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DETERMINATION OF MAJOR AND MINOR ELEMENTS IN MILK THROUGH ICP-AES

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Abstract

Milk products are a very important human nutrient since their consumption has increased in recent years. Good quality measurements are essential to control and maintain milk products and processes quality, both in manufacturing, trade and in research. The presence of toxic elements in powdered and liquid milk may create significant health problems for people. The aim of this paper was to determine the content of major and minor elements in different milk samples, sold in major supermarket chains in Romania. Inductively coupled plasma atomic emission spectrometry (ICP-AES) was used for the quantitative determination of elements in this matrix. Analyses were performed after the chemical mineralization of the samples with nitrogen acid. Detection limits ranged from 0.4 to7.03 ng/g.

Key words: milk, ICP-AES, major and minor elements

1. Introduction

Good quality measurements are essential to control and maintain products and processes quality, both in manufacturing, trade and in research. Milk products are a very important human nutrient since their consumption has increased in recent years. These products are also a good source of calcium and there biodisponibility is high.

Many dangerous elements or compounds, such as metals and metalloids, accumulate along the food chain. Furthermore their concentrations in the environment grow with the increase of urban, agricultural, and industrial emissions. The almost ubiquitous presence of some metal pollutants, especially Cd and Pb, facilitates their entry into the food chain and thus increases the possibility of them having toxic effects on humans and animals. Although heavy metals have industrial uses, their potential toxicity for people and animals is the object of several studies. For some elements the effects are accumulative and it is necessary to control them level in consumed food.

So, measurements of minor and trace metal contents, comprising Al, Pb, Cd, Cr, Cu, Fe, Mg, Mo, Mn, Ni, P, Sb, Si, Sn, Zn, Ti is also very helpful in assessment of quality of milk during its manufacturing treatment and production.

For carrying out these determinations were used different techniques: flame atomic absorption spectrometry (Kondyli et Prusisz, 2007; Pohl et al., 2007), capillary zone electrophoresis (Suarez-Luque et al., 2007), inductively coupled argon plasma emission spectroscopy (Park, 2000), differential pulse anodic stripping voltammetric technique (Tripathi et al., 1999), inductively coupled plasma optical emission spectrometry (Kira and Maihara, 2007), flow injection spectrometric methods (Nogueira Rita de Araujo et al., 1998), atomic fluorescence spectrometry (Cava-Montesinos et al., 2004) and stripping potentiometry (Munoz and Palmero, 2004).

Many reports indicate the presence of heavy metals in milk, and often it is needed to assess the levels of heavy metals in food. Lead, cadmium and mercury residues in milk are of particular concern because milk is largely consumed by infants and children (Caggiano et al., 2005; Licata et al., 2004; Tajkarimi et al., 2008; Zheng et al., 2007), and the determination of these heavy metals levels in milk is

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particularly attended by international organizations (Codex Alimentarius Commission, 2003).

The objective of this study was to determinate the Al, Pb, Cd, Cr, Cu, Fe, Mg, Mo, Mn, Ni, P, Sb, Si, Sn, Zn, Ti in milk samples by inductively coupled plasma atomic emission spectrometry (ICP-AES). This technique performs the simultaneous-sequential determination in a large number of elements from environmental and biological samples, being advantageous from the viewpoint of the short time and the low limit of detection.

2. Experimental

2.1 Reagents and solutions

All reagents used were of analytical reagent grade (Merck). Deionised water was used for the preparation of all solutions.

The working standard solutions were prepared by diluting the stock solutions (1000 mg/l) in 10% hydrochloric acid. All working standard solutions were stored in polypropylene bottles.

The nitric acid (65%) and hydrogen peroxide solutions used were of ultrapure grade, purchased from Merck.

All glassware was initially washed with detergent and water, and then the glassware was rinsed several times with deionized water and dried.

2.2. Sample preparation

Powder milk and cow milk (fresh and pasteurized from different producers) were the samples analyzed in this study and they were purchased in local markets in the city of Constanta, Romania.

A known volume of milk (25 mL) was evaporated to near dryness, wet-ashed and taken up in 10 ml of 0.25% HNO_3.

