm of the Agricultural Sciences (22°14′S and 54°49′W), which is situated 8 km from the Federal University of Grande Dourados (Dourados, MS, Brazil). Samples of the seeds of each species (1000 g) were randomly collected, stored in individual labeled paper bags, and then transported to the laboratory. The seeds were separately and thoroughly washed with running tap water, and then with deionized water. A 10.0 g subsample of each oilseed was dried at 70 °C for 168 h in a forced air oven, ground in a stainless steel mill and then sieved using a No. 20 sieve (0.84 mm opening size).

Samples (0.3000 g) were accurately weighed (±0.0001 g) and transferred into a 50 mL polypropylene flask followed by 10 mL acid leaching solution. The tubes were then subjected individually to an ultrasound energy corresponding to ultrasonication at 40 kHz for 10 min to leach the target elements from the seeds into the acid solution. After sonication, the obtained acid extracts were separated from the remaining solid materials using centrifugation for 3 min at 3500 rpm, followed by filtration (Ø = 150 mm, and 80 g m^2 filter paper) into 25 mL polypropylene flasks. All of the acid leaching solutions (samples and blanks) were prepared in 1.0% (w/v) La. Three replicates of each alternative oilseed samples and blank were used to optimize the analytical parameters of the extraction procedure. The final samples were diluted ten times before the determination of Ca and Mg. All of the measurements were performed using five replicates.

The alternative oilseeds materials were also mineralized using conventional acid digestion with a closed-vessel microwave-assisted system for comparative purposes. For this procedure, 0.3000 g of samples were accurately weighed and transferred into a microwave flask followed by 6.0 mL of HNO_3 and 2.0 mL of deionized water. The following optimized heating program involving step, power/ramp time/hold time was: step 1, 600 W/10 min/5 min; step 2, 1000 W/15 min/10 min; step 3, 0 W/0 min/15 min (ventilation). After the digestion and cooling, the resulting solutions obtained were transferred into 25 mL volumetric flasks, and a 5.0 mL aliquot of 5% (m/v) La solution was added, and the volume was completed with deionized water. Three sample replicates were used for the acid decompositions.

Two soybean reference materials PIATV 2/2010 and PIATV 5/2010 (0.84 mm particle size) from Embrapa Agropecuária Oeste (Dourados, MS, Brazil), which are used in national proficiency testing, were used to establish the optimal extraction conditions and were analyzed to check matrix effects and the efficiency of the method.

2.4. Measurement procedure

A fast sequential and multi-element determination were carried out using the main lines for Cu (324.8 nm), Mn (279.5 nm), and Ca (422.7 nm), and the secondary line for Mg (202.6 nm) under optimal instrumental conditions. The influences of the extracting acid, concentration, and sonication time on the sensitivity for Cu, Mn, Ca, and Mg were investigated using the PIATV 5/2010 reference material by varying the acid (HNO_3, HCl, or HNO_3:HCl (1:1, v/v)),

the acid concentration (0.14, 1.40, 2.80, 5.60, and 7.00 mol L^{-1}), and the sonication time (1, 5, 10, 20 min). At a 5.0 mL min^{-1} sample flow rate, multi-element calibration curves were consistently obtained within the 0.05–5.00 mg L^{-1} for Cu, 0.10–4.00 mg L^{-1} for Mn, 0.50–4.00 mg L^{-1} for Ca, and 0.30–4.00 mg L^{-1} for Mg ranges.

The accuracy was evaluated using recovery tests from spiked samples performed at two levels by adding aliquots of the 1000 mg L^{-1} single-element standard stock solutions to the *Crambe abyssinica Hochst* and *Raphanus sativus L var. oleiferus Metzg* oilseed samples before the extraction procedure. Final extracts contained 0.10 and 0.25 mg L^{-1} of Cu, 0.5 and 1.00 mg L^{-1} of Mn, and 1.00 and 2.00 mg L^{-1} of Ca and Mg. The limit of detection (LOD) and limit of quantification (LOQ) for all of the analytes were calculated using IUPAC recommendations (Currie, 1999). Statistical tests used in the data processing (mean, standard deviation, and precision) were performed using the Microcal OriginPro® 8.0 program and Microsoft® Office Excel 2007.

