

Analytical, Nutritional and Clinical Methods

Determination of major and minor elements in dairy products through inductively coupled plasma optical emission spectrometry after wet partial digestion and neutron activation analysis

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Abstract

A wet partial digestion procedure using hydrochloric acid was investigated to determine the concentration of Ca, Cr, Cu, Fe, K, Mg, Mn, Na, P and Zn in dairy products by Inductively Coupled Plasma Optical Emission Spectrometry (ICP OES) technique. The results of this partial digestion were satisfactory and no loss of analytes was observed. A comparison of the results obtained from this methodology was carried out with the other results from dry ashing digestion and Instrumental Neutron Activation Analysis (INAA) technique that do not require pre-treatment procedure.

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1. Introduction

Good quality measurements are essential to control and maintain products and processes quality, both in manufacturing, trade and in research. The growing importance of chemical measurements has greatly pressured the development of measures to improve the quality of analytical results and to guarantee quality to the end users.

Inorganic elements analyses are carried out by Health Control Agencies to determine nutrient content in food-stuffs so that product label accuracy can be verified producing product assurance. Although agencies apply official analytical methods they are analyte and matrix specific.

A review of the methodologies of the International Association of Official Analytical Chemists (AOAC) for inorganic element determination in food showed that almost all of them have used techniques such as UV/VIS

spectrometry, anodic stripping voltammetry or flame and graphite furnace atomic absorption spectrometry combined with dry ashing or wet digestion procedures for sample treatment (Association of official analytical chemists, 1995a, chap. 50). Only one of them applied Inductively Coupled Plasma Optical Emission Spectrometry – ICP OES (Association of official analytical chemists, 1995b, chap. 50). In this AOAC method a mixture of HNO₃ and HClO₄ is used to digest infant formula samples to determine Ca, Cu, Fe, K, Mg, Mn, Na, P and Zn in infant formula by ICP OES.

Some concerns with the HNO₃–HClO₄ digestion procedure are related to the use of these corrosive reagents, requiring constant control during the digestion in order to ensure that samples do not go to dryness avoiding risk of explosion and analyte losses (Hoening & Kersabiec, 1996; Sun, Waters, & Mawhinney, 2000; Amaro-López, Moreno-Rojas, Sánchez-Segarra, & Zurera-Cosano, 1996).

Sample digestion is a critical step in elemental analysis, due to the preparation time, risk of contamination and

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analytes loss, contributing for the systematic analysis errors (De La Fuente & Juárez, 1995; Zachariadis, Stratis, Kaniou, & Kalligas, 1995; Novozamsky, Lee, & Houba, 1995). The most frequently used digestion procedures have been the traditional dry ashing and wet digestion that allow destruction of organic matter of the sample.

The mineralization stage is time-consuming and prone to contamination problems. So, procedures that involve a minimal treatment of sample could be advantageous since time and effort would be saved and the incidence of re-runs on this original work can be dramatically decreased. Consequently analysis cost reduction could be achieved.

The effectiveness of digestion procedures using different acid mixtures for the mineralization of biological matrices has been extensively described, but there have been few reports on the analysis of dairy products by ICP OES (Krushavska, Barnes, & Amarasiriwaradena, 1993).

Dairy products are a very important human nutrient since their consumption has increased in recent years. Dairy products are also a good source of calcium and its bioavailability is high.

An ICP OES technique using wet digestion with HCl/H₂O (1:1) mixture was previously developed to analyze milk powder samples (Kira, Maio, & Maihara, 2004). In the present study, this methodology was applied to inorganic element determination in different kinds of dairy products. The results were compared to those obtained from the ICP OES technique using dry ashing digestion and the Instrumental Neutron Activation Analysis (INAA) technique.

Among the available techniques the use of INAA has proved to be beneficial for sample analysis since the samples can be analyzed directly without any mineralization (Maihara et al., 2001). This simplifies the analysis and minimizes the risk of contamination.

2. Experimental

2.1. Collection and pre-treatment sample

Chocolate milk, yogurt and Petit Suisse cheese were the samples analyzed in this study and they were purchased in local markets in the city of São Paulo, Brazil.

For the ICP OES the dairy product samples were analyzed without pre-treatment, while for the INAA the samples were freeze-dried and homogenized in a domestic blender before analysis.

2.2. Glassware

All glassware was initially washed with detergent and water. After that the glassware was soaked in 20% HNO₃ (v/v) solution for 24 h. This solution was discarded and the glassware was soaked again in 20% HNO₃ (v/v) solution for 24 h. This procedure was repeated again, and the glassware rinsed several times with deionized water and dried.

