Manganese and Zinc Analysis in Milk by Microwave Oven Digestion and Platform Graphite Furnace Atomic Absorption Spectrometry

Miguel Angel de la Fuente, Gonzalo Guerrero, and Manuela Juárez*

Instituto del Frío (CSIC), Ciudad Universitaria s/n, 28040 Madrid, Spain

A conventional microwave oven acid digestion system employing PTFE reactors was tested for sample digestion prior to the analysis of Mn and Zn in milk. The digestion procedure was based on sample dissolution with nitric acid using microwave heating in closed vessels. Sample treatment time in the microwave oven was reduced to 15 min. The resulting solutions, analyzed for Zn by flame atomic absorption spectrometry (FAAS) and by platform graphite furnace atomic absorption spectrometry with Zeeman background correction for Zn and Mn, showed good agreement with the certified milk values (SRM-1549 nonfat milk powder, National Institute of Standards and Technology), and results were comparable to those obtained by dry mineralization in real samples. The precision of the method was about 6% for Mn and 5% for Zn by graphite furnace atomic absorption spectrometry (GFAAS) with limits of detection of 0.07 and 0.28 μg L^{-1}, respectively. The digestion procedure can be used to determine Zn by FAAS and Mn by GFAAS in milk analysis. Using GFAAS, Zn can also be measured in milk fractions where it is found in smaller concentrations.

INTRODUCTION

Mn and Zn are decisive in human nutrition and metabolism and can be found in dairy products in different concentrations. Milk is a poor source of Mn, and its mean values in cow's milk, from different breeds, treatments, and countries, range from 10 to 50 μg L^{-1} (Koops and Westerbeek, 1993), the major part being found in the casein fraction (Lönnerdal et al., 1983). Dairy products are reported to contribute up to 25% of Zn in Western diets, and cow's milk contains between 3 and 5 mg kg^{-1} (International Dairy Federation, 1992a), the majority (>90%) being found in the skim fraction associated with casein micelles (Flynn and Power, 1985).

In general, the preparation of milk samples to determine trace elements is achieved by using conventional wet digestion (Emmett, 1988; Krushevska et al., 1992; Koops and Westerbeek, 1993; Alkanani et al., 1994) or dry ashing (Juárez and Martínez-Castro, 1979; Koops et al., 1986; International Dairy Federation, 1992b; Krushevska et al., 1992). Microwave oven digestion of a variety of samples has proven to be faster, safer, and more efficient (Taylor et al., 1994). In addition, the use of poly(tetrafluoroethylene) (PTFE) closed reactors results in lower blank values, less contamination, fewer acid fumes, more complete sample recovery, and the possibility of unattended operation (Fidler and Schöner, 1994).

Few papers have been published on the determination of microelements in dairy products using microwave digestion. The majority of procedures employ inductively coupled plasma atomic emission spectrometry (ICP-AES) for the final analysis (Emmett, 1988; White, 1988; Fagioli et al., 1990; Krushevska et al., 1992; Alkanani et al., 1994). This technique is very costly and relatively insensitive compared with graphite furnace atomic absorption spectrometry (GFAAS) when the concentrations of trace elements are low. GFAAS appears to be better suited to applications requiring high sensitivity for the analysis of small concentrations of trace elements. The stabilized temperature platform furnace concept (Slavin et al., 1981) and Zeeman effect background correction allow largely interference-free determinations.

This paper describes the application and evaluation of a commercial microwave digestion system using closed vessels for the digestion of milk samples prior to determination of Zn by flame atomic absorption spectrometry (FAAS) and traces of Zn and Mn by GFAAS. Validation of this method has been achieved using certified reference material and by comparing the results obtained in real samples with those carried out by dry ashing.