3. Results and discussion

Many studies describe the influence of the sample particle size (De La Rochebrochard, Naffrechoux, Drogui, Mercier, & Blais, 2013), acid (Deng, Feng, & Qiu, 2009), concentration and volume of the extraction solution (Filgueiras, Capelo, Lavilla, & Bendicho, 2000), sonication time (Güngör & Elik, 2007), sample mass (De La Calle et al., 2009), and the ultrasonic power (De La Rochebrochard et al., 2013) on the extraction procedure. Among them, the nature and concentration of the extraction solutions, and sonication time, have a significant influence and are often evaluated during ultrasound-assisted extractions of inorganic species (Domínguez-González et al., 2005; Krishna & Arunachalam, 2004; Lavilla, Vilas, Millos, & Bendicho, 2006; Nascentes et al., 2001). Therefore, to optimize the ultrasonic extraction conditions, the leaching solution and sonication time were varied, whereas the sample mass, extraction solution volume, and bath temperature were held constant at 0.3000 g (±0.0001 g), 10.0 mL, and 25 °C, respectively.

3.1. Optimization of ultrasound-assisted extraction procedures

In ultrasound-assisted extraction procedures, the extraction of analytes from solid matrices can be performed using acidic solutions. The presence of H^+ in the liquid phase can displace the metallic species from the solid sample into the liquid phase as inorganic ions (De Paula, Caldas, Brum, & Cassella, 2013).

Nitric acid is frequently reported in studies of the extraction of metals using ultrasonic energy (Deng et al., 2009); however, other acid solutions and/or mixtures have also been reported. In this work, different acid solutions (HCl, HNO_3, and HCl:HNO_3 (1:1)) at 1.00 mol L^{-1} were evaluated to determine the effectiveness of these reagents for leaching elements from samples using the PIATV 5/2010 reference material. The influence of these different acid solutions was determined using univariate analysis by fixing the solution volume, sonication time, sample mass, and bath temperature at 10 mL, 10 min, 0.3000 g, and 25 °C, respectively. The results obtained are shown in Fig. 1.

It can be seen that unsatisfactory recoveries were obtained with the 1.00 mol L^{-1} acid solutions. All three solutions had recoveries <80%, but had satisfactory relative standard deviations (<6.4%). However, in some cases, notably for the 1.00 mol L^{-1} HNO_3 solution, the recoveries varied in the 77–79% range for the reference soybean sample (PIATV 5/2010). It is important to point that the 1.00 mol L^{-1} HCl:HNO_3 (v/v) solution had recoveries that varied between 74–77%, which were similar and agreed statistically at the 95% confidence level (paired *t*-test) with those obtained with

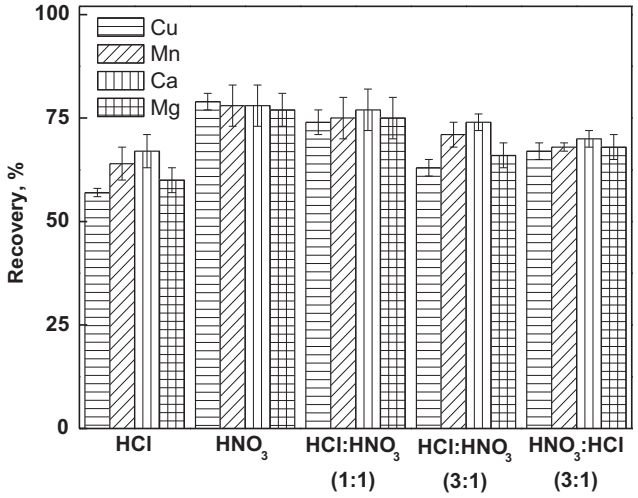


Fig. 1. Effect of different acid solutions on the recoveries of Cu, Mn, Ca, and Mg in the optimization of the ultrasound-assisted extraction procedure. Recoveries values were obtained using 0.3000 g of PIATV 5/2010 with 0.84 mm particle size, 10 mL of 1.0 mol L^{-1} extracting solution and 10 min of sonication at 25 °C.

1.00 mol L^{-1} HNO_3. Alternative acid mixtures, such as *aqua regia* (3:1 (v/v) HCl:HNO_3) and HCl:HNO_3 (1:3 (v/v)) at 1.00 mol L^{-1} were investigated for the extraction procedure (Fig. 1). In both cases, the results were no better than those obtained using 1.00 mol L^{-1} HNO_3, HCl or HCl:HNO_3 (v/v) solution. Because of the promising results obtained with 1.00 mol L^{-1} HNO_3, the remaining investigation was performed using HNO_3 solutions.

