Metals determination in milk powder samples for adult and infant nutrition after focused-microwave induced combustion

Juliana S.F. Pereira [a], Leticia S.F. Pereira [b], Lucas Schmidt [a], Clarissa M. Moreira [a], Juliano S. Barin [c], Erico M.M. Flores [a,*]

[a] Departamento de Química, Universidade Federal de Santa Maria, 97105–900, Santa Maria, RS, Brazil
[b] Departamento de Engenharia Química, Universidade Federal de Santa Maria, 97105–900, Santa Maria, RS, Brazil
[c] Departamento de Tecnologia e Ciência dos Alimentos, Universidade Federal de Santa Maria, 97105–900, Santa Maria, RS, Brazil

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ABSTRACT

In this study, a recently sample preparation method based on focused microwave-induced combustion (FMIC) is proposed for milk powder digestion (for adult and infant nutrition) for subsequent determination of Ba, Ca, Co, Cr, Cu, Fe, Mg, Mn, Sr, V and Zn by inductively coupled plasma optical emission spectrometry (ICP OES). Combustion was carried out under oxygen flow rate (2 to 15 l min^{-1}) using ammonium nitrate (50 μl of 6 mol l^{-1} solution) as ignition aid. Samples were pressed as pellets (up to 3 g) and placed on a quartz holder positioned inside the glass vessel. The concentration of the absorbing solution was investigated using nitric acid in the range of 2 to 14 mol l^{-1}. Sample digestion was also performed by microwave-assisted wet digestion (MAWD) and by microwave-induced combustion (MIC). Agreement higher than 95% was obtained for all analytes by comparison with certified reference materials of milk powder after FMIC using diluted nitric acid (2 mol l^{-1}) and by comparison of the results obtained by MAWD and MIC. The main advantage of FMIC when compared to MAWD and MIC is the possibility to digest higher sample masses (up to 3 g) achieving better limits of detection. It was possible to use diluted nitric acid solution for analytes absorption and digests were suitable for determination of metals by ICP OES avoiding the use of more expensive instrumentation as inductively coupled plasma mass spectrometry.

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1. Introduction

Determination of trace elements in food samples has received increased concern because some elements could present essential or toxic nature depending on their concentration. The information about metals content in food samples is an important aspect for consumers and also for legislation requirements and several works have reported the determination of trace elements in food samples [1–9]. Concerning the determination of metals in food, the Codex Alimentarius Commission (CAC) established limits especially for toxic elements as As, Cd, Hg and Pb [10]. However, the maximum content of other elements, as Cu, Fe, Mn, Zn, among others, is not informed. In addition, the levels of toxic elements especially in milk are established only for Pb [10]. In this sense, the determination of metals in food is of great importance since the deficiency or excess of metals could promote several clinical disorders, as respiratory system cancer, skin disorder, anemia, depression of growth, impaired reproductive performance, heart failure and gastrointestinal disturbances,

fatigue, decreased immunity and even death, resulting public health problems [2,11,12].

Milk could be considered as an important type of food especially for infants since it must contain all the essential nutrients at the required levels [13,14]. In some milk products, as the different types of milk powder, essential elements are normally added in order to attend nutritional requirements [13]. In contrast, it is necessary to control the level of elements added in milk samples since their excess could result in a potential source of exposure of toxic elements in humans. Therefore, some works have been recently recommended the quality control in milk and milk products related to trace elements determination [13–17].

For determination of metals in milk powder an appropriate sample preparation method should be used in order to obtain an efficient sample digestion and to achieve quantitative results, good accuracy and suitable limits of detection (LODs). The selected sample preparation method should promote sample decomposition as efficient as possible, preferentially with low reagent consumption and using diluted solutions [15,18–20].

It is important to mention that the use of concentrated reagents is hazardous, could require a dilution step of the digests before analytes determination and generates high volumes of concentrated acids as effluents [1,15,21,22]. In spite of good performance of sample preparation

* Corresponding author. Tel./fax: +55 55 3220 9445.
  E-mail address: ericommf@gmail.com (E.MM. Flores).

methods based on microwave-assisted wet digestion (MAWD) for different matrices, concentrated acids are generally required, increasing the blank values or could cause interferences in the determination step by some analytical techniques, such as inductively coupled plasma optical emission spectrometry (ICP OES) [23–25].

Combustion techniques could present high efficiency of sample oxidation, digestion of relatively high sample masses and low blanks due to purity of oxygen when compared to concentrated acids used in MAWD [26]. Different combustion systems have been proposed for sample digestion. Recently developed methods, as microwave-induced combustion (MIC) and focused microwave-induced combustion (FMIC) [27,28] have attended several premises related to sample preparation, as low reagent consumption, use of diluted acids for analytes absorption and high efficiency of digestion even for samples considered hard to bring into solution (e.g. samples with high fat content, polymers and crude oil) [27–31]. In these systems, organic samples are combusted under oxygen (pressurization in the range of 15 to 25 bar or in a continuous flow rate from 2 to 15 l min^{-1}) and ignition step is performed under microwave radiation. A small quartz holder, placed inside the vessel, is used for sample insertion. These systems allow to perform a subsequent reflux step that is not available in other combustion techniques such as oxygen flask and combustion bombs [27].

