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Analytical Methods

Quantification of trace elements in raw cow's milk by inductively coupled plasma mass spectrometry (ICP-MS)

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ABSTRACT

The levels of trace elements are an important component of safety and quality of milk. While certain elements such as chromium are essential at low levels, an excess can result in deleterious effects on human health. International quality control standards for milk are published by the Codex Alimentarious Commission and levels of heavy metals in milk intended for human consumption are routinely monitored. This paper describes a new method for demonstrating the levels of V, Cr, Mn, Sr, Cd and Pb in raw cow's milk, using an ICP-MS. Samples (n = 24) of raw cow's milk were collected from dairy farms close to mines in Gauteng and North West Provinces of South Africa. In order to destroy organic matrix, each freeze dried milk sample was mineralised by using a microwave assisted digestion procedure. Concentrations of trace elements in digested milk samples were measured by ICP-MS. A whole milk powder reference material (NIST SRM 8435) was used to evaluate the accuracy of the proposed method. It was found that the levels of V, Cr, Mn, Sr, Cd and Pb obtained using the new method showed concordance with certified values.

1. Introduction

Milk is recognized as an almost complete food product in the human diet because it provides all macronutrients (such as proteins, lipids and carbohydrates) and all micronutrients (elements, vitamins and enzymes) (http://www.idfa.org/facts/milk/milkfact/milk5.pdf). This fact is particularly true in the case of early childhood, because milk (human, cow or formula) is the only source of nutrients during the first months of a baby's life and the diet of growing children contains a high proportion of milk and milk products. An appropriate intake of milk is also recommended for adults as a source of calcium to retain bone mass so that fractures and osteoporosis can be prevented (Kira & Maio, 2004).

The trace elements in cow's milk are of interest because of their essential or toxic nature. For instance, Cr and Mn are essential but may become toxic at higher levels, while Pb and Cd are toxic and can be cumulative (Martino, Sánchez, & Medel, 2000; Onianwa, Adetola, Iwegbue, Ojo, & Tella, 1999; Underwood, 1977). Cd and Pb are amongst the elements that have caused most concern in terms of adverse effects on human health. This is because they are readily transferred through food chains and are not known to serve any essential biological function (Liu, 2003). Children have been shown to be more sensitive to Cd and Pb than adults and the effects are cumulative, the elements build up in the tissues (Tripathi, Raghunath, Sastry, & Krishnamoorthy, 1999). As a result, the regular absorption of small amounts of elements such as Pb may cause serious effects on the health of growing children, including retardation of mental development (e.g. reading and learning disabilities) and deficiencies in concentration, adverse effects on kidney function, blood chemistry and the cardiovascular system, as well as hearing degradation (Salma, Maenhaut, Dubtsov, Papp, & Záray, 2000). It is therefore important to monitor the levels of trace elements in cow's milk, which forms a major source of nutrition in childhood, consumed with breakfast cereals and as yoghurt or cheese.

The concentrations of selected trace elements such as Al, Ba, Cd, Co, Cr, Cu, Fe, Mg, Mn, Ni, Pb, Pt, Sr and Zn in raw cow's milk and cheese were determined using inductively coupled plasma-optical emission spectrometry after lyophilisation followed by ashing (Coni, Bocca, Ianni, & Caroli, 1995; Coni, Caroli, Ianni, & Bocca, 1994). Coni et al. (1996) later assessed the concentrations of the same elements in sheep and goats milk as well as in cheese employing the same method. The determination of Ca, Cu, Fe, K, Mg, Mn, Na, P and Zn in infant formulae, milk powders and liquid milk by slurry nebulisation and inductively coupled plasma-optical emission spectrometry were described by McKinstry, Indyk, and Kim (1999). Trace concentrations of Cd, Pb and Cu in milk were subsequently determined by potentiometric stripping analysis using a home-made flow cell after ashing (Muñoz & Palmero, 2004).

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Caggiano et al. (2005) measured Cd, Cr, Hg, Mn, and Pb levels in samples of fodder, sheep's milk, dairy products, and tissues collected from 12 ovine farms in the regions of Campania and Calabria (Southern Italy). Al-Awadi and Srikumar (2000) reported the concentration of Zn, Cu, Mn, and Fe in milk and plasma of Kuwaiti and non-Kuwaiti mothers during prolonged lactation. Studies in determination of Pb concentration in human milk were conducted by a number of authors (Saleh, Ragab, Kamel, Jones, & El-Sebae, 1996; Sowers et al., 2002).

Smit, Schönfeldt, de Beer and Smith (2000) investigated the effect of locality and season on the nutrient composition of South African cow's milk. Milk samples were collected from Gauteng, KwaZulu-Natal, Free State, Eastern Cape and Western Cape. The study focused on analysis of protein, lactose, fat, moisture, total solids, ash, energy, chloride, phosphorus, sodium, potassium, magnesium, calcium and vitamins.