Diluted nitric acid solutions are widely used in sample preparation using ultrasound-assisted extraction for the determination of inorganic species (Priego-Capote & de Castro, 2007). Satisfactory extraction should result in complete leaching of the analyte without the destruction of the sample matrix using a minimum amount of the selected acids. However, in some cases, the concentration of the acid solutions can reach 50% (Capelo et al., 2005). Based on this information, different concentrations of nitric acid (0.14, 1.40, 2.80, 5.60, and 7.00 mol L^{-1}) were used to evaluate their performance in the extraction procedure. The influence of these HNO_3 solutions on the element recoveries was evaluated by fixing the solution volume, sonication time, sample mass, and bath temperature.

With the 240 FS equipment adjusted to 5.0 mL min^{-1} aspiration flow rate, the 0.14, 1.40, and 2.80 mol L^{-1} HNO_3 solutions did not influence the aspiration flow rate of the extracts. However, the aspiration flow rates decreased to 4.0 mL min^{-1} for the 5.60 and 7.00 mol L^{-1} sample solutions. For sample introduction systems based on nebulization chambers, the efficiency of sample transport is highly dependent on its viscosity and surface tension (Raposo, Oliveira, Jones & Gomes Neto, 2012). Taking this into account, the sample flow rate is dependent on the viscosity of the extract solutions. Based on these results, only the 0.14, 1.40, and 2.80 mol L^{-1} HNO_3 solutions were evaluated (Fig. 2).

As illustrated in Fig. 2, a significant improvement was observed in the recoveries from the 0.14 to 1.40 mol L^{-1} HNO_3 solutions. The 1.40 mol L^{-1} HNO_3 solution was able to extract >50% of each element compared to the 0.14 mol L^{-1} HNO_3 solution. While the recoveries for 0.14 mol L^{-1} solution were in the 60–65% range, those of the 1.40 mol L^{-1} solution were 92%, 94%, 98%, and 94% for Cu, Mn, Ca, and Mg, respectively, and all with satisfactory relative standard deviations (<4.9%). The same behavior was observed in the results obtained for the 2.80 mol L^{-1} HNO_3 solution, because the extracted Cu, Mn, Ca, and Mg contents from the PIATV 5/2010 reference material were ~95%. No significant difference at the 95% confidence level (paired *t*-test), was observed between the 1.40

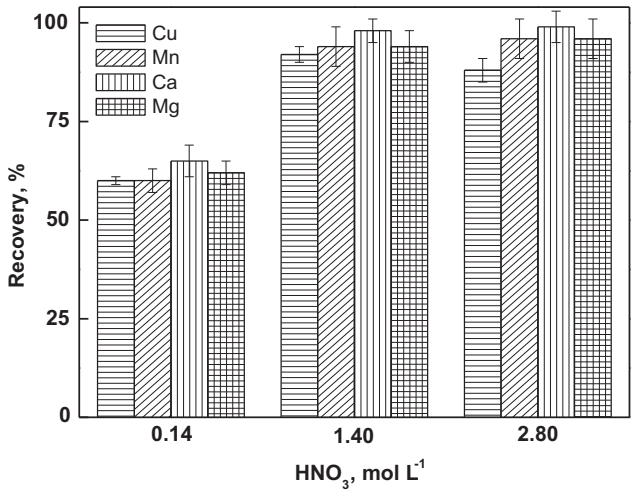


Fig. 2. Influence of variation of HNO_3 concentration on the recoveries of Cu, Mn, Ca, and Mg in the optimization of the ultrasound-assisted extraction procedure. Recoveries values were obtained using 0.3000 g of PIATV 5/2010 with 0.84 mm particle size, 10 mL of extracting solution and 10 min of sonication at 25 °C.

and 2.80 mol L^{-1} solutions. Given these results, the 1.40 mol L^{-1} HNO_3 solution was used for all subsequent extractions because of its complete extraction of the target elements and minimized acid concentration.

Even with these satisfactory results, the sonication time was evaluated to minimize the time required for the proposed procedure. For this, 0.3000 g of PIATV 5/2010 was subjected to 1, 5, 10, and 20 min of sonication under the previously optimized conditions (Fig. 3).