MATERIALS AND METHODS

Instrumentation. *Microwave Oven.* A domestic microwave oven, Texet Model 112, was used for microwave digestions. For monitoring the pressure and temperature during mineralization, a commercially available laboratory oven, Model MDS-2000 (CEM, Indian Trail, NC) rated at 650 W was used. This apparatus and its characteristics have been described previously (De la Fuente and Juárez, 1995). For safety reasons the microwave oven was placed in a separate room isolated from the rest of the laboratory.

Measuring Apparatus. A Model Zeeman 5100 PC atomic absorption spectrometer (Perkin-Elmer, Norwalk, CT) with an HGA-600 graphite furnace, Zeeman background correction, and AS-60 autosampler were used for Mn and Zn trace determinations. The instrument includes a graphics display unit; time-resolved signals were plotted with an Epson LX-800 printer. Analyte concentrations were determined using peak area measurements. Pyrolitic graphite-coated graphite tubes with L'vov platform inserted were used. Hollow cathode lamps of 15 mA for Mn (Activion Glass Ltd.) and of 20 mA for Zn (Intensitron, Perkin-Elmer), respectively, were employed. Operation parameters were as follows: wavelength, 213.9 (Zn) and 279.5 (Mn) nm; slit width, 0.7 (Zn) and 0.2 (Mn) nm. This apparatus was also utilized for measuring Zn by FAAS with impact bead in an air/acetylene flame (10/2 L min^{-1}).

Reactors and Glassware. The reactors used for the digestions were laboratory-made with PTFE and specially designed to withstand high pressures and temperatures. They had a volume of 125 mL with 10 mm wall thickness, 20 mm thread

depth, and tight-fitting screw-cap lids. This material was chosen because it has a softening point of about 250 °C and shows low surface adsorption of ions. To avoid the leaching of contaminating substances, we have adopted the cleanup procedure recommended by Kimber and Kokot (1990) for trace analysis: The reactors were heated at 448 W in the microwave for 10 min with 50% HNO_3 and then thoroughly rinsed with deionized water. Moreover, all reactors, glassware, and crucibles were kept in 10% HNO_3 and were rinsed thoroughly with distilled water before use.

Reagents and Standard Solutions. Analytical reagent grade water with a metered resistivity of 18 MΩ cm was used to prepare all samples and standards. All reagents used were of the highest purity available and at least of analytical reagent grade: 65% m/v HNO_3 Suprapur grade (Merck) and Zn and Mn standard solutions for spectrophotometry, 1 ± 0.002 g L^{-1} (Panreac). From these, external calibration standards for GFAAS were prepared containing 1 and 3 μg L^{-1} (Zn) and 2.00 and 5.00 μg L^{-1} (Mn). In the same way more concentrated Zn standard solutions (0.25 and 0.50 μg mL^{-1}) were made for use in FAAS. A magnesium chemical modifier for graphite furnace was prepared from $Mg(NO_3)_2$ hexahydrate Suprapur (Merck) in the concentrations recommended (1.78% w/v) by the manufacturer (Perkin-Elmer, 1984).

All solutions were prepared within a laminar-flow cabinet with a high-efficieny particulate airborne 0.3 μm filter.

Samples and Reference Material. Validation of the method described in this paper was performed by using a certified reference material from the National Institute of Standards and Technology, SRM-1549 nonfat milk powder; 2.5 g of this material was dissolved in water and diluted to 25 mL to reconstitute the liquid milk for subsequent use. Commercial ultrahigh-temperature (UHT) milks, skim and whole milk samples with 0.1 and 3.5% fat content, respectively, were also utilized in this study.

Procedures. The dry ashing mineralization method was carried out according to an IDF Standard (International Dairy Federation, 1992b). Milk samples were weighed into a porcelain crucible and dried on a hot plate. After charring, samples were incinerated in a muffle furnace at 450 °C. If necessary, the ash was bleached by treatment with HNO_3 and heating in the muffle furnace for 1 h. Finally, the ashes were diluted with concentrated nitric acid (2% v/v in the final sample solution) and distilled water and measured by atomic absorption.

