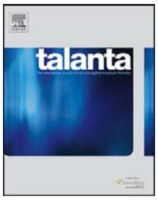
Talanta 81 (2010) 1357–1359

Contents lists available at ScienceDirect

Talanta

journal homepage: www.elsevier.com/locate/talanta



Use of slurry sampling for the direct determination of zinc in yogurt by high resolution-continuum source flame atomic absorption spectrometry

Geovani C. Brandao[a], Raildo M. de Jesus[a,b], Erik G.P. da Silva[c], Sergio L.C. Ferreira[a,*]

[a] Universidade Federal da Bahia, Instituto de Química, Grupo de Pesquisa em Química e Quimiometria, Campus Ondina, Salvador 40170-290, Bahia, Brazil
[b] Universidade Estadual de Santa Cruz, Departamento de Ciências Exatas e Tecnológicas, Ilhéus 45650-000, BA, Brazil
[c] Universidade do Estado da Bahia, Rua Silveira Martins, 2555 Cabula, Salvador 41195-001, Bahia, Brazil

ARTICLE INFO

Article history:
Received 27 December 2009
Received in revised form 5 February 2010
Accepted 8 February 2010
Available online 13 February 2010

Keywords:
Slurry sampling
Zinc determination
Yogurt samples
High resolution-continuum source flame atomic absorption spectrometry

ABSTRACT

This paper presents an analytical procedure for the direct determination of zinc in yogurt employing sampling slurry and high resolution-continuum source flame atomic absorption spectrometry (HR-CS FAAS). The step optimization established the experimental conditions of: 2.0 mol L^{-1} hydrochloric acid, a sonication time of 20 min and a sample mass of 1.0 g for a slurry volume of 25 mL. This method allows the determination of zinc with a limit of quantification of 0.32 $\mu g\,g^{-1}$. The precision expressed as relative standard deviation (RSD) were 0.82 and 2.08% for yogurt samples containing zinc concentrations of 4.85 and 2.49 $\mu g\,g^{-1}$, respectively. The accuracy was confirmed by the analysis of a certified reference material of non-fat milk powder furnished by the National Institute of Standard and Technology. The proposed method was applied for the determination of zinc in seven yogurt samples. The zinc content was varied from 2.19 to 4.85 $\mu g\,g^{-1}$. These results agreed with those reported in the literature. The samples were also analyzed after acid digestion and zinc determination by FAAS. No statistical difference was observed between the results obtained by both of the procedures performed.

1. Introduction

Yogurt is defined as the product obtained from milk fermentation by the action of two lactic acid bacteria that live symbiotically: *Lactobacillus delbrueckii* ssp. *bulgaricus* and *Streptococcus thermophilus*. These bacteria convert the milk sugar lactose into lactic acid during the fermentation [1,2]. This product is widely consumed because it is a good source of minerals such as calcium, magnesium, phosphorus and zinc in the human diet and it is digested and assimilated more easily than fresh milk [3,4]. In addition, it can provide beneficial effects to human health due its therapeutic, probiotic and antitumoral effects [5,6].

Zinc is an essential nutrient for human metabolism. It is present in more than 300 enzymes involved in several physiological functions, such as protein synthesis and energy metabolism. Zinc deficiency in humans causes dwarfism, hypogonadism, diarrhea and dermatitis [7]. The daily recommended intake of zinc depends on life stage [8]. Thus, the quantization of this metal in yogurt is of great relevance.

Yogurt is a complex matrix that presents a high content of organic compounds, such as proteins and fats. This way, the sample digestion procedures proposed for the decomposition of yogurt samples are often complicated. Mehmet and co-workers compared digestion procedures using dry, wet and microwave ashing, proposed for the determination of copper, manganese and lead in yogurt employing FAAS. The results showed that use of a microwave oven is the best option. It was also observed that a procedure using dry ashing with an incineration temperature of 450 °C for 8 h is efficient for the determination of copper and manganese, but considerable lead losses were observed [9]. For all these reasons, the slurry sampling appears to be an alternative technique for the pre-treatment of yogurt samples with many advantages, including: simplification of the sample digestion step, reduced risk of contamination and minimization of the use of reagents [10–13]. Actually, slurry sampling is an analytical strategy used for the determination of metals and metalloids in different samples employing spectrometry techniques, such as: inductively coupled plasma optical emission spectrometry (ICP OES) [14,15], hydride generation atomic absorption spectrometry (HG-AAS) [16], cold vapor atomic absorption spectrometry (CV AAS) [17], electrothermal atomic absorption spectrometry (ET AAS) [18–20] and (FAAS) [21,22].