According to the results shown in Fig. 3, an increase in the recoveries was observed from 1 to 10 min of sonication. The amount of Cu, Mn, Ca, and Mg extracted from the PIATV 5/2010 improved from 66% to 93% (Cu), 69% to 94% (Mn), 86% to 98% (Ca), and 63% to 95% (Mg) between 1 and 10 min, respectively. To confirm the results obtained after 10 min, a 20 min sonication was also performed. From Fig. 3, there was no significant difference

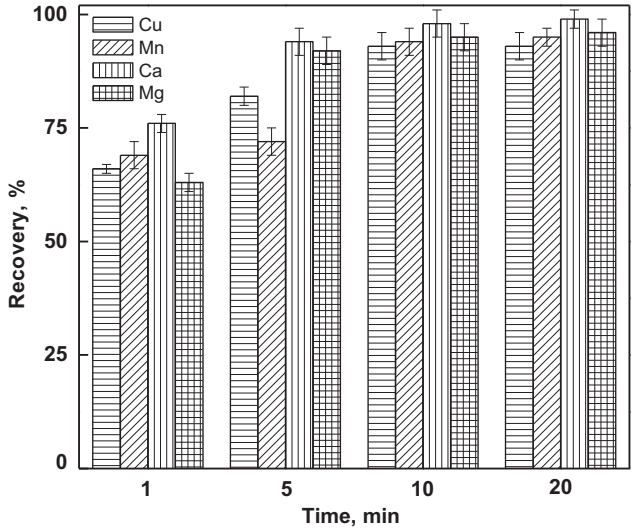


Fig. 3. Influence of sonication time on the recoveries of Cu, Mn, Ca, and Mg in the optimization of the ultrasound-assisted extraction procedure. Recoveries values were obtained using 0.3000 g of PIATV 5/2010 with 0.84 mm particle size, 10 mL of 1.40 mol L^{-1} HNO at 25 °C.

observed at the 95% confidence level (paired *t*-test) for the Cu, Mn, Ca, and Mg recovered between 10 and 20 min of sonication. The precision, which was calculated as relative standard deviation (% RSD), for the recoveries of Cu, Mn, Ca, and Mg extracted from the PIATV 5/2010 after 10 min of sonication were close to 3.2%, 4.3%, 3.2% and 3.3%, respectively. Sonication at 40 kHz for 10 min was satisfactory and minimized the extraction time. Typically, sonication times range from minutes to hours (Capelo et al., 2005), and analyte–matrix interactions can contribute to this (De La Calle et al., 2009).

After optimizing the acid solution and sonication time, the optimal conditions for the ultrasound system when used to leach Cu, Mn, Ca, and Mg from the PIATV 5/2010 reference material were determined to be 10 mL of 1.40 mol L^{-1} HNO_3 solution, 0.84 mm particle size, 0.3000 g sample mass, and 10 min of sonication time at 25 °C. These conditions were used to check the matrix effects of the proposed method and for the analysis of samples.

3.2. Analytical features and validation method

Under the optimum conditions of the 240 FS FAAS equipment, analytical curves were constantly built up in the ranges of 0.05–5.00 mg L^{-1} for Cu, 0.10–4.00 mg L^{-1} for Mn, 0.50–4.00 mg L^{-1} for Ca, and 0.30–4.00 mg L^{-1} for Mg, and typical linear correlation coefficients of 0.9992, 0.9994, 0.9988, and 0.9995 were obtained for Cu, Mn, Ca, and Mg, respectively. The limits of detection, which were calculated using LOD = $3.SD_{blk}/b$, where SD_{blk} was the standard deviation of twelve consecutive blanks and b was the slope of the calibration curve (Cu = 0.0755, Mn = 0.1223, Ca = 0.0214, and Mg = 0.0137), were 666.7, 416.7, 333.4 μg g^{-1}, and 3.5 mg g^{-1} for Cu, Mn, Ca, and Mg, respectively. The precisions, which are expressed as the relative standard deviation (%RSD) for $n = 5$, were 1.2%, 4.1%, 2.9%, and 2.6% for the determination of Cu, Mn, Ca, and Mg using FAAS, respectively.

The accuracy of the proposed extraction procedure and determination method was evaluated using two reference materials (PIATV 5/2010 and PIATV 2/2010), and are presented in Table 1. A paired *t*-test was applied to verify the agreement between the reference and measured values of the materials, and the results obtained for Student's *t*-test revealed no significant differences at the 95% confidence level. Using the proposed extraction procedure, the results obtained for the reference materials were suitable for determination of the analytes in the selected oilseed samples.

