Food Chemistry 115 (2009) 1048–1055

Contents lists available at ScienceDirect

Food Chemistry

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

Analytical Methods

Optimization of a slurry dispersion method for minerals and trace elements analysis in infant formulae by ICP OES and FAAS

Cristina Sola-Larrañaga, Iñigo Navarro-Blasco *

University of Navarra, Faculty of Sciences, Department of Chemistry and Soil Science, Pamplona, Navarra 31.080, Spain

ARTICLE INFO

Article history:
Received 17 April 2008
Received in revised form 18 September 2008
Accepted 7 December 2008

Keywords:
Inductively coupled plasma optical emission spectrometry (ICP OES)
Flame atomic absorption spectrometry (FAAS)
Slurry
Infant formula
Minerals
Trace elements

ABSTRACT

Infant formula developed by manufacturers requires a rigorous control of composition, particularly those elements added routinely in an attempt to mimic the mineral composition of human milk. A total of 97 different types of powdered infant formulae (preterm, adapted starter, adapted follow-up, toddler, specialised and soy-based formulae) commercially available in Spain were studied. It is noteworthy great differences in mineral (Ca, P, Mg) and trace element (Zn, Fe, Cu, Mn) contents found between analysed and listed in label information. The development of a fast, simple and direct slurry method for the determination of these essential micronutrients in infant formula by inductively coupled plasma optical emission spectrometry (ICP OES) and flame atomic absorption spectrometry (FAAS) was performed in order to help in quality control tasks. Infant formula samples were solubilised using different amounts of several different solvents. An addition of 250 μL of a solution 10% tetramethylammonium hydroxide and 25% ammonium hydroxide were required for the accurate quantification of Ca and P, Mg, Zn, Fe, Cu and Mn, respectively. The standard reference material 1549 non-fat milk powder was solubilised to compare the validity of assayed methodology following slurry nebulisation and traditional microwave-assisted acid digestion method. Good agreement of the analytical results by both ICP OES and FAAS, with the certified values was obtained. Method performance parameters (accuracy, precision and methodological detection limits) were determined for studied elements to check the quality and usefulness of the optimised slurry method. The analytical procedure was applied successfully to the analysis of a representative group of infant formulae. Levels of analysed elements were graphically represented, showing an acceptable comparability between slurry and acid-mineralisation method set by linear correlation coefficients and slopes close to the unit. The described simple and slurry method is appropriate, as an attractive alternative, for routine control analysis of added essential elements in infant formulae regardless of predominant protein type used in manufacture.

1. Introduction

Proper nutrition is particularly critical during infancy when growth and development are most rapid and therefore, the consequences of inadequate nutrition are most severe. Breast milk is the most adequate food for babies, but in some cases it is not sufficient to feed up the infant and the infant formula use is imperative (Delagne & West, 2003).

Likewise, infant formulae are manufactured by modifying cow milk composition so as to resemble that of human milk. It involves mainly an adaptation of the total levels of protein, fat, carbohydrates and minerals in cow milk. Most formulae are based on whole or skim milk with or without demineralised whey, vegetable oils or vegetable oils–milk fat mixtures, and added vitamins and trace elements. Optimal growth and development of infants may be guaranteed when both, food and water intakes provides the required doses of all essential (major and minor) elements and delivers only ineffectual concentration of potentially toxic elements. The adjustment of electrolytes and major minerals content of infant formulae has become the most sophisticated step manufacturing. Main electrolytes (sodium and potassium) and major elements (calcium, phosphorous and magnesium) contained at high levels in cow milk, must be reduced by means of electrodialysis ion exchange or/and ultrafiltration in the standardization process to obtain a minor level of these minerals, which consumed by infants at high concentrations could lead to renal overcharge, calcifications and bone demineralisation (World Health Organization & Food & Agricultural Organization, 2004). Membrane technology is now well established and has widespread use in the dairy industry. During the ultrafiltration process, fat and proteins are retained; thus those elements partly or wholly bound to protein are also

* Corresponding author. Address: Dpto. de Química y Edafología, Fac. de Ciencias, Universidad de Navarra, Irunlarrea 1, 31.080 Pamplona, Navarra, Spain. Tel.: +34 948 42 56 00; fax: +34 948 42 56 49.
E-mail address: inavarro@unav.es (I. Navarro-Blasco).

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doi:10.1016/j.foodchem.2008.12.037

removed. In reverse osmosis, theoretically all components other than water are separated, but in practice a very small loss of certain elements (calcium, magnesium and phosphorous) occurs. In short, the dynamic equilibrium of mineral components between aqueous and colloidal phases of milk is affected (Scott, 1989). It brings about partial replacement of all the minerals removed which must be added under inorganic salts in an attempt to mimic the mineral composition of human milk. Moreover, during these treatments others minor elements are also removed and as a consequence these essential micronutrients are normally added to infant formula at higher level than that which are present in human milk in order to compensate its lower bioavailability. Usually no remark is made for the intrinsic trace element content of the formula ingredients and actual contents show normally wide different in comparison with those values that label claims.

From the chemical point of view, infant formula is essentially a suspension of proteins, homogenised oils and sparingly soluble minerals in a solution of carbohydrates and minor ingredients. Thus, these formulations are a complex matrix offering significant challenge to the analyst. Industry analysts have usually used several techniques for mineral and trace elements determinations in infant formula, among others flame or graphite furnace atomic absorption spectrometry (FAAS, GF AAS), inductively coupled plasma optical emission spectrometry (ICP OES) or mass spectrometry (ICP MS). Most element quantification procedures are usually performed in solution. Traditional mineralisation in order to destroy the organic matter is the most critical step during analysis. Digestion in a closed vessel with pressure control and microwave heating is often recommended to avoid any contamination and to increase the sample throughput rate.