The recommended procedure for conventional microwave oven digestion of samples is as follows: Two milliliters of sample (UHT milks or reconstituted certified milk) was placed in a PTFE reactor and 2 mL of 65% m/v HNO_3 was added. Six reactors were closed and situated in outer positions to ensure maximum irradiation inside a lidded plastic container, which was placed on the rotating turntable as described by De la Fuente and Juárez (1995). Samples were irradiated at a 583 W power setting for 5 min, and then the power was decreased to 380 W for 10 min and the reactors were removed from the oven. After the reactors were cooled to room temperature in an ice bath to reduce the internal pressure, the screw caps were removed. The yellowish and transparent solution obtained was diluted to enable AAS measurements in the optimum linear range for Mn and Zn in the different assays. Finally, the procedure involved simultaneous injection in the platform furnace by the autosampler of 5 μL of the modifier solution and 20 μL of sample or standard solution.

The procedure using the analytical microwave oven to evaluate pressure and temperature was similar to that just cited and was described in a previous paper (De la Fuente and Juárez, 1995).

RESULTS AND DISCUSSION

Digestion Conditions. The most frequently used acid for mineralization by microwave oven is nitric acid. This acid behaves ideally under microwave energy excitation, has a relatively low boiling point, can be obtained in ultrahigh purity, and lacks the hazards and
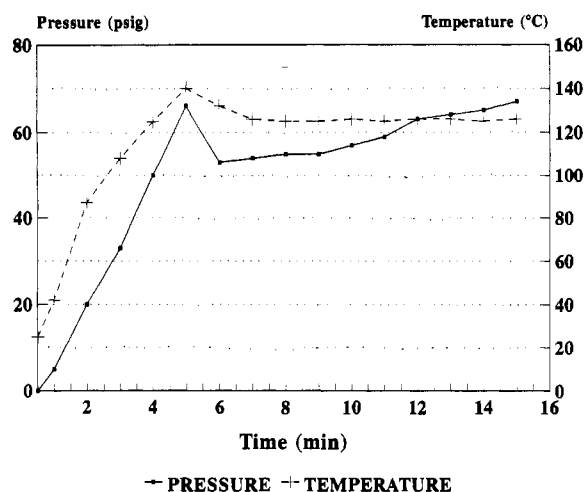

Figure 1. Development of pressure and temperature during mineralization in the microwave oven: 5 min at 583 W followed by 10 min at 247 W.

inconveniences of other acids. HNO_3 often requires temperatures above 120 °C and the addition of other strong oxidizing agents such as peroxide or perchloric acid to completely destroy the organic matter. White (1988) employed the microwave oven to digest samples of different foodstuffs with HNO_3 and H_2O_2 in open and semiclosed reflux vessels. Mineralization periods that exceeded 60 min were required. In view of the positive results obtained in an earlier study with the use of HNO_3 for the digestion of milk samples (De la Fuente and Juárez, 1995), we omitted the H_2O_2 addition. The mineralization was done in closed vessels. Such vessels have the disadvantage, however, that only small volumes of sample can be used, a problem inherent to trace element analysis. Nevertheless, diminishing the risk of contamination and reducing the loss of those elements represent considerable advantages.

A range of volumes of acid, sample sizes, and power settings of the microwave oven were used, employing two stages of power and time setting to ensure total recovery of Mn and Zn after sample treatment. The addition of 2 mL of HNO_3 to 2 mL of milk with the microwave program cited above achieved an efficient digestion, producing a pale yellow transparent solution appropriate for final measurement.

