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# Microwave-assisted wet digestion with H<sub>2</sub>O<sub>2</sub> at high temperature and pressure using single reaction chamber for elemental determination in milk powder by ICP-OES and ICP-MS



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## ABSTRACT

In this work a green digestion method which only used H<sub>2</sub>O<sub>2</sub> as an oxidant and high temperature and pressure in the single reaction chamber system (SRC-UltraWave™) was applied for subsequent elemental determination by inductively coupled plasma-based techniques. Milk powder was chosen to demonstrate the feasibility and advantages of the proposed method. Samples masses up to 500 mg were efficiently digested, and the determination of Ca, Fe, K, Mg and Na was performed by inductively coupled plasma optical emission spectrometry (ICP-OES), while trace elements (B, Ba, Cd, Cu, Mn, Mo, Pb, Sr and Zn) were determined by inductively coupled plasma mass spectrometry (ICP-MS). Residual carbon (RC) lower than 918 mg L<sup>-1</sup> of C was obtained for digests which contributed to minimizing interferences in determination by ICP-OES and ICP-MS. Accuracy was evaluated using certified reference materials NIST 1549 (non-fat milk powder certified reference material) and NIST 8435 (whole milk powder reference material). The results obtained by the proposed method were in agreement with the certified reference values (*t*-test, 95% confidence level). In addition, no significant difference was observed between results obtained by the proposed method and conventional wet digestion using concentrated HNO<sub>3</sub>. As digestion was performed without using any kind of acid, the characteristics of final digests were in agreement with green chemistry principles when compared to digests obtained using conventional wet digestion method with concentrated HNO<sub>3</sub>. Additionally, H<sub>2</sub>O<sub>2</sub> digests were more suitable for subsequent analysis by ICP-based techniques due to of water being the main product of organic matrix oxidation. The proposed method was suitable for quality control of major components and trace elements present in milk powder in consonance with green sample preparation.

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## 1. Introduction

Milk powder is a complex matrix composed of several organic molecules, such as proteins, carbohydrates and fat. It is a kind of food that is normally a source of essential minerals, but it can also contain toxic elements. In order to ensure health properties, quality control of milk powder should be carefully performed [1]. To avoid mistakes in this step, mainly those related to matrix effects during elemental determination, samples should be previously digested to bring the analytes into solution for subsequent analysis by using suitable analytical techniques. In this sense, a lot of methods are available in the literature to oxidize refractory matrices and the most common are dry ashing, combustion in closed systems and wet digestion methods in high pressure systems [2–9].

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The dry ashing method is usually performed by calcination at atmospheric pressure in a muffle furnace at temperatures around 450 °C. The main advantage of dry ashing for milk powder is the possible oxidation of a large sample mass and subsequent dissolution of ash in a small volume of acids that allow better limits of detection (LODs) when compared with other digestion methods. However, this method is prone to several drawbacks, such as losses of analyte and contamination during sample preparation [3,10,11].

Nowadays, access to commercial microwave-induced combustion (MIC) systems has allowed the efficient digestion of several refractory organic matrices. Diluted acid or alkaline solutions are used to absorb analytes during combustion and final digest solutions are suitable for determination of trace elements using ICP-based techniques. In this sense, MIC has been used for milk and related matrices, thus allowing for digests with very low residual carbon content (RCC) [12,13].

Undoubtedly, wet digestion methods are widely used for the digestion of organic matrices [14]. Among the different oxidants

used in wet digestion methods,  $\text{HNO}_3$  is preferred because it allows for oxidation of almost all organic compounds and can be obtained in high purity [14]. However, for efficient digestion of refractory organic matrices high temperature and pressure systems are required to improve the oxidation capacity of  $\text{HNO}_3$  [15,16].

By contrast, hydrogen peroxide presents weak acidity (a solution of 50%  $\text{H}_2\text{O}_2$  presents a pH of 4.3) and can oxidize organic compounds with the generation of water as the only theoretical byproduct [14]. In this sense, digests containing only  $\text{H}_2\text{O}_2$  were less prone to signal suppression using plasma-based techniques compared to digests prepared with mineral acids. The explanation of signal suppression of analytes in acid digests with respect to water is complex due to the combination of several possible effects, such as a decrease in the sample aspiration rate as a result of increased viscosity, a change in nebulizer efficiency and droplet size distribution, a variation in the aerosol transport efficiency and a change in plasma conditions [17–19]. For ICP-OES, when analyses were carried out using robust conditions (MgII/MgI ratio higher than 8) the changes in thermal characteristics of plasma were minimized and signal suppression could be attributed to the reduction of the analyte transport to the plasma [17]. In regard to ICP-MS analysis, changes in aerosol properties or plasma temperature caused by mineral acids affect the distribution of analyte ions close to the sampling orifice, and suppression of the signal can be observed. According to the literature, and depending on the operating conditions employed, signal suppression is more pronounced for elements with high ionization potential. In order to minimize drawbacks related to acid effect on ICP-MS, robust plasma conditions should also be used [18,19]. Additionally, the use of  $\text{H}_2\text{O}_2$  for oxidation of organic compounds is compatible with green chemistry principles because it is relatively cheap and environmental friendly [20]. According to the literature  $\text{H}_2\text{O}_2$  is also useful for the extraction of trace elements from refractory matrices, but the digests can contain solid residues that cause interference in determination with plasma based techniques [21,22]. However, applications that only use  $\text{H}_2\text{O}_2$  for digestion of organic matrices are scarce in the literature and it is usually used in combination with other concentrated acids [14].