2.3. Sample analysis

A Spectroflame P (Spectro Company, Germany) ICP-AES 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. For each sample three determinations were performed and average results were reported. Detection limits of the elements studied in milk samples (Table 2) were determined from the standard addition curves of each element in different samples. It was based on the usual definition as the concentration of the analyte yielding a signal equivalent to three times the standard deviation of the blank signal. The detection limits of the method are good and permit the determination of the elements in milk at background concentrations.

Table 1. ICP-AES operating conditions

Operating conditions	
RF frequency	27.12 Hz
RF power	2.5 Kw
Outer gas flow rate	Ar 17 L/min
Intermediate gas flow rate	Ar 1 L/min
Carrier gas flow rate	Ar 1 L/min
Observation height	18 mm above work coil
Plasma's temperature	8000-9000 K

Table 2. Detection limits for ICP-AES method

Element	***Detection limit (ng/g)***	***Element***	***Detection limit (ng/g)***
Al	1.02	Mn	1.87
Pb	7.03	Ni	1.03
Cd	0.63	P	0.4
Cr	1.87	Sb	6.5
Cu	0.90	Si	1.0
Fe	0.5	Sn	5
Mg	2.27	Zn	4
Mo	1.16	Ti	2

3. Results and discussion

The results of the mineral analysis of milk samples are given in table 3 and 4. The P content of powder milk was lower then the value reported by Park (Park, 2000) and the concentrations of fresh cow milk samples were comparable with those encountered in goat milk samples (Kondyli et al., 2007). This mineral plays an essential role in the human organism and it is well known that milk and dairy products are good dietary sources of P and their contributions to the total P daily intake have been reported to be 30–45% (Cashman, 2003).

The concentration levels of Mg in fresh cow milk observed in this study are higher than those observed in raw goat milk: 151-167 ppm (Kondyli et al., 2007). Also, the concentration levels of Mg in commercial milk samples observed in this study were higher than those observed in commercial milk samples from Spain: 126 ppm (Suarez-Luque et al., 2007).

Table 3. P and Mg contents of milk samples collected from local markets

Element	***Concentration (ppm)***				
	powder milk	**fresh cow milk**	**pasteurized milk**		
			Brenac	**La Dorna**	**Diami**
P	3933.00	1608.00	2736.00	914.00	922.00
Mg	919.80	214.00	344.00	139.21	155.24

As far as trace minerals are concerned, there were no indications of abnormal levels of Cr, Cu, Fe, Zn, Al, B, Mn, Mo, Ni, Sb, Sn and Ti in the milk samples collected from local markets.

The level of iron in fresh cow milk is slightly higher than the report of Park (Park, 2000)

where the average Fe concentration in fluid goat milk was 0.55 mg/L. The mean Fe content (ppm) of the pasteurized milk samples in this study was 4.64 mg/l, which is significantly lower than that of powdered milk (Table 4).

Table 4. Mineral contents of milk samples collected from local markets

Element	*Concentration (ppm)*				
	powder milk	fresh cow milk	pasteurized milk		
			Brenac	La Dorna	Diami
Cr	0.18	0.04	0.10	0.04	0.06
Cu	0.54	0.17	0.10	0.08	0.16
Fe	21.73	0.72	11.84	1.30	0.80
Zn	3.24	0.98	1.54	0.52	0.48
Al	1.90	1.18	4.16	4.14	1.22
B	0.10	0.04	0.04	0.04	0.04
Mn	0.29	0.08	0.09	0.04	0.07
Mo	0.18	0.04	0.04	0.04	0.04
Ni	0.18	0.04	0.04	0.04	0.05
Si	0.49	0.44	1.08	0.66	0.52
Sb	0.45	0.10	0.10	0.10	0.10
Sn	0.45	0.10	0.10	0.10	0.10
Ti	0.19	0.04	0.04	0.04	0.04

The mean Zn concentration in the analyzed fresh cow milk samples (0.98 ppm) was lower than those reported in raw bovine milk (0.29-4.96 ppm) (Licata et al., 2004). The mean Zn concentration in powdered milk is 3.24 ppm and the Zn concentrations in the commercial cow milk samples are in range 0.48-1.54 ppm. These concentrations were lower then those determined in powdered and commercial goat milk (32.10 ppm, respectively 3.10 ppm) (Park, 2000).