Pressure and Temperature of the Digestion. Serious consideration has been given to the safety aspects of microwave pressure digestion. The mineralization temperature should be controlled to avoid excessive heating of the reactors. PTFE vessels are not recommended for use above 200 °C (Kimber and Kokot, 1990). Experiments were made to assess the pressure and temperature generated during digestion in the conditions described above (Figure 1). The pressure in the first stage gradually increased to 66 psig, settled down to 53 psig immediately after the second stage of irradiation commenced, and started to rise again, but more slowly, to 55 psig during the final stage of the program. The temperature increased exponentially during the first moments of digestion up to 100 °C, thereafter rising more gently up to 140 °C for the final part of the first stage (5 min) of high-power irradiation (583 W). During the second mineralization stage, the temperature dropped to 125 °C and then remained steady. These parameters did not constitute hazards for the integrity of the PTFE vessels. In addition, these temperatures are above the boiling point of nitric acid
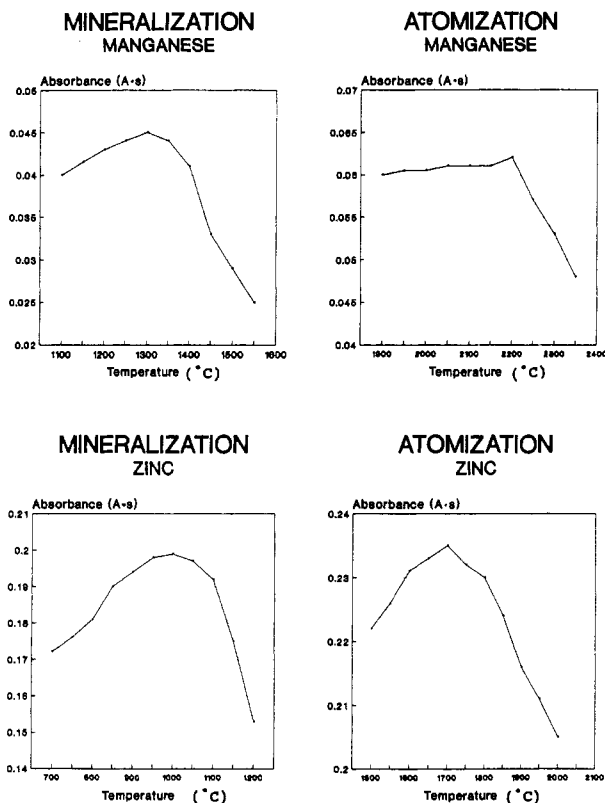
Figure 2. Mineralization and atomization absorbance curves for Mn and Zn in milk samples mineralized by microwave oven.

Figure 3. Typical signals for analytes Mn (A) and Zn (B) and background in milk samples mineralized in microwave oven. Solid lines correspond to absorbance readings and broken lines to background readings. Atomization temperatures were 2200 °C (Mn) and 1700 °C (Zn).

Table 1. Temperature Programs for Determination of Zn and Mn in Milk by Graphite Furnace Atomic Absorption Spectrometry

| | furnace (°C) | | ramp | | hold | | internal flow rate |
step	Zn	Mn	Zn	Mn	Zn	Mn	(mL min^{-1})
1, drying	80	80	1	1	10	10	300
2, drying	103	103	10	10	50	50	300
3, drying	120	120	10	10	20	20	300
4, ashing	1000	1300	10	10	20	20	300
5, cooling	20	20	1	1	15	15	300
6, atomization	1700	2200	0	0	4	5	0 (read)
7, cleaning	2600	2600	1	1	5	5	300
8, cooling	20	20	1	1	15	15	300

(120 °C), which substantially increases the rate of digestion.

Optimization of the Graphite Platform in Furnace Program. The temperature–time programs in the graphite furnace were optimized to provide maximum matrix decomposition without loss of analyte, compatible with minimum background and maximum Mn and Zn absorbances in the atomization stage. These programs are shown in Table 1.

The influence of the temperature on the development of the analytical signal for ashing and atomization was also evaluated (Figure 2). An additional cooling step was inserted between the ashing and the atomization. The use of a cooling step prior to atomization maximized the heating rate and extended the isothermal zone within the tube immediately after heating. The extended isothermal zone improved sensitivity and reduced peak tailing in both elements.