The first application using only  $\text{H}_2\text{O}_2$  reported in the literature was proposed for the digestion of sample masses of up to 15 g of more than thirty organic matrices (such as milk, honey, margarine and meat) mixed with 150 mL of 30% ( $\text{w w}^{-1}$ )  $\text{H}_2\text{O}_2$ . According to the author, the reaction rate of organic substances with  $\text{H}_2\text{O}_2$  is increased by high temperature and pressure, and especially constructed high-pressure vessel was necessary to ensure the security. The maximum temperature achieved during the heating program was 370 °C (using a saltpetre bath or electric furnace), and the resulting digests with low acidity were suitable for subsequent analysis using different analytical techniques. Accuracy was evaluated by determining of spike of radiotracers ( $^{85}\text{Sr}$ ,  $^{106}\text{Ru}$ ,  $^{131}\text{I}$  and  $^{137}\text{Cs}$ ) using gamma spectrometry, and recoveries higher than 96% were observed for these elements [23]. Later, the same author proposed the wet digestion with  $\text{H}_2\text{O}_2$  as oxidant for different fatty matrices (such as cocoa butter, olive oil and sunflower oil) and temperature up to 450 °C were necessary to ensure the efficiency of the digestion [24].

More recently, digestion of dried wood samples was also carried out using only  $\text{H}_2\text{O}_2$  for subsequent analysis of digests using electrothermal vaporization inductively coupled plasma optical emission spectrometry (ETV-ICP-OES). A sample mass of up to 120 mg was digested with 1.5 mL of 50% ( $\text{w w}^{-1}$ )  $\text{H}_2\text{O}_2$  in a polytetrafluoroethylene (PTFE) bomb heated up to 125 °C (conventional heating) during 4 h. Final digests did not present wood residue in the solution and determination of 21 elements was carried out using ETV-ICP-OES. The authors of this manuscript

recommended that such procedure must be carefully evaluated for larger sample masses and higher concentration of  $\text{H}_2\text{O}_2$  to obtain a safe method. Additionally, the authors recommended avoiding temperatures higher than 125 °C to prevent the leakage from PTFE bomb vessels [25].

For safety reasons digestion of organic matrices that only use  $\text{H}_2\text{O}_2$  should be performed in systems especially designed for working under high temperature and pressure [23,25]. Recently, the single reaction chamber system (SRC-UltraWave™) with microwave-assisted heating has become commercially available, and it allows maximum temperature and pressure up to 300 °C and 199 bar, respectively [15]. This new system has been used to digest large sample masses even of refractory samples such as active pharmaceutical ingredients and nuts. The combination of high pressure and high temperature allows for the efficient digestion of these samples. Final digests with low RCC were obtained that are suitable for analysis using ICP-based techniques [26,27].

In the present study, a green method using a single reaction chamber (SRC-UltraWave™ system) was evaluated for milk powder digestion using only  $\text{H}_2\text{O}_2$  as an oxidant reagent for subsequent elemental determination by ICP-based techniques. To evaluate the digestion efficiency of the proposed method, sample masses of up to 1 g were digested, and the digestion efficiency was evaluated by the determination of residual carbon content (RCC) and residual carbon (RC) in final digests. The accuracy of the proposed method, was evaluated using reference materials (RMs) and also by comparison with results obtained using digestion with concentrated  $\text{HNO}_3$ .

## 2. Experimental section

### 2.1. Instrumentation

In this study sample digestion was performed using SRC system (UltraWave™, Milestone, Sorisole, Italy) equipped with a five quartz vessel (internal volume of 40 mL). This system has a microwave cavity (1 L) made of stainless steel and covered with PTFE vessel which was sealed and pressurized with 40 bar of argon 99.996% (White Martins, São Paulo, Brazil) before heating. All experiments using SRC system were carried out using 1500 W of microwave irradiation and a maximum temperature and pressure of 250 °C and 199 bar, respectively.

Determination of C, Ca, Fe, K, Mg and Na was carried out in an inductively coupled plasma optical emission spectrometer (Ciros CCD model, Spectro, Kleve, Germany) equipped with a Scott-type double pass spray chamber, a cross-flow nebulizer, a torch and a quartz injector. Additionally, an inductively coupled plasma mass spectrometer (Nexion model, Perkin Elmer, Shelton, USA) equipped with concentric nebulizer and cyclonic spray chamber was used for determination of B, Ba, Cd, Cu, Mn, Mo, Pb, Sr and Zn. For plasma generation, nebulization and auxiliary gas, argon with a purity of 99.996% was used. The conditions used for element determination by ICP-OES and ICP-MS are summarized in Table 1.

### 2.2. Reagents, solutions and samples

Water was purified in Milli-Q system (Millipore Corp. Bedford, USA). Purified water was used to prepare all reference solutions and reagents used in this study. Stabilized 30% ( $\text{w w}^{-1}$ ) and 50% ( $\text{w w}^{-1}$ )  $\text{H}_2\text{O}_2$  (Sigma Aldrich, USA, product numbers H3410 and 516,813, respectively) were used as an oxidant agent. Digestion of milk powder samples was also performed using  $\text{HNO}_3$  (65%,  $\text{w w}^{-1}$ , Merck, Germany) doubly distilled in a quartz sub-boiling device (model duoPUR 2.01E, Milestone, Sorisole, Italy).

A multi-element stock solution (PlasmaCal SCP33MS, SCP Science, Quebec, Canada) containing 10 mg  $\text{L}^{-1}$  of all the evaluated

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