Cu levels are in the line with those reported by other authors (Kira et Maihara, 2007; Kondyli et al., 2007; Tripathi et al., 1999). The low concentrations of Cu could be due to Zn contained in food that interferes with the copper absorption system, explaining the presence of low levels of this metal in milk (Doull's, 2000).

The range obtained for aluminium in this study was (1.18 - 4.16 ppm). These values are higher than those reported in other research papers (Ikem et al., 2002). There is concern because of the possibility of increased amounts of aluminium being deposited in the brain and the resulting risk of brain dysfunction (Walker, 2000) and aluminium is now being implicated as interfering with a variety of cellular and metabolic processes (American Academy of Pediatrics, 1998).

The trace minerals contents of the commercial cow milk products in this study generally were lower than the content of powdered milk.

The concentrations of ''toxic'' metals (Cd and Pb) in milk samples are reported in Table 5. The lowest levels were those of Cd (0.001-0.005 ppb). This study demonstrates that, in milk from Romania, there are highest concentrations only of lead among ''toxic'' metals. From a more detailed analysis of the results obtained, it appears that milk samples show a range of Pb (0.04-0.16 ppb) higher than those reported in literature (Caggiano et al., 2005; Tajkarimi et al., 2008) and lower than those reported by Licata (Licata et al., 2004).

Table 5. Cd and Pb (toxic metals) contents of milk samples collected from local markets

Element	*Concentration (ppb)*				
	powder milk	fresh cow milk	pasteurized milk		
			Brenac	La Dorna	Diami
Cd	0.001	0.004	0.005	0.004	0.003
Pb	0.16	0.12	0.04	0.11	0.04

However, it is of particular interest to note the presence of Pb in all samples studied were not in dangerous concentrations. If the maximum limits of lead for milk and secondary milk products were taken as 0.05 ppm each, the total exposure in the European diet (European diet provides maximum potential for weekly intake of lead through food) would be 4.631 g of lead per kg body weight (GEMS/food regional diets, 2003).

The results obtained show how this metal is ever more frequently found in milk samples, not only in regions with great industrial activity. The presence of Pb in milk samples could be due to various factors: transhumance along roads and/or motorways, fodder contamination, climatic factors, such as winds, and the use of pesticide compounds. One of the most important sources of lead contamination in milk is water, especially in more contaminated areas (Codex Alimentarius Commission, 2003); so, water testing should be one of the important topics for future study. Therefore, it is necessary to monitor this metal over time to better clarify its presence in milk.

At present, the CE Regulation no. 2001/466 (CE Regulation, 2001) establishes a limit for Pb in milk (MRL= 0.02 mg/kg w.w.). Therefore, the Pb concentrations below MRLs found in powdered, fresh and pasteurized milk samples from local markets indicate that the milks products are safe for the consumers. As regards Cd, its presence at low concentrations in milk samples shows that there are no toxicological risks in Romania.

4. Conclusions

The dry ashing procedure has proved to be precise and accurate sample preparation procedure for multi-element determination of Cr, Cu, Fe, Zn, Al, B, Mn, Mo, Ni, Sb, Sn and Ti in the powdered, fresh and pasteurized milk samples.

The results of this study showed that the studied cow milk samples generally, contained sufficient quantity of trace elements, a fact which has a great impact on its nutritional quality. The trace minerals contents of the commercial cow milk products in this study generally were lower than the content of powdered milk

The mean concentrations of the macroelement P in fresh cow milk samples were similar to those reported in the literature and the mean concentrations of the macroelement Mg in fresh and

commercial cow milk samples were higher than those reported in the literature.

Further studies are necessary to evaluate the contents of ''essential'' and ''toxic'' heavy metals on a greater number of milk samples from various producers in Romania and to confirm the absence of possible toxicological risks.

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