



# A new approach to mineralization of flaxseed (*Linum usitatissimum* L.) for trace element analysis by flame atomic absorption spectrometry



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## ABSTRACT

A new approach to the analysis of Cu, Fe, Mn and Zn in flaxseed was developed based on infrared-assisted acid digestion. Quantitation by flame atomic absorption spectrometry yields results in agreement with those arising from aggressive total decomposition using conventional microwave-assisted (MW) digestions. A full factorial design in two levels was applied to evaluate the impact of significant variables for all elements to determine optimal experimental conditions. A desirability function revealed these to be: 2.0 g sample mass, 8 mL of HNO<sub>3</sub> and 8 min of heating time in the IR system. Precision better than 10% (RSD) was obtained, superior to that of a combined IR-MW approach. Sample preparation based on IR-assisted digestion provides a rapid and inexpensive alternative to other conventional techniques for the analysis of complex samples and is able to accommodate relatively large masses of sample, alleviating potential homogeneity issues as well as enhancing detection power.

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## 1. Introduction

Flaxseed (*Linum usitatissimum* L.) belongs to the family of Linaceae, and exists as both brown and golden varieties, depending on the geographical region where they are grown. The brown flaxseed is found in tropical climates (e.g., Latin America) whereas the golden variety originates in countries having milder temperatures, such as North America and Europe; Canada is the largest producer (Oomah & Mazza, 1999). Both present similar characteristics in composition (32–35% protein) and are considered to be an excellent source of arginine, glutamine and histidine, amino acids well-known for their immunological function. High cysteine and methionine levels are present as well, contributing to antioxidant activity, helping to stabilize DNA during cell division and reduce the risk of colon cancer (Oomah, 2001).

Flaxseed proves to be a complex matrix because, in addition to its high protein content, a 40% lipid composition comprised of 51–55% alpha linolenic acid and 15–18% linoleic acid is present (Carter, 1993). The main advantage for health is that flaxseed oil reduces the risk of cardiovascular problems as well as prevents cancer due to the presence of biologically active phytochemicals (Caragay, 1992).

Approximately one third of all proteins and enzymes contain strongly bound elements in their structures, especially transition

metals such as copper, cobalt, iron, manganese, molybdenum and zinc (Bittencourt et al., 2014). Biochemical processes in enzymes and proteins, including activation of substrate, transport and storage, are performed by these elements, which are called minerals (Naozuka, Marana, & Oliveira, 2010; Soetan, Olaiya, & Oyewole, 2010). Due to the high content of proteins, flaxseed is expected to be a rich source of these elements.

Although flaxseed is comprehensively described in the literature (Caragay, 1992; Carter, 1993; Marthe, Augusti, & Costa, 2015; Oomah, 2001; Oomah, Der, & Godfrey, 2006; Oomah & Mazza, 1993, 1999; Sosulski & Sarwar, 1973), its mineral composition is not well known. Marthe et al. (2015), describe the quantification of trace elements bound to proteins in flaxseed samples after removal of the lipid fraction. Several extraction media were studied for this purpose and the defatted samples were digested using a cavity microwave oven to permit quantitation of Cu, Fe and Zn by flame atomic absorption spectrometry (FAAS). The separated protein fractions were also isolated using a TRIS buffer and mineral contents quantified by graphite furnace AAS (GFAAS) (Marthe et al., 2015). Lipid removal steps are very time consuming and the solvents used may introduce contamination to the sample. Nevertheless, this step also accomplishes a pre-concentration of analytes present in the protein phase, which allows their quantification by less sensitive techniques such as FAAS.

Microwave-assisted digestion in closed systems is one of the most used techniques for sample preparation. Commonly, considering samples containing a significant organic fraction, nitric acid

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is used as the oxidizing reagent and high pressures and temperatures ensure complete decomposition of the organic matter (Dantas, Matos, Gouveia, & Lopes, 2013; Krug, 2009; Kubrakova & Toropchenova, 2008; Market, 1995), making the elements of interest available in a simple solution. However, in order to reach high pressures and temperatures, small masses of samples, typically less than 250 mg (depending on their organic carbon content), are required so as not to exceed the safe pressure limits of the digestion system. Such a limitation directly affects subsequent quantitation of minerals present at low concentration and may give rise to large imprecisions in the results when heterogeneous samples are encountered and representative sample masses cannot be utilized.

Most recently, microwave-induced combustion has become available for the preparation of sample masses up to 500 mg. Efficient combustion of organic matter in quartz tubes pressurized with oxygen followed by a conventional microwave assisted reflux of the residue ensures absorption of elements of interest in either acid or alkaline medium for their subsequent analysis (Flores, Barin, Paniz, Medeiros, & Knapp, 2004).

Focused microwave radiation has also been used as an alternative approach for the digestion of large masses of sample (0.5–5 g) (Matusewicz, 1999; Santos & Oliveira, 2001), however, this technique consumes large volumes of acid, and requires extensive dilutions before analysis (Nóbrega, Trevisan, Araújo, & Nogueira, 2002).

