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Determination of Zn and Mg in Milk Powder Samples Using Conventional and Alternative Sample Preparations and FAAS

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Abstract: Conventional procedures for sample preparation, such as calcination and acid digestion, were compared with an alternative procedure: alkaline solubilization and ultrasound-assisted extraction. The procedures were evaluated by the application of the mentioned sample preparation and subsequent determination of Mg and Zn in milk powder samples by flame atomic absorption spectrometry (FAAS). The results indicated that ultrasound-assisted extraction was not suitable for Zn and Mg extraction, whereas alkaline solubilization using TMAH was efficient only for determination of Mg.

Key words: Milk powder, trace elements, ultrasound-assisted extraction, alkaline solubilization, FAAS.

1. Introduction

Milk powder is obtained by dehydrating cow milk applying the appropriate unit operations. It presents advantages when compared to liquid milk, such as ease of storage and transport, and perishability. Considering the internationally marketed dairy products, milk powder is the product with the highest volume of transactions, and Brazil stands out as one of the largest producers of whole milk powder [1].

Elements required for the development of different tissues and functioning of several enzymatic systems could be found in milk powder [2], and their qualification depends on numerous parameters, among them the evaluation of the minerals that constitute it [3]. The Brazilian Health Regulatory Agency (ANVISA), through resolution RDC 360, dated December 23, 2003, establishes that the reference values for daily intake of minerals Mg and Zn are 260 and 7 mg, respectively [3].

Determination of Mg and Zn in food samples could be performed using spectrometric methods such as flame atomic absorption spectrometry (FAAS), which is well established and suitable for chemical analysis laboratories [4]. However, this analytical technique requires a sample pretreatment [2]. The conventional methods of sample preparation involve digestion with oxidizing acids and heating or calcination, and both techniques are laborious and require a high operating time, besides the risk of contamination and volatilization due to the number of steps [1, 2].

Alternative methods are studied as milk powder sample pretreatment, such as alkaline solubilization using TMAH, which is a strong organic base, soluble in water and alcohols and can complex and stabilize volatile elements at room temperature without the application of energy sources for heating [3], and ultrasound-assisted extraction, based mainly on the cavitation phenomenon, which results in an effective

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rupture of the solid particles, favoring the metal extraction [5]. Both techniques allow the use of less toxic reagents and shorter preparation time [6, 7].

The objective of this study was to compare the determination of Mg and Zn in milk powder samples by FAAS using conventional (calcination and acid digestion) and alternative (alkaline solubilization using TMAH and ultrasound-assisted extraction) sample preparations.

2. Materials and Methods

2.1 Instrumentation

Weight measurement and phase separation of samples were performed using an analytical balance (Mark 205A, BEL ENGINEERING) and a centrifuge (DM0412S, SCILOGEX), respectively. Calcination, acid digestion and ultrasound-assisted extraction were performed in muffle (318D24, QUIMIS), digestion system (SL 25/40, SOLAB) and ultrasonic bath (USC-1400A, UNIQUE), respectively. A flame atomic absorption spectrometry (AAnalyst 700, PERKIN ELMER-SCIEX) carried out in an air/acetylene flame of 17:2.0 and 8:1.8 $L \cdot min^{-1}$, wavelength of 285.2 and 213.9 nm and slit of 0.7 nm was applied for Mg and Zn determination, respectively.

2.2 Chemicals and Samples

All reagents used were of analytical grade. Ultrapure water with resistivity of 18.1 MΩ·cm (MS2000, GEHAKA), nitric acid 65% (mm^{-1}), hydrogen peroxide 30% (vv^{-1}) and TMAH solution 25% (mv^{-1}) in methanol were used for sample preparation. Two milk powder samples obtained in supermarkets located in the city of Ponta Grossa–PR, Brazil were analyzed.

2.3 Calcination and Acid Digestion as Conventional Sample Treatments

Calcination involved a carbonization of 2.0 g of milk powder sample in porcelain crucibles in muffle for 5 h at 500 °C. After cooling, the samples received 1.0 mL of HNO_3 and ultrapure water up to 25 mL, and were filtered.

Acid digestion was performed by the attachment of test tubes containing 4.0 mL HNO_3 (65% vv^{-1}), 2.0 mL H_2O_2 (30% vv^{-1}) and 1.0 g of milk powder sample in a digestion system at 80 °C for 30 min, and subsequently at 130 °C for 1.5 h. Ultrapure water was added to the remaining solutions up to 50 mL.

2.4 Alkaline Solubilization and Ultrasound-Assisted Extraction as Alternative Sample Treatments

Alkaline solubilization was performed using polypropylene tubes containing 500 μL of TMAH (25% mv^{-1}) and 0.1 g of milk powder sample in a bath at 95 ± 5 °C for 30 min. Ultrapure water was added to the remaining solutions up to 14 mL and the samples were centrifuged at 4,500 rpm for 5 min.

Ultrasound-assisted extraction was executed using polypropylene tubes containing 2.0 mL of 30% (vv^{-1}) HNO_3 and 0.2 g of milk powder sample in an ultrasonic bath at ambient temperature for 20 min. After extraction, ultrapure water was added to the remaining solutions up to 12 mL and the solutions were filtered.

3. Results and Discussion

The determination of Mg and Zn was concluded for two different milk powder samples denominated A and B. Table 1 presents the results as a function of the mean and standard deviation obtained for the replicates of each method submitted to the Tukey test with 5% significance.

The results indicated that there was no significant difference between calcination and alkaline solubilization with TMAH in determination of Mg. Therefore, alkaline solubilization with TMAH is an alternative to the conventional sample preparations. Ultrasound-assisted extraction and acid digestion were not efficient.

In the determination of Zn, it was observed that

Table 1 Concentration of Mg and Zn in milk powder samples using FAAS.

Mg (g/(100g))				
Sample	Calcination	Alkaline solubilization	Acid digestion	Ultrasound-assisted extraction
A	0.128 ± 0.005	0.124 ± 0.006	0.094 ± 0.007	0.100 ± 0.004
B	0.122 ± 0.001	0.124 ± 0.004	0.091 ± 0.003	0.099 ± 0.007
Zn (mg/kg)				
Sample	Calcination	Alkaline solubilization	Acid digestion	Ultrasound-assisted extraction
A	39.988 ± 2.379	35.931 ± 1.277	40.175 ± 0.913	37.041 ± 0.485
B	42.560 ± 1.703	30.559 ± 0.763	28.340 ± 0.809	32.717 ± 0.686

there was a significant difference between conventional and alternative sample preparations, and this outcome may be due to a possible formation of low solubility zinc hydroxides that made the reading less effective, as well as high element volatilization.

4. Conclusion

In order to determine Mg in milk powder samples, alkaline solubilization using TMAH was effective, whereas ultrasound-assisted extraction was not.

Both alkaline solubilization using TMAH and ultrasound-assisted extraction were not efficient to determine Zn in milk powder samples. A high element volatilization may have been the reason.

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