International standard methods for the analysis of some elements in milk and milk products are well documented. These include determination of lead in evaporated milk by atomic absorption spectrometry after dry ashing and extraction with 1-pyrrolidinecarbodithioate, and by anodic stripping voltammetry after dry ashing and dissolving the residue in HNO_3 (AOAC, 1990). The Codex Alimentarius Commission recommended method AOAC 972.25, is for the evaluation of lead levels in butter, edible casein products and whey powders (Codex Alimentarius Commission, 1998). In that method, the final quantification of lead is conducted by atomic absorption spectrometry. Iron in milk products is evaluated by atomic absorption spectrometry after dry ashing (Codex Alimentarius Commission, 1998).

ICP-MS has become accepted as the most powerful analytical tool for the simultaneous determination of trace elements due to its extreme sensitivity, selectivity and capability of multielemental and isotopic analysis. Martino et al. (2000) analysed essential and toxic elements in milk whey using a double focusing ICP-MS after dilution with ultrapure water. Milk elemental analysis by direct nebulisation of aqueous solutions is hampered by blockage of cones, deposition of organic matter in the injector tube of the torch, and spectral and non-spectral interferences due to the fatty nature of the matrix. The use of a high resolution mass spectrometer such as a double focusing ICP-MS reduces the influence of spectral interferences. Although, the double focusing ICP-MS offers the advantage of high resolving power, it is significantly slower than the quadrupole based ICP-MS. With the increasing demand for analyses required by public health programmes and private companies, it is important to use a quadrupole ICP-MS for routine, high-throughput trace element analyses. This study involved the development of an alternative method for the evaluation of selected trace elements in raw cow's using ICP-MS after lyophilisation of milk samples by a freeze-drying unit followed by microwave digestion. Lyophilisation allows the quick destruction of organic matrix and pre-concentration of analyte by minimising dilution.

The primary objective of this study is to contrast the efficiency of the method developed for the evaluation of V, Cr, Mn, Sr, Cd and Pb with the results obtained from certified reference materials in order to validate the method. Field samples were analysed to further validate the method.

2. Experimental

2.1. Apparatus

A LP3 model freeze dryer (Jouan, France) was used to dry liquid milk samples. The MARS 5 microwave digestion system (CEM Corporation, USA) was employed for mineralisation of freeze-dried milk samples. A Teflon XP-1500 Plus Vessel, allowing maximum decomposition pressure of 800 psi and temperature of 240 °C, was used for digestion. The High Pressure Digestion Vessel Accessory Sets (CEM Corporation, USA) permit simultaneous processing of up to 12 XP-1500 Plus vessels. At full power, the MARS delivers approximately 1200 watts of microwave energy at a magnetron frequency of 2450 MHz. All glassware was washed with detergent and water. After being rinsed with de-ionised water (18.2 MΩ cm) three times, it was soaked in 10% HNO_3 (v/v) for 24 h. This solution was discarded and the glassware was soaked again in 10% HNO_3 (v/v) for 24 h. The glassware was then rinsed three times with de-ionised water with a resistivity of 18.2 MΩ cm, and dried.

2.2. Instrumentation

ICP-MS measurements were performed by a quadrupole ELAN DRC-e spectrometer (PerkinElmer SCIEX, Concord, Ontario, Canada), equipped with a PerkinElmer auto sampler model AS-93 Plus and with as93f.try tray. A cross-flow nebuliser with a Scott type double pass spray chamber sample introduction system was employed in this study. Details on the instrumentation and the operating conditions are summarised in Table 1.

2.3. Reagents

All solutions were prepared using ultra-pure reagents. The water used in this work was doubly de-ionised with the final stage of de-ionisation provided by a Milli-Q water purification system (Millipore, Bedford, MA, USA). High purity HNO_3 (65%, Suprapur, Merck, Darmstadt, Germany) was used for cleaning glassware and digesting milk samples throughout this work. A stock standard solution containing 1000 mg/L of each element (TEKNOLAB A/S, Kolbotn, Norway) was used in preparing calibration standards. The calibration solutions were prepared from the stock solution using de-ionised water (18.2 MΩ cm) immediately before analysis. An internal standard solution containing 10 mg/L of each of Ga, In and Tl was prepared from single-element standard solutions (1000 mg/L) (TEKNOLAB A/S, Kolbotn, Norway). The mass calibration stock solution containing Ba, Be, Ce, Co, In, Mg, Pb, Rh and U at 10 μg element/L was obtained from PerkinElmer (Concord, Ontario, Canada). Argon (N 4.8) of 99.998% purity was supplied by Afrox Boc gases (Afrox, South Africa).

Table 1
Instrumental operating conditions of PerkinElmer ELAN DRC-e ICP-MS

Operating parameter	Setting
Plasma power output	1300 W
RF generator frequency	40 MHz
Analog stage voltage (V)	−1850
Pulse stage voltage (V)	800
Main water temperature (°C)	19
Interface water temperature (°C)	31
Torch box temperature (°C)	32
Lens voltage (V)	7
Argon flow rate ($L\ min^{-1}$)	Plasma: 15, auxiliary: 1.2, nebuliser: 0.89–1.02
Nebuliser type	Cross-flow
Spray Chamber type	Ryton®, double-pass
Interface	Ni sampler and skimmer cones, i.d. 1.1 and 0.9 mm, respectively
Torch	Standard quartz torch
Data acquisition	Peak hopping; dwell time per AMU 40 ms, sweeps/reading 60, number of replicates 3