This paper proposes a procedure that employs slurry sampling for the determination of zinc in yogurt samples by high resolution-continuum source flame atomic absorption spectrometry (HR-CS FAAS).

---

[*] Corresponding author. Tel.: +55 71 32355166; fax: +55 71 32355166.
E-mail address: slcf@ufba.br (S.L.C. Ferreira).

0039-9140/$ – see front matter © 2010 Published by Elsevier B.V.
doi:10.1016/j.talanta.2010.02.033

Table 1
Equations of the analytical curves.

System	Linear regression equations
Aqueous media^{ECT}	$\mathrm{Abs} = (0.3168 \pm 0.0125)C_{Zn} + (0.0040 \pm 0.0038)\ r = (0.9995 \pm 0.0052)$
Sample 1^{AAT}	$\mathrm{Abs} = (0.2921 \pm 0.0144)C_{Zn} + (0.0724 \pm 0.0043)\ r = (0.9992 \pm 0.0060)$
Sample 2^{AAT}	$\mathrm{Abs} = (0.2961 \pm 0.0181)C_{Zn} + (0.0686 \pm 0.0050)\ r = (0.9991 \pm 0.0070)$
Sample 3^{AAT}	$\mathrm{Abs} = (0.3058 \pm 0.0166)C_{Zn} + (0.0371 \pm 0.0050)\ r = (0.9991 \pm 0.0069)$
Sample 4^{AAT}	$\mathrm{Abs} = (0.3034 \pm 0.0099)C_{Zn} + (0.0450 \pm 0.0030)\ r = (0.9997 \pm 0.0041)$
Sample 5^{AAT}	$\mathrm{Abs} = (0.3038 \pm 0.0123)C_{Zn} + (0.0384 \pm 0.0037)\ r = (0.9995 \pm 0.0051)$

^{ECT}: analytical curve using external calibration technique; ^{AAT}: analytical curves using analyte addition technique. C_{Zn} (μg L^{-1}).

2. Experimental

2.1. Instrumentation

An Analytik Jena Model ContrAA 300 High Resolution-Continuum Source Flame Atomic Absorption Spectrometer (GLE, Berlin, Germany) equipped with a xenon short-arc lamp XBO 301 with a nominal power of 300 W operating in a hot-spot mode as a continuum radiation source was used for the analysis. An air–acetylene flame was used for the atomization of Zn. All measurements of absorbance were carried out in triplicate for blanks, analytical solutions and samples using the main line of Zn (213.875 nm). The equipment was operated under optimum conditions.

An Ultrasonic Benchtop Cleaner VWR Model 75 D (Cortland, NY, USA) was used for slurry preparation.

A Tecnal Model TE-040/25 Aluminum Heating Block (Piracicaba, São Paulo, Brazil) was used for the mineralization of samples.

An Eppendorf Model 5804 centrifuge was used for the centrifugation of the slurries.

2.2. Reagent and samples

All reagents were of analytical grade unless otherwise stated. Ultrapure water was obtained from an EASY pure RF (Barnstedt, Dubuque, IA, USA). Nitric and hydrochloric acid were of Suprapur quality (Merck, Darmstadt, Germany). Laboratory glassware was kept overnight in 10% (v/v) nitric acid solution. Before use the glassware was rinsed with deionized water and dried in a dust-free environment.

Zinc solution (100.0 μg mL^{-1}) was prepared by diluting a 1000 μg mL^{-1} zinc solution (Merck) with a 1% (v/v) hydrochloric acid solution.

The certified reference material used for the confirmation of the accuracy was SRM 1549 non-fat milk powder (National Institute of Standard and Technology, NIST, Gaithersburg, MD, USA).

The yogurt samples investigated in this study were locally available brands, collected in supermarkets from Salvador City, Brazil.

2.3. Slurry preparation

A 1.0 g mass of yogurt sample was directly weighted in a 25-mL volumetric flask and diluted with 2.0 mol L^{-1} acid hydrochloric solution. After, the slurries were placed in an ultrasonic bath for 20 min and then aspirated directly through the nebulizer for zinc determination by HR-CS FAAS. All samples were analyzed in triplicate. The blanks were prepared in the same way as the slurries. A standard calibration technique was used for quantification, and the analytical curves were established using aqueous standards.