2.3. Reagents and standards

- Deionized water – obtained from a Milli-Q system (Millipore, Mildford, MA, USA). Specific resistance, 18 M Ω cm⁻¹.
- Hydrochloric acid (10%) – analytical grade (Merck, Darmstadt, Germany).
- Nitric acid (65%) – analytical grade (Merck, Darmstadt, Germany).
- Standard stock solution of Ca, Fe, K, Mg, Na, P and Zn – (10.00 \pm 0.03) mg mL⁻¹ (High Purity Standards).
- Standard stock solution of Cr, Cu, Mn – (1 \pm 0.002) g L⁻¹ (Merck).

The working standard solutions were prepared by diluting the stock solutions in 10% hydrochloric acid. All working standard solutions were stored in Nalgene polypropylene bottles. The multi-elemental standard solutions ranged from: 2.5 to 100.0 mg L⁻¹ for Ca, K, Na, P; 0.25 to 10.0 mg L⁻¹ for Fe and Zn; 0.025 to 1.0 mg L⁻¹ for Cr; 0.125 to 5.0 mg L⁻¹ for Cu; 0.625 to 25.0 mg L⁻¹ for Mg; and 0.0125 to 0.5 mg L⁻¹ for Mn.

2.4. Certified reference material

The accuracy of the study was determined using two reference materials: National Institute of Standards and Technology (NIST) Standard Reference Material (SRM) Non Fat Milk Powder SRM-1549 and Whole Milk Powder RM-8435 (NIST, 2003; NIST, 1999).

2.5. Apparatus

2.5.1. ICP OES technique

An Optima 3000DV (Perkin Elmer Corp., Norwalk, CT, USA) ICP OES instrument was used. After scanning a blank, a standard solution and a sample solution in the programmed wavelength range, the background correction wavelengths were selected manually at appropriate background positions for each analyte peak. Instrument configuration and general experimental conditions are summarized in Table 1.

2.5.2. INAA technique

For the INAA technique the samples were counted with a Ge detector (model POP TOP – EG&G ORTEC) with a resolution of 1.90 keV for the 1332.49 keV γ -ray peak of ⁶⁰Co. γ -ray spectrum was performed using the VISPECT 2 software (Maihara et al., 2001).

2.6. Sample preparation

2.6.1. ICP OES technique

2.6.1.1. Procedure A: wet digestion on a hot plate. Chocolate milk sample. A 10.0 mL sample was transferred into 125 mL conical flask; 10.0 mL HCl/H₂O (1:1) mixture

Table 1
ICP OES operating conditions

Operation conditions	
RF power (W)	1350
Sample uptake rate (mL min ⁻¹)	1.5
Nebulization gas flow rate (L min ⁻¹)	0.85
Plasma flow rate (L min ⁻¹)	15
Sample flow rate (L min ⁻¹)	1.5
Observation height	15 mm above load coil
Nebulizer	Cross flow
Spray chamber	Scott
Elements, wavelengths (nm)	Ca(422.673), Cr(267.716), Cu(327.396), Fe(259.940), K(766.491), Mg(280.270), Mn(257.610), Na(589.592), P(213.618), Zn(213.856)

was added and the flask was covered with a watch glass. The sample was heated on a hot plate at 100–150 °C for about 2 h with a gentle boil. During this time the sample was refluxed so the mixture was not allowed to dry. The digested solution was then filtered through Whatman no. 40, 125 mm filter paper into 25.0 mL volumetric flask and made up to the mark with deionized water.

Yogurt sample. A 10.0 g sample was weighed into 125 mL conical flask and 10.0 mL HCl/H₂O (1:1) mixture was added. The digestion followed the same procedure of the chocolate milk sample.

Petit Suisse cheese sample. A 2.0 g sample was weighed into 125 mL conical flask and some water was added in order to dilute the sample, then 10.0 mL HCl/H₂O (1:1) mixture was added. The digestion followed the same procedure of the chocolate milk sample.

Evaluation of acid effect. Since digestion on a hot plate was only applied to the samples, differences in acid concentration between standards and samples might lead to change in efficiency of aerosol formation and transport and could influence the analytical signal. Experiments were performed in order to evaluate the effect of acid concentration as described: aliquots of 10.0 mL digested sample were put into a 25 mL beaker and heated on a hot plate to dryness. After drying, the sample was quantitatively transferred into a 10.0 mL volumetric flask with 10% HCl (v/v) (standard solution medium) and measurements were performed in ICP OES equipment.