Figure 3 depicts the shape and size of the atomic absorption peaks for Mn and Zn and the corresponding background values when microwave digestion was employed in milk samples. While the background signal
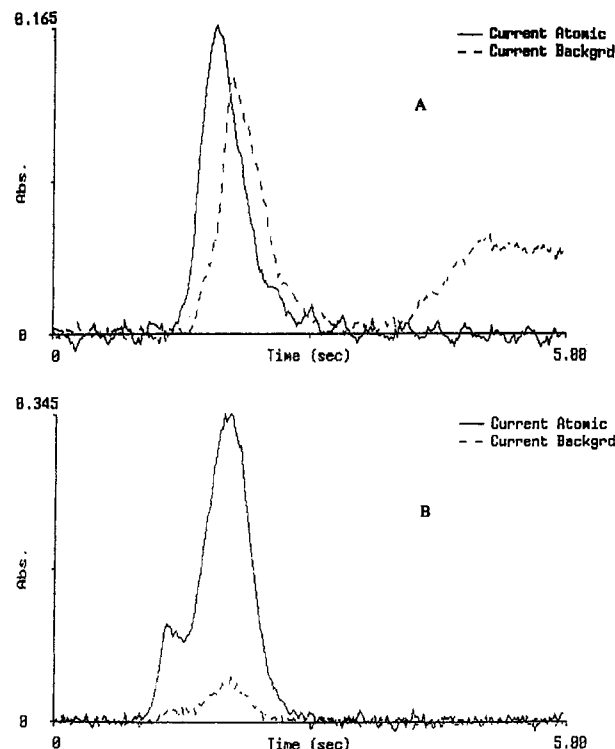
Table 2. Analytical Performance Characteristics, Sensitivity (S) (Absorbance Units per Microgram per Liter), Detection Limit (DL) (Micrograms per Liter), and Characteristic Mass (Picograms) (m_0) for Mn by GFAAS and for Zn by FAAS and GFAAS

| | FAAS | | GFAAS | |
element	S	DL	m_0	DL
Zn	18	9.61	1.05	0.28
Mn			3.65	0.07

showed clearly in Mn analysis, it was distinctly lower for Zn. In both cases Zeeman background correction permits correction of these signals.

Analytical Characteristics. To check the validity of the proposed methods for the determination of Mn and Zn in milks, the analytical characteristics such as sensitivity (S), detection limit (DL), and characteristic mass (m_0) were evaluated; they are shown in Table 2. S was established from the mean value of the slopes of the external standard (FAAS) and expressed in absorbance units per microgram per liter; m_0 is the mass of analyte in picograms required to produce an integrated peak area signal of 0.00044 absorbance seconds (A·s). DL, defined as the analyte concentration in micrograms per liter of milk which provides an absorbance reading statistically different from that of the blank, was calculated by dividing 3 times the standard deviation of the absorbance readings of the reagent blanks by the sensitivity. m_0 was 2.2 and 1.05 pg, respectively, for Mn and Zn, comparable to values achieved for Mn (about 2.9 pg) under similar experimental conditions (Koops and Westerbeek, 1993). DL found for Mn (0.07 μg L^{-1}) confirms that the concentration obtained, although remaining far from the values established theoretically (International Dairy Federation, 1992a) (0.01 μg L^{-1}), is better than that obtained in studies on ICP-AES (Alkanani et al., 1994), where in some cases

Mn and Zn Analysis in Milk

J. Agric. Food Chem., Vol. 43, No. 9, 1995 **2409**

Table 3. Content of Manganese in Commercial Skim and Whole Milk (Micrograms per Kilogram) and Reconstituted Certified Milk (SRM-1549) Mineralized by Dry Ashing and Microwave Oven and Measured by Graphite Furnace Atomic Absorption Spectrometry