2.4. Digestion of yogurt samples

A mass of 1.0 g of yogurt sample was directly weighed in a digestion tube, and 5.0 mL of concentrated nitric acid and 4 mL of 30% (v/v) hydrogen peroxide were added. Then, the mixture was heated and evaporated to dryness. Afterward, the residual solution was transferred to a 25-mL volumetric flask and diluted with 2.0 mol L^{-1} acid hydrochloric solution.

3. Results and discussion

3.1. Optimization of the experimental conditions

The optimization was performed using univariate methodology involving the followings variables: nature and concentration of acid, sonication time and sample mass. All the experiments were performed using a slurry volume of 25 mL.

Hydrochloric, nitric and formic acid were investigated as the liquid phase for slurries preparation in the concentration range of 0.5–3.0 mol L^{-1}. This study was performed at the experimental conditions of a sample mass of 1.0 g and a sonication time of 20 min. The results demonstrated that there is no difference in the analytical signals for the acids, and a maximum sensitivity was obtained for a concentration of 0.5 mol L^{-1}, which remained constant up to 3.0 mol L^{-1}. However, it was observed that slurries prepared with acid concentrations less than 2.0 mol L^{-1} caused occasional blockage in the nebulization system of the spectrometer. Thus, hydrochloric acid at a 2.0 mol L^{-1} concentration was established as the liquid phase for slurry preparation.

The effect of sonication time on the preparation of the slurries was also studied. The results demonstrated that this variable in the range of 0–40 min does not affect the analytical signal. However, it was observed that slurries prepared with sonication times less than 20 min caused occasionally problems of obstruction in the nebulization system. Thus, a sonication time of 20 min was established for this method.

Slurries were prepared with sample masses ranging from 0.25 to 2.0 g, using 2.0 mol L^{-1} hydrochloric acid solution and a sonication time of 20 min. Then, zinc was determined, and the results showed that the mass limit is 1.5 g. Thus, the procedure recommends a sample mass of 1.0 g for preparation of the slurries.

The efficiency of the extraction of the proposed method was assessed under optimized experimental conditions for four yogurt samples. It was calculated with a relationship among the absorbance obtained for the slurry and the absorbance obtained for the liquid phase of the slurry after centrifugation. The results varied from 96 to 103% demonstrating that the zinc extraction process is complete under the experimental conditions established by the procedure proposed.

3.2. Analytical validation

The calibration technique of the method was evaluated by comparison of the slopes of curves obtained with aqueous standards and with analyte addition in five yogurt samples. The results showed good similarity among the slopes of the curves, all with correlation coefficients >0.999, as can be seen in Table 1.

Table 2
Determination of zinc in yogurt samples using slurry sampling and acid digestion ($N = 3$).

Sample	Results found by slurry sampling technique ($\mu g\,g^{-1}$)	Results found by acid digestion procedure ($\mu g\,g^{-1}$)
1	4.85 ± 0.33	4.82 ± 0.06
2	4.66 ± 0.07	4.70 ± 0.12
3	2.49 ± 0.11	2.44 ± 0.08
4	2.86 ± 0.07	2.95 ± 0.11
5	3.44 ± 0.31	3.36 ± 0.29
6	2.19 ± 0.08	2.12 ± 0.27
7	3.02 ± 0.23	3.08 ± 0.17

These results demonstrated that the external calibration technique using aqueous standards is efficient for this procedure.

The limits of detection (LOD) and quantification (LQ) were determinate as IUPAC recommendation. They were found to be 0.10 and 0.32 $\mu g\,g^{-1}$, respectively.

The precision, expressed as the relative standard deviation (RSD) and calculated from ten consecutive measurements of the slurries, were 0.82 and 2.08% for two yogurt samples with concentrations of zinc of 4.85 and 2.49 $\mu g\,g^{-1}$, respectively.

The accuracy was evaluated by the analysis of a certified reference material (CRM) NIST SRM 1549 of non-fat milk powder, which has a certified value of $46.1 \pm 2.2\ \mu g\,g^{-1}$ for zinc. Using the proposed method a zinc concentration of $44.9 \pm 0.8\ \mu g\,g^{-1}$ ($N = 3$) was found, confirming the accuracy of this method.