2.6.1.2. Procedure B: dry ashing. Chocolate milk sample. Aliquots of 10.0 mL sample were put into a porcelain crucible and dried in an oven at 100 °C. The sample was pre-heated in a Bunsen burner until evolution of smoke was ceased. The crucible was transferred into a muffle furnace and the temperature was increased at a rate of about 50 °C per 30 min up to 450 °C. This temperature was kept constant for 4 h. If ashes still contained carbon (black particles), 1 mL of HNO₃ was added, followed by evaporation on a hot plate and a new ashing cycle. This procedure was repeated until the ashes contained no more carbon. Ashes were dissolved with 10% HCl under careful heating on a

hot plate and the solution was transferred quantitatively into a 25.0 mL volumetric flask.

Yogurt and Petit Suisse cheese sample. Portions of 10.0 g sample were weighed into a porcelain crucible and put into an oven at 100 °C to dry. Mineralization step followed the same procedure of the chocolate milk sample.

2.6.2. INAA technique

The lyophilized samples were put into plastic irradiation vials and no other treatment was used.

The samples were irradiated for a short and long time. For a short irradiation time, the samples were irradiated for 2 min under a flux of a thermal neutron of 1×10^{11} n cm⁻² s⁻¹ and the long-lived nuclides were measured after irradiation for 8 h under a flux of 1×10^{13} n cm⁻² s⁻¹.

About 0.100 g sample was weighed into plastic irradiation vial for the short-lived nuclides (Na, K, Mn, Mg and Ca) determination and about 0.200 g sample was used for the long-lived nuclide (Fe and Zn) determination.

An appropriate weight of standard reference material was put into the same kind of vial as the samples. Samples and standards were neutron irradiated simultaneously in the reactor IEA-R1 from Instituto de Pesquisas Energéticas e Nucleares/Comissão Nacional de Energia Nuclear – São Paulo (IPEN/CNEN-SP). After the cooling time, the vials were transferred to the counting device and the radioactivity was measured in γ -ray spectrometer. After counting, the areas measured under the photopeaks, corresponding to the γ -rays of ²⁷Mg (843 keV), ⁴⁹Ca (3083 keV), ²⁴Na (1368 keV), ⁵⁶Mn (846 keV), ⁴²K (1524 keV), ⁵⁹Fe (1099 keV), ⁶⁵Zn (1115 keV) were compared in samples and standards for the calculation of the unknown quantity of the determined element in each sample.

3. Results and discussion

Samples used in this study consisted of different dairy products, e.g., chocolate milk, yogurt and Petit Suisse cheese. The consumption of these dairy products has increased in recent years. Besides growing interest there has been an emphasis in food labeling due to consumers demand for healthy diets.

Concentrations of inorganic elements (Ca, Fe, K, Mg, Mn, Na and Zn) were measured using both ICP OES and INAA techniques.

Many alternatives for wet sample digestion using oxidant reagents have been tried by various authors (Sun et al., 2000; Moreno-Torres, Navarro, Ruiz-López, Artacho, & López, 2000; Karadjova, Girousi, Iliadou, & Stratis, 2000; De La Fuente, Carazo, & Juárez, 1997), but in order to reduce the spend time in the mineralization stage and the risk of explosion provoked by using an oxidant acid, in this study a HCl/H₂O (1:1) mixture was used for sample digestion.

A bright to dark brown colour solution was obtained after the samples were wet digested on a hot plate. Although the colour of the digested solution indicated a

partial dissolution of the samples, this fact did not affect the determination of the elements using the ICP OES technique.

To evaluate the efficiency of the wet digestion using hydrochloric acid, a comparison was made for the results of the analysis obtained by wet digested procedure, with the dry ashing procedure with complete destruction of the organic matrix and the INAA technique that do not require dissolution of the sample. The results are shown in Table 2.

It was not possible to determine Cr and Cu by the INAA technique due to their low concentrations in these dairy products. P was also not analyzed by the INAA as this technique is not appropriate to determine its concentration.

In order to evaluate the acid effect between standards and samples experiments were performed as described in Section 2.6.1. The results obtained by the samples previously digested on a hot plate with the acid reflux and by the processed samples as described in Section 2.6.1 (evaluation of acid effect) were not statistically different, indicating that differences in acid concentration between standards and samples were not significant.

The statistical tests ANOVA, one way analysis of variance, and Tukey–Kramer were applied to compare the means obtained for the inorganic elements determined in samples (chocolate milk, yogurt and Petit Suisse cheese) with the ICP OES technique after the two different digestion procedures and INAA technique. The statistical comparison of the results obtained for the elements determined in dairy products are presented in Table 3.