| assay | SRM-1549 (26 ± 6)[a] | | whole milk | | | skim milk | |
	microwave	microwave[b]	dry ashing	microwave	microwave[b]	dry ashing	microwave
1	25.25	28.00	20.90	18.75	17.38	28.30	29.50
2	24.75	22.88	22.10	21.88	20.25	27.10	25.38
3	25.00	24.88	19.90	19.63	18.25	28.90	29.63
4	24.00	26.75	23.80	20.75	21.34	29.30	26.13
5	23.13	28.88	20.10	20.10	22.13	28.40	27.76
6			19.80	18.88	21.88	29.30	26.13
7			21.10	18.38	21.25	27.00	27.13
8			21.50	21.50	21.00	29.30	29.63
av	24.43	26.28	21.15	19.98	20.44	28.45	27.69
SD	0.86	2.42	1.34	1.31	1.73	0.95	1.70
RSD %	3.53	9.22	6.34	6.53	8.45	3.30	6.14

[a] Certified value ± 95% confidence interval. [b] Determined by standard additions.

Table 4. Determination of Zn in SRM-1549 Reconstituted and Commercial Milk (Whole and Skim) (Milligrams per Kilogram) Mineralized in Microwave Oven by Graphite Furnace Atomic Absorption Spectrometry

| assay | SRM-1549 (4.61 ± 0.22)[a] | | skim milk | whole milk |
	A[b]	B[c]		
1	4.53	4.67	4.63	3.63
2	4.72	4.47	4.41	3.61
3	4.55	4.73	4.45	3.52
4	4.74	5.10	4.41	3.52
5	4.65	4.63	4.08	3.97
6			4.13	3.59
7			4.11	3.45
8			4.33	3.80
av	4.64	4.72	4.32	3.64
SD	0.10	0.23	0.20	0.17
RSD %	2.07	4.94	4.52	4.68

[a] Certified value ± 95% confidence interval. [b] External calibration. [c] Standard addition.

Table 5. Determination of Zn in SRM-1549 Reconstituted and Commercial Milk (Whole and Skim) (Milligrams per Kilogram) Mineralized by Dry Ashing and Microwave Oven by Flame Atomic Absorption Spectrometry

| assay | SRM-1549 (4.61 ± 0.22)[a] | skim milk | | whole milk | |
		dry ashing	microwave	dry ashing	microwave
1	4.71	4.10	4.50	3.42	3.49
2	4.70	4.06	4.50	4.11	3.94
3	4.68	4.24	4.38	3.73	3.99
4	4.75	4.50	4.63	3.39	3.64
5	4.75	4.20	4.41	3.79	3.70
6		4.20	4.59	3.40	3.78
7		4.46	4.43	3.65	3.75
8		4.44	4.34	3.27	3.79
av	4.72	4.28	4.47	3.60	3.76
SD	0.03	0.17	0.10	0.28	0.16
RSD %	0.63	3.96	2.27	7.72	4.24

[a] Certified value ± 95% confidence interval.

(Fagioli et al., 1990) Mn can be undetected. With regard to Zn, the use of impact bead reduces the DL (9.61 μg L^{-1}) for FAAS to concentrations that are approximately half those generally obtained by flow spoiler (Munro and Sneddon, 1987), which makes it comparable to ICP-AES (Krushevska et al., 1992; Alkanani et al., 1994). For the analysis of samples having lower concentrations, such as milk serum or soluble milk fractions, GFAAS provides a lower DL (0.28 μg L^{-1}).

Analysis of Standard Reference Material. To test the accuracy of the method, Mn and Zn were analyzed in certified material, SRM-1549, under specified conditions and using the graphite furnace programs given in Table 1 with calibration against matrix-free reference solutions. Five independent analyses were carried out on the standard reference material (Tables 3–5). The high level of accuracy of the method is demonstrated by the agreement of the results obtained in the analysis of the SRM-1549 with the certified values.

A comparison of methods using external standard calibrations versus standard additions for the determination of manganese in SRM-1549 and whole milk (Table 3) and zinc in SRM-1549 (Table 4) shows no significant differences between the two procedures. However, the relative standard deviation (RSD) was higher for data obtained by the method of standard additions. It appears that standard addition procedures are unnecessary with these types of milk samples, and it is possible to obtain accurate data from a direct determination with external aqueous standards.