3.3. Application

The proposed method was used for the determination of zinc in eight yogurt samples bought in supermarkets from Salvador City, Brazil. The samples were also analyzed after complete digestion using nitric and hydrogen peroxide, and the zinc was determined by HR-CS FAAS. All results are expressed with interval confidence (at the 95%) and are shown in Table 2. The zinc content found in these samples varied from 2.19 to 4.85 $\mu g\,g^{-1}$. These results are in agreement with data reported in the literature [3]. Applying the paired *t*-test at the level of 95% confidence no statistical difference was observed among the values obtained by the slurry method and those after complete digestion.

4. Conclusion

The proposed method presented analytical features necessary for zinc determination in yogurt samples. Furthermore, the results showed that the method developed is feasible, rapid, simple and adequate for routine analyses.

Acknowledgements

The authors are grateful to Conselho Nacional de Desenvolvimento Científico e Tecnalógico (CNPq) and to Coordenação de Aperfeiçoamento de Pessoal de Nível Superior (CAPES) for providing grants and fellowships and for financial support.

References

[1] M. Khanmohammadi, A.B. Garmarudi, K.G. Ghasemi, S. Garrigues, M. de la Guardia, Microchem. J. 91 (2009) 47.
[2] E.J.G. Hernandez, R.G. Estepa, I.R. Rivas, Food Chem. 53 (1995) 315.
[3] M.A. de la Fuente, F. Montes, G. Guerrero, M. Juarez, Food Chem. 80 (2003) 573.
[4] P.J. Sanchez-Segarra, M. Garcia-Martinez, M.J. Gordillo-Otero, A. Diaz-Valverde, M.A. Amaro-Lopez, R. Moreno-Rojas, Food Chem. 70 (2000) 85.
[5] G. Perdigon, J.C. Valdez, M. Rachid, J. Dairy Res. 65 (1998) 129.
[6] S.N. Meydani, W.-K. Ha, Am. J. Clin. Nutr. 71 (2000) 861.
[7] P.C. Onianwa, A.O. Adeyemo, O.E. Idowu, E.E. Ogabiela, Food Chem. 72 (2001) 89.
[8] IOM (Institute of Medicine), National Academy of Sciences on Dietary Reference Intakes (DRIs): Dietary Reference Intakes: Applications in Dietary Planning, National Academy Press, Washington, 2003.
[9] G. Kaya, I. Akdeniz, M. Yaman, At. Spectrosc. 29 (2008) 99.
[10] M.J. Cal-Prieto, M. Felipe-Sotelo, A. Carlosena, J.M. Andrade, P. Lopez-Mahia, S. Muniategui, D. Prada, Talanta 56 (2002) 1.
[11] C.E.C. Magalhaes, M.A.Z. Arruda, Quim. Nova 21 (1998) 459.
[12] M.G.R. Vale, N. Oleszczuk, W.N.L. dos Santos, Appl. Spectrosc. Rev. 41 (2006) 377.
[13] S.L.C. Ferreira, M. Miro, E.G.P. da Silva, G.D. Matos, P.S. dos Reis, G.C. Brandao, W.N.L. dos Santos, A.T. Duarte, M.G.R. Vale, R.G.O. Araujo, Appl. Spectrosc. Rev. 45 (2010) 44.
[14] M.C. Santos, J.A. Nobrega, Appl. Spectrosc. Rev. 41 (2006) 427.
[15] H. Matusiewicz, M. Slachcinski, Microchem. J. 86 (2007) 102–111.
[16] S.M. Macedo, R.M. de Jesus, K.S. Garcia, V. Hatje, A.F.D. Queiroz, S.L.C. Ferreira, Talanta 80 (2009) 974.
[17] S.R. Segade, J.F. Tyson, Talanta 71 (2007) 1696.
[18] Z. Arslan, J.F. Tyson, Microchem. J. 86 (2007) 227.
[19] K.G. Fernandes, A.R.A. Nogueira, J.A. Gomes Neto, J.A. Nobrega, Talanta 71 (2007) 1118.
[20] R.G.O. Araujo, N. Oleszczuk, R.T. Rampazzo, P.A. Costa, M.M. Silva, M.G.R. Vale, B. Welz, S.L.C. Ferreira, Talanta 77 (2008) 400.
[21] R.A. Bugallo, S.R. Segade, E.F. Gomez, Talanta 72 (2007) 60.
[22] H.S. Ferreira, W.N.L. dos Santos, R.P. Fiuza, J.A. Nobrega, S.L.C. Ferreira, Microchem. J. 87 (2007) 128.