From Table 3, it can be seen that both technique used (ICP OES technique after the dry and wet digestion using hydrochloric acid and INAA technique) arrived at the similar results. The results obtained for chocolate milk and yogurt samples by the ICP OES technique were not significantly different from those obtained by the INAA technique. So, there is no need to destroy all the organic matter in order to determine the inorganic elements in the studied samples. Using a simple procedure of wet digestion of 2 h with a mixture of HCl/H₂O (1:1) it is possible to analyze Ca, Cr, Cu, Fe, K, Mg, Mn, Na, P and Zn by ICP OES. This procedure can improve the productivity in the laboratory without risk of contamination or losses that can occur when dry ashing is adopted as a pretreatment of a sample.

Phosphorus concentration obtained from Petit Suisse cheese sample after wet digestion was 10% lower than that obtained after dry ashing sample treatment. The inferior value of phosphorus concentration could be related to the fact that this element could be associate with the casein present in dairy products that was not released from the matrix.

The relative standard deviation (RSD) values for the data were 5% below for most of the determined elements in all dairy product samples.

The SRM-1549 Non Fat Milk Powder and RM-8435 Whole Milk Powder was used for quality control purposes and to evaluate the effectiveness of the procedures. The

Table 2
Results for minerals and trace elements determined in chocolate milk, yogurt and Petit Suisse cheese samples, with the INAA technique and ICP OES technique after the different procedures (dry ashing and wet digestion), in mg kg⁻¹

Element	Chocolate milk			Yogurt			Petit Suisse cheese		
	Procedure A ICP/ wet digestion	Procedure B ICP/ dry ashing	Method C INAA	Procedure A ICP/ wet digestion	Procedure B ICP/ dry ashing	Method C INAA	Procedure A ICP/ wet digestion	Procedure B ICP/ dry ashing	Method C INAA
Ca	723 ± 9	715 ± 9	731 ± 14	927 ± 24	934 ± 11	923 ± 6	2153 ± 70	2136 ± 30	2181 ± 39
Cr	0.06 ± 0.01	0.06 ± 0.01	*	0.04 ± 0.01	0.04 ± 0.01	*	0.07 ± 0.01	0.07 ± 0.01	*
Cu	0.52 ± 0.03	0.54 ± 0.03	*	0.05 ± 0.01	0.07 ± 0.01	*	0.22 ± 0.01	0.19 ± 0.03	*
Fe	5.48 ± 0.05	5.44 ± 0.09	5.33 ± 0.34	1.94 ± 0.10	1.97 ± 0.40	1.93 ± 0.34	29.1 ± 0.1	30.1 ± 1.2	32.2 ± 0.4
K	1756 ± 29	1758 ± 29	1760 ± 136	1358 ± 11	1396 ± 24	1366 ± 26	980 ± 6	936 ± 6	957 ± 51
Mg	146 ± 1	151 ± 3	155 ± 5	81.3 ± 1.1	81.8 ± 4.9	83.4 ± 2.1	74.5 ± 1.3	77.0 ± 3.0	74.6 ± 5.9
Mn	0.63 ± 0.02	0.63 ± 0.03	0.63 ± 0.12	0.28 ± 0.01	0.30 ± 0.03	0.28 ± 0.04	0.35 ± 0.02	0.36 ± 0.01	0.36 ± 0.03
Na	655 ± 18	661 ± 18	660 ± 12	346 ± 11	330 ± 10	357 ± 2	283 ± 8	265 ± 14	283 ± 2
P	639 ± 7	640 ± 10	na	700 ± 7	692 ± 45	na	1410 ± 16	1557 ± 41	na
Zn	3.02 ± 0.07	3.00 ± 0.18	2.93 ± 0.12	3.27 ± 0.20	3.29 ± 0.53	3.28 ± 0.05	3.15 ± 0.23	3.16 ± 0.08	3.38 ± 0.13

(Mean value ± standard deviation); number of determinations: 3; *, not detected; na, not analyzed.