3.3. Analysis of samples

Initially, an optimization study of the ultrasound-assisted extraction procedure was performed to establish the optimum conditions for determining Cu, Fe, Mn, Zn, Ca, and Mg. However, the Fe and Zn contents measured using preliminary results from the PIATV 5/2010 reference material were statistically different at the 95% of confidence level (paired *t*-test) from those observed in the reference material. The Fe and Zn contents extracted from PIATV 5/2010 at the beginning of the optimization study were,

Table 1
Results (mean ± standard deviation) for the determination ($n = 3$) of Cu, Mn, Ca, and Mg (mg g^{-1}) in PIATV 5/2010 reference material by FAAS employing the ultrasound-assisted extraction procedure.

Element	PIATV 2/2010		PIATV 5/2010	
	Reference	Found	Reference	Found
Cu	ND	ND	0.11 ± 0.01	0.102 ± 0.003
Mn	1.39 ± 0.04	1.28 ± 0.03	0.32 ± 0.03	0.301 ± 0.013
Ca	24.59 ± 1.04	23.60 ± 0.99	10.11 ± 0.86	9.91 ± 0.32
Mg	2.27 ± 0.11	2.11 ± 0.08	3.34 ± 0.28	3.17 ± 0.10

respectively, ~40 and 130% of that expected (0.174 ± 0.027 mg g^{-1} for Fe and 0.018 ± 0.002 mg g^{-1} for Zn). Although these preliminary results were unsatisfactory, the optimization of the extraction procedure was performed including Fe and Zn in the analysis. After optimizing all of the extraction parameters, the recoveries of Fe and Zn were still not improved beyond 50% (0.087 ± 0.007 mg g^{-1}) and 140% (0.025 ± 0.003 mg g^{-1}), respectively. The relative standard deviations of Zn were always >12% and those of Fe were ~8.0%. A high stability of the chelate between Fe^{2+} (in non-heme iron form) with organic matter is very common in vegetable species, and might have contributed to the low recoveries obtained by the proposed procedure. However, the higher recoveries for Zn can be explained by nitrogen monoxide molecular absorption bands, which overlap the atomic line for Zn at 213.9 nm in an air–acetylene flame (Welz, Becker-Ross, Florek, & Heitmann, 2005). This interference can only be eliminated using a least-squares background correction (LBSC) technique (Oliveira, Raposo, & Gomes Neto, 2009) using the instrumental features of high-resolution continuum source atomic absorption spectrometry (HR-CSAAS). Because Fe and Zn cannot be determined by LS FAAS because of the drawbacks cited above, only Cu, Mn, Ca, and Mg were determined in the alternative oilseed samples.

The analytical results for the determination of Cu, Mn, Ca, and Mg in five alternative oilseed samples are shown in Table 2. It shows that the concentrations ranges obtained for Cu, Mn, Ca, and Mg using FAAS with the ultrasound-assisted extraction procedure were in the ranges of 3.45 ± 0.21–18.65 ± 0.79 mg g^{-1} for Cu, 13.03 ± 0.80–51.97 ± 0.86 mg g^{-1} for Mn, 0.83 ± 0.04–3.47 ± 0.11 mg g^{-1} for Ca, and 1.77 ± 0.06–2.35 ± 0.07 mg g^{-1} for Mg, and these results are in agreement at the 95% confidence level (paired *t*-test) with those obtained using the microwave-assisted digestion (MAD) comparative sample preparation. To complement the evaluation of the proposed method and/or to check matrix effects, an addition and recovery test was also performed using *Crambe abyssinica Hochst* and *Raphanus sativus L var. oleiferus Metzg* oilseed samples. For the addition of the analytes, aliquots of single-element standard stock solutions were added to 0.3000 g samples in order to contain 0.10 and 0.25 mg L^{-1} of Cu, 0.5 and 1.00 mg L^{-1} of Mn, and 1.00 and 2.00 mg L^{-1} of Ca and Mg. The spiked samples were subjected to the optimized extraction procedure and recoveries of 95.5–102.7% for Cu, 89.0–93.7% for Mn, 99.1–105.9% for Ca, and 98.8–100.4% for Mg were obtained, which indicated that the extraction procedure was free of matrix interferences. The RSD (n = 12) for all of the elements varied within the ranges of 0.52–6.13% for ultrasound-assisted extraction and 0.42–5.35% for MAD.