Despite the good efficiency of MIC to digest samples with complex matrix for subsequent determination of metals using diluted acids, the amount of sample that can be burnt is limited to 500 mg due to the high pressure generated inside the closed vessel [25,29,32]. However, using the FMIC method, it has been possible to digest sample masses up to 3 g that is an important aspect related to trace elements determination [28]. The FMIC system operates at atmospheric pressure using a glass vessel especially designed to allow an entrance of oxygen flow inside the vessel. In addition, a modified water-cooled condenser was also used in order to avoid analyte losses by volatilization [27,28].

In the present work FMIC method is proposed for the first time for biological sample (different types of milk powder and for adult and infant nutrition) digestion for further metals determination. Some limitations of MIC and also MAWD concerning the digestion of high sample masses and the use of concentrated acids are overcome using the proposed FMIC method. The concentration of absorbing solution for analytes retention was studied using a reflux step after sample combustion. For results comparison, milk powder digestion was also performed by MAWD and MIC in closed vessels. As a relatively high sample mass was digested, the determination of Ba, Ca, Co, Cr, Cu, Fe, Mg, Mn, Sr, V and Zn was performed by ICP OES. Accuracy was evaluated using certified reference materials (CRMs) of milk powder. Residual carbon content (RCC) in digests was determined in order to evaluate the efficiency of the investigated sample preparation methods for milk powder digestion.

2. Experimental

2.1. Instrumentation

A commercial microwave oven with focused microwave radiation with two cavities (Star System 2, 800 W, CEM, Matthews, NC, USA) equipped with glass vessels of 180 ml of capacity and lab-made condenser was used for milk powder digestion by FMIC. For ignition step using FMIC, the maximum microwave power and temperature applied were 800 W and 430 °C, respectively. The focused microwave oven was equipped with a vapor collection and automatic reagent addition modules (CEM, model reagent addition EX4, model number 560980). For combustion process, the system was modified to allow an oxygen flow entrance and introduction of a sample quartz holder inside the vessel [27,28] as shown in Fig. 1.
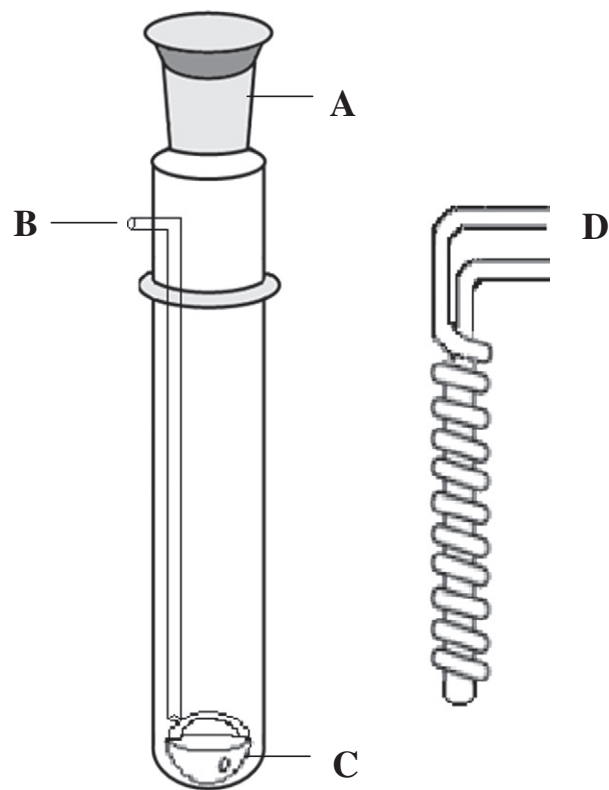

Fig. 1. Apparatus used for FMIC digestion of milk powder samples: (A) modified glass vessel, (B) device used for oxygen entrance inside the vessel, (C) sample quartz holder and (D) water-cooled condenser.

In order to minimize losses of analytes, a water-cooled condenser was used instead of the conventional air-cooled system provided by the manufacturer in view of better efficiency. Cooling was performed using water (10 °C). The design of sample quartz holder and its position inside the vessel was set according to previous works [27,28].

For sample digestion by MAWD and MIC, a microwave sample preparation system (Multiwave 3000, Anton Paar, Graz, Austria) equipped with high-pressure quartz vessels (internal volume of 80 ml, maximum temperature and pressure of 280 °C and 80 bar, respectively) was used. For MIC digestion, commercial quartz holders (Anton Paar, part number 16427) were used and the software version of the equipment was changed to v1.27-Synt allowing running with a maximum pressure rate of 3 bar s^{-1}.

Determination of Ba, Ca, Co, Cr, Cu, Fe, Mg, Mn, Sr, V and Zn was carried out using an inductively coupled plasma optical emission spectrometer (Optima 4300 DV, PerkinElmer, Shelton, USA) with axial view configuration. A concentric nebulizer and cyclonic spray chamber were used. Argon 99.996% (White Martins, São Paulo, Brazil) was used for plasma generation, nebulization and as auxiliary gas. This equipment was also used for residual carbon content determination in digests obtained by MAWD, MIC and FMIC according previous work [33]. The instrumental parameters like measurements of the signal to background ratio and signal to noise ratio, varying radio frequency, nebulizer gas flow rate, torch configuration and wavelengths were evaluated. The operational conditions selected are shown in Table 1.

2.2. Reagents and standards

Distilled and deionized water was further purified using a Milli-Q system (18.2 MΩ cm, Millipore Corp., Bedford, USA) and it was used