Although a less popular technique, application of infrared radiation (IR) for sample preparation has been shown to be a viable alternative, utilizing inexpensive materials and providing efficiencies comparable to other preparation methodologies. Dantas et al. (2013) described a system that combined an IR source with a conventional microwave assisted digestion system to realize the complete decomposition of up to 1.0 g of food for the determination of trace elements by ICP OES. Relative standard deviations of better than 8% were obtained for all elements of interest. A short period of initial IR heating of the sample in the presence of a small volume of nitric acid accomplished a pre-digestion of up to 80% of the carbon content, thereafter allowing the mixture to be easily accommodated by the closed microwave oven system. Gouveia, Fatibello-Filho, and Nóbrega (2000) used a system comprising three tungsten lamps for the extraction of metals from apple leaves and bovine liver Standard Reference Materials for determination of element content by GFAAS. Good precision was obtained (RSDs <10%) with results in agreement with certificate values.

The aim of this study was to evaluate the effectiveness of an IR heating source for the digestion of two varieties of flaxseed in order to quantify Cu, Fe, Mn and Zn by FAAS without the need for complete digestion of the sample.

## 2. Experimental

### 2.1. Samples and reagents

Flaxseed samples, purchased from a local market in Fortaleza, Ceara, Brazil, were ground using a coffee grinder fitted with stainless steel blades and stored in previously decontaminated vials. The mill was also cleaned before use by grinding a sacrificial sub-sample of flaxseed and discarding it before processing the final material used for analysis.

Solutions were prepared using ultrapure water (18.2 M $\Omega$  cm resistivity) obtained from a Milli-Q water purification system (Millipore, Bedford, MA, USA). All glassware was immersed in nitric acid 10% v v<sup>-1</sup> (Vetec, Rio de Janeiro, Brazil) for 24 h and thoroughly rinsed with ultrapure water. The extraction procedures and digestions were accomplished using 65% w w<sup>-1</sup> nitric acid (Vetec), 37% w w<sup>-1</sup> hydrochloric acid (Sigma Aldrich, Germany)

and 30% w w<sup>-1</sup> hydrogen peroxide (Vetec). The lipid extraction was accomplished using 98.5% w w<sup>-1</sup> methanol (Sigma Aldrich) and 98% w w<sup>-1</sup> chloroform (Vetec). Standard calibration solutions were prepared after successive dilutions of their 1000 mg L<sup>-1</sup> Cu, Fe, Mn and Zn (Acros Organics, Belgium) stock solutions.

### 2.2. Instrumentation

Samples were dried in an oven (Micronal, Piracicaba, SP, Brazil) for 1 h at 105 °C.

Fig. 1 illustrates the IR digestion system, which consisted of a medium-density fibreboard (MDF) box 30 cm × 17 cm × 20 cm, internally coated with aluminum foil and fitted with a removable lid having an orifice large enough to accommodate a quartz vessel of 50 mL from an Anton Paar microwave digestion system. The latter is supported by the orifice in the lid at the top and rests on a glass plate placed on the bottom of the box. A tungsten halogen lamp (500W, FLC, China) 1.8 cm long and 0.6 cm diameter, served as the IR source, located at one end of the box and approximately 3 cm from the sample tube. A parabolic shaped aluminum reflector was located on the opposite side of the sample tube, approximately 5 cm from the tube in order to maximize the irradiation of the sample with the IR lamp. Temperature measurements of the contents of the quartz vessel were periodically made using a hand held radiation thermometer (Power First, Canada; temperature range – 30 °C to 550 °C with resolution 0.1 °C), focused onto the vessel through an observation window on the side of the box.

For comparison of analytical performance, digestion of the sample was also accomplished using the IR-MW system described by Dantas et al. (2013) which utilized an E-27 – ES PHILCO 250W/220V IR source and an Anton Paar Multiwave digestion system (Graz, Austria) equipped with a rotor containing six 50 mL quartz vessels.

A Varian AS 240FS Flame AA Spectrometer (Mulgrave, Australia) equipped with deuterium lamp for background correction and air-acetylene flame was used for quantification of the elements. The wavelengths and spectral bandwidths (SBWs) used for the analysis are, respectively, described as follows: 324.7 nm, 0.5 nm (Cu), 372.0 nm, 0.2 nm (Fe), 279.5 nm, 0.2 nm (Mn), 213.9 nm, 1.0 nm (Zn). The linear ranges were: 0.03 – 10 mg L<sup>-1</sup> (Cu), 1.0–100 mg L<sup>-1</sup> (Fe), 0.02–5 mg L<sup>-1</sup> (Mn) and 0.01–2 mg L<sup>-1</sup> (Zn)

Near IR analysis of undigested sample residue was conducted with a Vertex 70 spectrometer (Bruker Billerica, MA, USA) equipped with an attenuated total reflectance accessory (diamond ATR Miracle).

### 2.3. Lipid phase removal

Extraction of the lipid phase was undertaken using the method described by Bittencourt et al. (2014). To 1.0 g of the dried sample was added 5 mL of a mixture of methanol and chloroform (1:2 v v<sup>-1</sup>). The solution was then stirred manually for 15 min and centrifuged at 3000 rpm for 10 min. The process was repeated 3 times. As a final step, the sample was dried in an oven for 1 h at 100 °C to remove residual solvent.

### 2.4. Sample preparation using combined IR-MW

Sample digestion using the IR-MW system described by Dantas et al. (2013) permitted verification of the accuracy of the proposed method. Typically, 6 mL of 65% w w<sup>-1</sup> HNO<sub>3</sub> were added to a 1.0 g mass of sample and exposed to IR radiation for 20 min. Addition of 1 mL 30% w w<sup>-1</sup> H<sub>2</sub>O<sub>2</sub> before subsequent digestion in the microwave oven was necessary. The microwave-heating program consisted of four steps, as follows: first, power ramp 100–600 W

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