Table 2
Comparative results (mean ± standard deviation) for the determination (n = 3) of Cu and Mn (μg g^{-1}), Ca and Mg (mg g^{-1}) in oilseed samples by FAAS using the proposed ultrasound-assisted extraction and microwave-assisted digestion procedures.

Sample	Element	Ultrasound-assisted extraction	Microwave-assisted digestion
Crambe abyssinica Hochst	Cu	3.45 ± 0.21	3.74 ± 0.13
	Mn	13.03 ± 0.80	13.72 ± 0.68
	Ca	2.72 ± 0.15	2.92 ± 0.10
	Mg	2.08 ± 0.07	2.21 ± 0.09
Guizotia abyssinica	Cu	14.43 ± 0.29	15.39 ± 0.38
	Mn	26.52 ± 1.40	27.92 ± 0.40
	Ca	2.40 ± 0.12	2.66 ± 0.09
	Mg	2.19 ± 0.03	2.36 ± 0.08
Brassica napus var. oleífera	Cu	4.59 ± 0.21	4.82 ± 0.19
	Mn	51.97 ± 0.86	53.96 ± 0.23
	Ca	3.47 ± 0.11	3.74 ± 0.20
	Mg	2.30 ± 0.09	2.52 ± 0.10
Carthamus tinctorius L.	Cu	18.65 ± 0.79	19.18 ± 0.76
	Mn	21.27 ± 0.40	22.86 ± 0.48
	Ca	0.83 ± 0.04	0.86 ± 0.04
	Mg	1.77 ± 0.06	1.82 ± 0.02
Raphanus sativus L. var. oleiferus Metzg	Cu	5.01 ± 0.21	5.22 ± 0.15
	Mn	19.30 ± 0.10	20.78 ± 0.55
	Ca	2.67 ± 0.08	2.74 ± 0.03
	Mg	2.35 ± 0.07	2.39 ± 0.07

4. Conclusions

A fast, accurate, and efficient sample preparation based on ultrasound-assisted extraction was proposed and evaluated for the determination of Cu, Mn, Ca, and Mg in alternative oilseed crop samples using fast-sequential flame atomic absorption spectrometry. In general, the proposed sample preparation resulted in the minimal generation of wastes or residues, which saves the consumption of reagents, and therefore contributes to a green chemistry procedure.

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References

Aleixo, P. C., Júnior, D. S., Tomazelli, A. C., Rufini, I. A., Berndt, H., & Krug, F. J. (2004). Cadmium and lead determination in foods by beam injection flame furnace atomic absorption spectrometry after ultrasound-assisted sample preparation. *Analytica Chimica Acta, 512*(2), 329–337.

Bakkali, K., Martos, N. R., Souhail, B., & Ballesteros, E. (2009). Characterization of trace metals in vegetables by graphite furnace atomic absorption spectrometry after closed vessel microwave digestion. *Food Chemistry, 116*(2), 590–594.

Capelo, J. L., Maduro, C., & Vilhena, C. (2005). Discussion of parameters associated with the ultrasonic solid–liquid extraction for elemental analysis (total content) by electrothermal atomic absorption spectrometry. An overview. *Ultrasonics Sonochemistry, 12*(3), 225–232.

Currie, L. A. (1999). Nomenclature in evaluation of analytical methods including detection and quantification capabilities. *Analytica Chimica Acta, 391*(2), 105–126.

Dancsak, S. E., Silva, S. G., Nóbrega, J. A., Jones, B. T., & Donati, G. L. (2014). Direct determination of sodium, potassium, chromium and vanadium in biodiesel fuel by tungsten coil atomic emission spectrometry. *Analytica Chimica Acta, 806*, 85–90.

De La Calle, I., Cabaleiro, N., Lavilla, I., & Bendicho, C. (2009). Analytical evaluation of a cup-horn sonoreactor used for ultrasound-assisted extraction of trace metals from troublesome matrices. *Spectrochimica Acta Part B: Atomic Spectroscopy, 64*(9), 874–883.

De La Rochebrochard, S., Naffrechoux, E., Drogui, P., Mercier, G., & Blais, J.-F. (2013). Low frequency ultrasound-assisted leaching of sewage sludge for toxic metal removal, dewatering and fertilizing properties preservation. *Ultrasonics Sonochemistry, 20*(1), 109–117.