Although these data for Zn are similar to those obtained in other studies on certified samples mineralized by microwave and measured by ICP-AES (Emmett, 1988; White, 1988; Alkanani et al., 1994), Mn data obtained by GFAAS are closer to the certified values.

With the aim to test the efficiency of FAAS for the determination of Zn, SRM-1549 samples digested in the microwave oven were less diluted than those used for GFAAS and their concentration was determined by FAAS with bead impact. The results obtained (Table 5), 4.72 ± 0.03 mg L^{-1}, are close to the certified values (4.61 ± 0.22 mg L^{-1}) and are similar to those obtained by Koops et al. (1986) for the same certified sample mineralized by muffle furnace and measured by FAAS as well. Munro and Sneddon (1987), also utilizing microwave oven heating and FAAS, produced optimal though slightly lower values for certified samples, which was probably due to a "milder" mineralization process by microwave than the one used in this study.

Precision of the Method. Precision is expressed as the RSD of eight independent analyses of the same milk samples. The determination of the precision was carried out using dry mineralization and microwave oven digestion procedures with Zn and Mn in skim and whole market milks.

Manganese in both cases was measured by GFAAS. The mean values obtained by the two methods of mineralization used are comparable (Table 3). With a confidence level of 95% the F values of Snedecor exceed the ratio between the variances of the two series of

measurements (1.05 and 3.20 versus 3.87), from which it can be deduced that the differences are not sufficiently significant to be attributed to the method. The values of RSD obtained for Mn (about 6%) were similar for whole milk by both methods of mineralization; in skim milk the spread was less (RSD = 3.30) when mineralization was by dry ashing. The above values are within the RSD values reported in the recent literature in similar studies (Koops and Westerbeek, 1993) and are superior to those produced when a simple dilution of the milk sample with water is applied before introduction into the graphite furnace. In a GFAAS study on several microelements, one of them being Mn measured by GFAAS, Salvato et al. (1989) made use of reconstituted milk powder (1:10). Although accurate values were found in certified samples, their variation of around 20% is unacceptable. This is probably due to the casein micelles, which bind about 80% (Lönnerdal et al., 1983) of the Mn in milk and tend to settle on prolonged standing of the diluted milk in the autosampler cups. Thus, recovery after atomization of the milk powder solution can be variable (Koops and Westerbeek, 1993).

The results obtained with Zn for both types of milk by the different methods, FAAS (with muffle furnace and microwave oven) and GFAAS (microwave), produced average values that are similar (Tables 4 and 5). Yet, precision is better (2.27 and 4.24%) in samples processed by microwave and measured by FAAS. The values obtained by GFAAS, preceded by digestion in the microwave oven, show an equal spreading, or less, as the same milk samples mineralized in the muffle furnace and measured by FAAS. The F values of Snedecor, in a comparison of the variances of the classic mineralization processes with the two by microwave, did not show significant differences in the two types of milk used.

Conclusions. Milk digestion in pressurized PTFE closed vessels using microwave heating proved to be a rapid and effective method for the digestion of milk to determine Zn and Mn by GFAAS, an improved alternative to conventional dry and wet mineralization. Sample preparation times are reduced from hours to 15 min. The use of GFAAS allows lower analyte concentrations, and the agreement between reference values and results illustrates the viability of the described procedure. Additionally, it is clear that with this type of digestion none of these elements are lost from the samples and that the risks of contamination are reduced. Mn and Zn can easily be measured, in different concentrations, by using this combination: microwave mineralization followed by measurement by atomic absorption.

LITERATURE CITED

Alkanani, T.; Friel, J. F.; Jackson, F. E.; Longerich, H. P. Comparison between digestion procedures for the multielemental analysis of milk by inductively coupled plasma mass spectrometry. J. Agric. Food Chem. 1994, 42, 1965–1970.