Table 3

Comparison between the average concentrations obtained for the elements determined in chocolate milk, yogurt and Petit Suisse cheese samples with the ICP OES after the two digestion procedures and with the INAA technique, applying the Tukey–Kramer statistical test

Element	Chocolate milk		Yogurt		Petit Suisse cheese	
	Method A × B	Method A × C	Method A × B	Method A × C	Method A × B	Method A × C
Ca	+	+	+	+	+	+
Cr	+	*	+	*	+	*
Cu	+	*	+	*	+	*
Fe	+	+	+	+	+	–
K	+	+	+	+	+	+
Mg	+	+	+	+	+	+
Mn	+	+	+	+	+	+
Na	+	+	+	+	+	+
P	+	na	+	na	–	na
Zn	+	+	+	+	+	+

Method A: ICP OES technique with wet digestion on a hot plate procedure; Method B: ICP OES technique with dry ashing procedure; Method C: INAA technique; +, the mean concentrations are not considered significantly different at the significance level of 95%; –, the mean concentrations are considered significantly different at the significance level of 95%; *, Not detected; na, not analyzed.

Table 4

Results obtained for the elements determined in SRM-1549 non fat milk powder by the ICP OES and INAA technique (in mg kg⁻¹)

Element	Methods of dissolution ICP OES technique		INAA technique	Certified value
	Procedure A wet digestion on a hot plate	Procedure B dry ashing		
Ca	13122 ± 373	13128 ± 355	13218 ± 274	13000 ± 500
Cu	0.64 ± 0.05	0.66 ± 0.07	*	0.7 ± 0.1
Fe	1.75 ± 0.29	1.84 ± 0.09	1.79 ± 0.34	1.78 ± 0.1
K	16807 ± 721	16881 ± 495	16034 ± 443	16900 ± 300
Mg	1103 ± 10	1149 ± 48	1205 ± 22	1200 ± 30
Mn	0.22 ± 0.02	0.21 ± 0.02	0.22 ± 0.03	0.26 ± 0.06
Na	4990 ± 242	5139 ± 232	4975 ± 144	4970 ± 100
P	10117 ± 138	10603 ± 374	na	10600 ± 200
Zn	40.4 ± 2.8	40.5 ± 0.9	43.9 ± 2.6	46.1 ± 2.2

*, not detected; na, not analyzed; number of determinations, 6.

Table 5

Results obtained for the elements determined in RM-8435 whole milk powder by the ICP OES and INAA technique (in mg kg⁻¹)

Element	Methods of dissolution ICP OES technique		INAA technique	Certified value
	Procedure a wet digestion on a hot plate	Procedure B dry ashing		
Ca	9209 ± 147	9331 ± 207	9097 ± 192	9220 ± 490
Cu	0.40 ± 0.04	0.44 ± 0.05	*	0.46 ± 0.08
Fe	1.95 ± 0.43	1.87 ± 0.13	1.88 ± 0.14	1.8 ± 1.1
K	13484 ± 288	13844 ± 263	13410 ± 230	13630 ± 470
Mg	794 ± 17	813 ± 27	798 ± 13	814 ± 76
Mn	0.16 ± 0.01	0.17 ± 0.02	0.20 ± 0.04	0.17 ± 0.05
Na	3555 ± 54	3670 ± 98	3559 ± 99	3560 ± 400
P	7632 ± 228	7871 ± 135	na	7800 ± 490
Zn	26.7 ± 2.0	27.7 ± 2.0	29.0 ± 1.9	28.0 ± 3.1

*, not detected; na, not analyzed; number of determinations, 6.

results obtained by both techniques were compared with certified values. The ICP OES and INAA results for the analyzed elements in SRM-1549 and RM-8435 are summarized in Tables 4 and 5, respectively. The concentrations obtained for SRM-1549 and RM-8435 agreed well with reference values. No statistical difference was found at the 95% confidence level.

4. Conclusions

The wet digestion using a HCl/H₂O (1:1) mixture has proved to be fast, precise and accurate sample preparation procedure for multi-element determination of Ca, Cr, Cu, Fe, K, Mg, Mn, Na, P and Zn in dairy products (chocolate milk, yogurt and Petit Suisse cheese). This

sample pretreatment has shown to be faster than the conventional dry ashing procedure.

The employment of a hot plate to digest the samples could avoid the acquisition of high cost equipment in the laboratory. Besides, many samples can be digested at the same time depending on the size of the hot plate.

The proposed wet digestion has also eliminated the problem with the intensive monitoring since the use of hydrochloric acid avoids risk of explosion caused when oxidant reagents are used. In addition, only 2 h are required to digest the samples, saving time and consequently reducing problems with contamination. This is an important point when large volumes of samples must be processed routinely.

The INAA technique was useful to determine inorganic elements since there is no need to digest the samples. Thus, the INAA has proved to be beneficial to compare results obtained from different sample pre-treatment procedures.

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