Deng, J., Feng, X., & Qiu, X. (2009). Extraction of heavy metal from sewage sludge using ultrasound-assisted nitric acid. *Chemical Engineering Journal, 152*(1), 177–182.

De Paula, C. E. R., Caldas, L. F. S., Brum, D. M., & Cassella, R. J. (2013). Development of a focused ultrasound-assisted extraction method for the determination of trace concentrations of Cr and Mn in pharmaceutical formulations by ETAAS. *Journal of Pharmaceutical and Biomedical Analysis, 74*, 284–290.

Domínguez-González, R., Moreda-Piñeiro, A., Bermejo-Barrera, A., & Bermejo-Barrera, P. (2005). Application of ultrasound-assisted acid leaching procedures for major and trace elements determination in edible seaweed by inductively coupled plasma-optical emission spectrometry. *Talanta, 66*(4), 937–942.

Farago, M. E. (1994). *Plants and the chemical elements: Biochemistry, uptake, tolerance and toxicity*. Weinheim, New York: VCH.

Filgueiras, A. V., Capelo, J. L., Lavilla, I., & Bendicho, C. (2000). Comparison of ultrasound-assisted extraction and microwave-assisted digestion for determination of magnesium, manganese and zinc in plant samples by flame atomic absorption spectrometry. *Talanta, 53*(2), 433–441.

Gómez-Nieto, B., Gismera, M. J., Sevilla, M. T., & Procopio, J. R. (2015). Fast sequential multi-element determination of major and minor elements in environmental samples and drinking waters by high-resolution continuum