Subsequently, alternative methods to the conventional acid attack based on slurries or extract improve inherent advantage of required time, speed and ease of analysis, and are readily adapted to repetitive analysis of relatively large numbers of samples with a minimised risk of potential losses or contamination. Thus, some simple and attractive dissolution methods have been developed for several matrices (Nóbrega et al., 2006). Nóbrega, Gélinas, Krushevska, and Barnes (1997a, 1997b) have proposed the use of tertiary amine and ethylenediaminetetracetic acid (EDTA) for biological and dairy materials by ICP MS. Thixotropic agent (Triton X-100) were applied to determination of mineral elements (Ca, Mg, K, Na and Zn) in milk samples by means of ICP OES (McKinstry, Indyk, & Kim, 1999; Murcia et al., 1999). Although, in case of certain milk products, the attempt to determine Ca, P, Mg and Zn, by direct aqueous slurry nebulization was failed (Hua, Kay, & Indyk, 2000). Slurry sampling offers several benefits to the analysis of trace elements in different types of samples by GF AAS or electrothermal vaporisation ICP MS, demonstrated in several literature reports (Campillo, Viñas, López-García, & Hernández-Córdoba, 1998; Miller-Ihli, 1997; Pozebon, Dressler, & Curtius, 1998). Also, the sample dispersion in tetramethylammonium hydroxide (TMAH) was investigated (Martins, Pozebon, Dressler, & Kemieciki, 2002; Matusiewicz & Golik, 2004; Ribeiro, Moretto, Arruda, & Cadore, 2003; Stürup & Buchert, 1996).

In short, infant formula developed by manufacturers requires a rigorous control of composition with special concern related to minerals and trace elements, particularly those elements added routinely. Thereby, the tune-up of a direct, fast and low cost methodology represents a clear interest for the quality control operations of these essential micronutrients in this kind of matrices to the dairy sector manufacturers.

This paper shows the substantial differences between the values of mineral and trace elements measured and those indicated on the label information of infant formula sold commercially in Spain. To solve this difficulty, it was developed a simple dispersion methodology, evaluating different solvents, for the determination of Ca, P Mg, Fe, Zn, Cu and Mn in different types if infant formulae by ICP OES with conventional pneumatic nebulisation, taking into account its good performance, multielement ability and great linear dynamic range and FAAS, chosen for good reproducibility, easiness and quickness analysis and reasonable precision for quality control in integrated laboratories programs rather than other instrumental techniques listed above (Bermejo, Domínguez, & Bermejo, 1997). Also, in order to compare the validity and versatility of dispersion analysis following slurry nebulization and traditional microwave-assisted acid digestion method, the analysis of a standard reference material was carried out. The method was applied to real samples to establish its accuracy by comparing with pressured microwave-assisted digestion method.

2. Experimental

2.1. Apparatus and experimental conditions

A Perkin Elmer Aanalyst 800 atomic absorption spectrometer equipped with a stainless steel nebulizer and impact bead, and deuterium lamp as a background correction system was used. Assays by FAAS were performed at 422.7, 285.2, 213.9, 248.3, 324.8 and 279.5 nm for Ca, Mg, Zn, Fe, Cu and Mn, respectively. Hollow cathode lamps operated at 20, 20, 15, 30, 15 and 20 mA and bandwidths of 0.7, 0.7, 0.7, 0.2, 0.2 and 0.2 nm for each element listed above. An air/acetylene flame was used.

A Jobin-Ybon JY38S Plus ICP OES spectrometer powered by a 40.68 MHz radiofrequenzy generator at 1400 W was used for elemental determination. This instrument operates in the sequential measurement mode (radial measurements) and has a Czerny-Turner mounting with a 2400 grooves mm^{-1} holographic plane grating, the focal length is 1 m. The main argon flow was 12 L min^{-1}, and the cooling flow 0.45 L min^{-1}. The nebulizer was a Meinhard type with Scott concentric nebulization chamber, operated at 34 psi, with argon aerosol gas and a 0.6 L min^{-1} flow-rate. Sample aspiration was forced by means of a Spetec Perimax 12 peristaltic pump with a 1.4 mL min^{-1} sample delivery rate. The analytical lines (type of spectral line and the integration times) used for the different elements were: Ca, 317.933 nm (II, 0.5 s); Mg, 383.231 nm (I, 0.5 s); P, 213.618 nm (I, 1.0 s); Fe, 259.940 nm (II, 0.5 s); Zn, 213.856 nm (I, 0.5 s); Cu, 324.754 nm (I, 0.5 s); Mn, 257.610 nm (II, 0.5 s). Nebulizer clogging was avoided by using suitable uptake and rinsing cycles. A 30 s pre-observation aspiration time and a 30 s rinse time with ultrapure deionised water were applied. Warm-up time (plasma on) was 30 min.

Mineralisation of infant formulae and certified reference material for comparison purposes was carried out in PTFE closed vessels using Ethos Plus microwave labstation with computer easywave software (Millestone s.r.l., Sorisole, Italy).

A Transsonic 310 by Elma ultrasonic bath of 14 W constant power was used.

2.2. Sample collection

Infant formulae analysed are commercially available in Spain. A total of 97 different powdered infant formulae from nine different manufactures were studied. Both types, based on cow's milk ($n = 90$) and soy-based formulae ($n = 7$), were investigated. Cow's milk-based formulae included: preterm formula ($n = 6$), adapted starter formula ($n = 19$), adapted follow-up formula ($n = 17$), toddler formula ($n = 5$) and specialised formula (hypoallergenic ($n = 10$), lactose-free ($n = 10$), designed to avoid regurgitation ($n = 15$) and functional type ($n = 8$) formula).