De la Fuente, M. A.; Juárez, M. Rapid determination of calcium, magnesium, sodium and potassium in milk by flame atomic spectrometry after microwave oven digestion. Analyst 1995, 120, 107–111.

Emmett, S. E. Analysis of liquid milk by inductively coupled plasma mass spectrometry. J. Anal. At. Spectrom. 1988, 3, 1145–1146.

Fagioli, F.; Landi, S.; Locatelli, C.; Righini, F.; Settimo, R.; Magarini, R. Determination of elements in biological materials by inductively coupled plasma atomic emission spectrometry with sampling of a carbonaceous slurry. J. Anal. At. Spectrom. 1990, 5, 519–522.

Fidler, R.; Schöner, A. A by-pass for sampling bottleneck. Anal. Eur. 1994, 1, 39–42.

Flynn, A.; Power, P. Nutritional aspects of minerals in bovine and human milks. In Developments in Dairy Chemistry—3; Fox, P. F., Ed.; Elsevier Applied Science Publishers: London, 1985; pp 183–215.

International Dairy Federation. Trace elements in milk and dairy products. Bull. Int. Dairy Fed. 1992a, 278, 57.

International Dairy Federation. Milk and milk products. Determination of Zn content. Flame atomic absorption method. International IDF Standard 119, 1992b.

Juárez, M.; Martínez Castro, I. Atomic absorption spectrophotometric determination of sodium, potassium, calcium, magnesium, iron, copper, zinc, and manganese of market milk. Rev. Agroquim. Tecnol. Alim. 1979, 19, 45–54.

Kimber, G. M.; Kokot, S. Practical options for microwave digestions. Trends Anal. Chem. 1990, 6, 203–207.

Koops, J.; Klomp, H.; Westerbeek, D. Spectrophotometric and flame atomic absorption spectrometric determination of zinc in milk and milk products. Comparison of methods. Neth. Milk Dairy J. 1986, 40, 337–350.

Koops, J.; Westerbeek, D. Manganese in dutch powder. Determination by Zeeman-corrected stabilized-temperature platform-furnace atomic-absorption spectroscopy. Neth. Milk Dairy J. 1993, 47, 1–13.

Krushevska, A.; Barnes, R. M.; Amarasiriwaradena, C. J.; Foner, H.; Martines, L. Comparison of sample decomposition procedures for the determination of Zinc in milk by inductively coupled plasma atomic emission spectrometry. J. Anal. At. Spectrom. 1992, 7, 851–858.

Lönnerdal, B.; Keen, C. L.; Hurley, L. S. Manganese binding in human milk and cow's milk—an effect on bioavailability. Fed. Proc. 1983, 42, 926.

Munro, J. L.; Sneddon, J. Determination of six elements in infant formula by flame and furnace atomic absorption spectrometry. At. Spectrosc. 1987, 8, 92–95.

Perkin-Elmer. Analytical methods for furnace atomic absorption spectrometry. Uberlingen, Germany B332, 1984.

Salvato, N.; Banfi, G.; Taccani, F.; Rottoli, A.; Banderari, G. In Applicazioni dell'ETA-AAS Zeeman nel Laboratorio Chimico e Tossicologico; Minoia, C., Caroli, S., Eds.; Edizioni Libreria Cortina: Padova, Italy, 1989; Vol. 1, pp 323–342.

Slavin, W.; Manning, D. C.; Carnrick, G. R. The stabilized temperature platform furnace. At. Spectrosc. 1981, 2, 137–145.

Taylor, A.; Branch, S.; Crews, H. M.; Halls, D. J.; White, M. Atomic spectrometry update—clinical and biological materials, foods, and beverages. J. Anal. At. Spectrom. 1994, 9, 87R–132R.

White, R. T., Jr. Open reflux vessels for microwave digestion: Botanical, biological, and food samples for elemental analysis. In Introduction to Microwave Sample Preparation. Theory and Practice; Kingston, H. M., Jassie, L. B., Eds.; ACS: Washington, DC, 1988; pp 53–77.