source flame atomic absorption spectrometry. *Analytica Chimica Acta, 854*, 13–19.
Güngör, H., & Elik, A. (2007). Comparison of ultrasound-assisted leaching with conventional and acid bomb digestion for determination of metals in sediment samples. *Microchemical Journal, 86*(1), 65–70.
Kassem, M. A., & Amin, A. S. (2013). Spectrophotometric determination of iron in environmental and food samples using solid phase extraction. *Food Chemistry, 141*(3), 1941–1946.
Krishna, M. V. B., & Arunachalam, J. (2004). Ultrasound-assisted extraction procedure for the fast estimation of major, minor and trace elements in lichen and mussel samples by ICP–MS and ICP–AES. *Analytica Chimica Acta, 522*(2), 179–187.
Lavilla, I., Vilas, P., & Bendicho, C. (2008). Fast determination of arsenic, selenium, nickel and vanadium in fish and shellfish by electrothermal atomic absorption spectrometry following ultrasound-assisted extraction. *Food Chemistry, 106*(1), 403–409.
Lavilla, I., Vilas, P., Millos, J., & Bendicho, C. (2006). Development of an ultrasound-assisted extraction method for biomonitoring of vanadium and nickel in the coastal environment under the influence of the Prestige fuel spill (North east Atlantic Ocean). *Analytica Chimica Acta, 577*(1), 119–125.
Liu, H., Cheng, T., Xian, M., Cao, Y., Fang, F., & Zou, H. (2014). Fatty acid from the renewable sources: A promising feedstock for the production of biofuels and biobased chemicals. *Biotechnology Advances, 32*(2), 382–389.
López-García, I., Viñas, P., Romero-Romero, R., & Hernández-Córdoba, M. (2007). Fast determination of phosphorus in honey, milk and infant formulas by electrothermal atomic absorption spectrometry using a slurry sampling procedure. *Spectrochimica Acta Part B: Atomic Spectroscopy, 62*(1), 48–55.
Nabi, M. N., Rahman, M. M., Islam, M. A., Hossain, F. M., Brooks, P., Rowlands, W. N., ... Brown, R. J. (2015). Fuel characterisation, engine performance, combustion and exhaust emissions with a new renewable Licella biofuel. *Energy Conversion and Management, 96*, 588–598.
Naozuka, J., Vieira, E. Carvalho, Nascimento, A. N., & Oliveira, P. V. (2011). Elemental analysis of nuts and seeds by axially viewed ICP OES. *Food Chemistry, 124*(4), 1667–1672.
Nascentes, C. C., Korn, M., & Arruda, M. A. (2001). A fast ultrasound-assisted extraction of Ca, Mg, Mn and Zn from vegetables. *Microchemical Journal, 69*(1), 37–43.
Neves, R. C. F., Moraes, P. M., Saleh, M. A. D., Loureiro, V. R., Silva, F. A., Barros, M. M., ... Padilha, P. M. (2009). FAAS determination of metal nutrients in fish feed after ultrasound extraction. *Food Chemistry, 113*(2), 679–683.
Nigam, P. S., & Singh, A. (2011). Production of liquid biofuels from renewable resources. *Progress in Energy and Combustion Science, 37*(1), 52–68.
Nunes, L. S., Barbosa, J. T. P., Fernandes, A. P., Lemos, V. A., dos Santos, W. N. L., Korn, M. G. A., & Teixeira, L. S. G. (2011). Multi-element determination of Cu, Fe, Ni and Zn content in vegetable oils samples by high-resolution continuum source atomic absorption spectrometry and microemulsion sample preparation. *Food Chemistry, 127*(2), 780–783.
Oliveira, S. R., Gomes Neto, J. A., Nóbrega, J. A., & Jones, B. T. (2010). Determination of macro- and micronutrients in plant leaves by high-resolution continuum source flame atomic absorption spectrometry combining instrumental and sample preparation strategies. *Spectrochimica Acta Part B: Atomic Spectroscopy, 65*(4), 316–320.
Oliveira, S. R., Raposo, J. L., & Gomes Neto, J. A. (2009). Fast sequential multi-element determination of Ca, Mg, K, Cu, Fe, Mn and Zn for foliar diagnosis using high-resolution continuum source flame atomic absorption spectrometry: Feasibility of secondary lines, side pixel registration and least-squares background correction. *Spectrochimica Acta Part B: Atomic Spectroscopy, 64*(6), 593–596.
Pohl, P. (2009). Determination of metal content in honey by atomic absorption and emission spectrometries. *TrAC Trends in Analytical Chemistry, 28*(1), 117–128.
Priego-Capote, F., & de Castro, L. (2007). Ultrasound-assisted digestion: A useful alternative in sample preparation. *Journal of Biochemical and Biophysical Methods, 70*(2), 299–310.
Raposo, J. L., Jr., Oliveira, A. P., Jones, B. T., & Neto, J. A. G. (2012). Internal standardization combined with dilute-and-shoot preparation of distilled alcoholic beverages for Cu determination by high-resolution continuum source flame atomic absorption spectrometry. *Talanta, 92*, 53–57.
Rodríguez-Solana, R., Salgado, J. M., Domínguez, J. M., & Cortés, S. (2014). Assessment of minerals in aged grape marc distillates by FAAS/FAES and ICP–MS. Characterization and safety evaluation. *Food Control, 35*(1), 49–55.
Ruiz-Jiménez, J., Luque-García, J. L., & Luque de Castro, M. D. (2003). Dynamic ultrasound-assisted extraction of cadmium and lead from plants prior to electrothermal atomic absorption spectrometry. *Analytica Chimica Acta, 480*(2), 231–237.
Sabarudin, A., Oshima, M., & Motomizu, S. (2003). Ultratrace determination of phosphorus in ultrapurified water by a slope comparison method. *Analytica Chimica Acta, 481*(2), 311–319.
Sandroni, V., & Smith, C. M. M. (2002). Microwave digestion of sludge, soil and sediment samples for metal analysis by inductively coupled plasma–atomic emission spectrometry. *Analytica Chimica Acta, 468*(2), 335–344.
Stelmach, E., Pohl, P., & Szymczycha-Madeja, A. (2013). The suitability of the simplified method of the analysis of coffee infusions on the content of Ca, Cu, Fe, Mg, Mn and Zn and the study of the effect of preparation conditions on the leachability of elements into the coffee brew. *Food Chemistry, 141*(3), 1956–1961.
Szydłowska-Czerniak, A., & Szłyk, E. (2003). Spectrophotometric determination of total phosphorus in rape seeds and oils at various stages of technological process: Calculation of phospholipids and non-hydratable phospholipids contents in rapeseed oil. *Food Chemistry, 81*(4), 613–619.
Tarafder, P. K., & Thakur, R. (2005). Surfactant-mediated extraction of iron and its spectrophotometric determination in rocks, minerals, soils, stream sediments and water samples. *Microchemical Journal, 80*(1), 39–43.
Welz, B., Becker-Ross, H., Florek, S., & Heitmann, U. (Eds.). (2005). *High-resolution continuum source AAS: The better way to do atomic absorption spectrometry*. Weinheim: Wiley-VCH (Great Britain).