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Analytical Note

Simultaneous determination of bromine and iodine in milk powder for adult and infant nutrition by plasma based techniques after digestion using microwave-induced combustion ☆

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ABSTRACT

In this work, bromine and iodine determination in milk powder for adult and infant nutrition was performed by inductively coupled plasma mass spectrometry (ICP-MS) and inductively coupled plasma optical emission spectrometry (ICP-OES) after digestion by microwave-induced combustion (MIC). Contrarily to previous works using MIC, a higher sample mass was digested (700 mg). Water and ammonium hydroxide (10 to 100 mmol L^{-1}) were investigated as absorbing solutions and accurate results were achieved using a 25 mmol L^{-1} NH_4OH solution. Moreover, the high stability of analytes after digestion (up to 30 days) using this solution was observed. The accuracy of the proposed MIC method was evaluated using certified and reference materials of milk powder (NIST 1549 and NIST 8435). No statistical difference was observed between results obtained by MIC-ICP-MS and reference values. Results for samples were also compared with those obtained by ICP-OES and no statistical difference was observed. Microwave-assisted alkaline extraction (MW-AE) was also evaluated for milk powder using NH_4OH and tetramethylammonium hydroxide solutions. Solutions obtained after digestion by MIC (whole milk powder) presented low carbon content in digests (<25 mg L^{-1}) while solutions obtained after alkaline extraction presented up to 10,000 mg L^{-1} of C. MIC method was preferable in view of the possibility of obtaining solutions with low carbon content even using a relatively high sample mass (up to 700 mg) avoiding additional dilution prior to ICP-MS analysis, thus allowing better detection limits. Limits of detection obtained by MIC-ICP-MS were 0.007 and 0.003 μg g^{-1} for Br and I, respectively, while for MW-AE were 0.1 and 0.05 μg g^{-1} respectively for Br and I. Among the main advantages of the proposed method are the use of diluted alkaline solutions that is in agreement with green analytical chemistry recommendations, the high stability of analytes in solution and the suitability of digests for analysis by ICP-MS and also ICP-OES, minimizing memory effects and being advantageous for routine analysis.

1. Introduction

Milk and milk related products are widely recognized as an important source of nutrients, including proteins, lipids, carbohydrates, vitamins, minerals and enzymes [1,2]. On the other hand, milk can also represent a source of exposure to halogens and information about their concentrations is important for consumers. In this context halogens play an important role in metabolism and their excess or absence can cause serious damages to human organism [3,4].

Iodine is considered an important trace element required for human organism functioning. Deficiency or excess intake of iodine can lead to disorders commonly related to thyroid gland [5]. With regard to bromine, it is considered nonessential to human health and it can be combined with hemoglobin causing hematologic diseases. Bromide intake can reduce iodide accumulation, not only in the thyroid but also in mammary glands, and to increase iodide elimination through the kidneys [6]. In this sense, the determination of bromine and iodine in milk powder for adult and infant nutrition is of great importance since the deficiency or excess of these elements could promote several health problems.

However, halogens determination in biological samples, as milk, is not a simple task mainly due to problems related to sample preparation step [7,8]. Analytical techniques such as spectrophotometry [9], potentiometry using ion-selective electrode [10], ion chromatography

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(IC) [11], molecular absorption spectrometry (MAS) [12,13], inductively coupled plasma optical emission spectrometry (ICP-OES) [14], and inductively coupled plasma mass spectrometry (ICP-MS) [15–17] have been employed for bromine and iodine determination after a suitable sample pretreatment [7]. On this aspect, organic samples, as milk powder, are commonly digested using concentrated nitric acid and conditions during digestion (temperature and pressure) must be selected according to the difficulty to bring samples into solution. However, the use of acids when working for halogens determinations should be avoided due to analyte losses by volatilization of respective acids. In this sense, European Committee for Standardization (Method EN 15111:2007) recommends an extraction method for further iodine determination in foodstuff samples by ICP-MS. In this procedure iodine compounds are extracted with tetramethylammonium hydroxide (25% TMAH) in a dry oven at 90 °C [37]. Moreover microwave-assisted extraction [19,20], pyrohydrolysis [21], alkaline fusion [22], and microwave-assisted acid digestion in open vessels followed by precipitation [18] methods are also alternatives for sample preparation for further halogens determination. However, due to their suitability for digestion of organic samples, combustion methods are commonly used for milk powder for further determination of halogens [23–25].

Combustion can be considered as the method of choice particularly for halogens determination. The method recommended by the Official Methods of Analysis of AOAC International (Method 974.36) involves the determination of bromine and iodine by titration after digestion using oxygen flask system. This method presents some advantages in comparison with other procedures as low residual carbon content of digests and the suitability for determination by many analytical techniques. However, the disadvantage of this method is limited by the low throughput (one sample processed by each run), the low sample mass that can be digested (50 to 100 mg for a 500 mL flask), and by the impossibility of using a reflux step to improve analyte recoveries [7,26,27].

As an alternative, microwave-induced combustion (MIC) has been successfully applied for the digestion of biological samples in closed vessels mainly due to the high efficiency of sample oxidation [8,28–30]. Digestion by MIC method involves the combustion of samples in closed quartz vessels pressurized with oxygen and ignition by microwave radiation. An optional reflux step enables additional dissolution of remaining inorganic compounds and allows quantitative analyte recoveries [31].

In this work, the feasibility of ICP-MS for simultaneous bromine and iodine determination in milk powder for adult and infant nutrition after MIC digestion was evaluated. The operational parameters of MIC, such as sample mass (500 to 800 mg) and the concentration of absorbing solutions (water or 10 to 100 mmol L^{-1} NH_4OH) were investigated. Microwave-assisted alkaline extraction (MW-AE) in closed vessels was also investigated for comparison of results. The efficiency of MIC digestion was evaluated by the determination of residual carbon in digests. Accuracy of the proposed MIC method with ICP-MS determination was evaluated using certified reference materials (CRM) of milk powder. For comparison of results, the determination of bromine and iodine by ICP-OES in MIC digests was also evaluated.

2. Experimental

2.1. Instrumentation

A microwave-assisted sample preparation system (Multiwave 3000, Anton Paar, Graz, Austria) equipped with eight high-pressure quartz vessels (internal volume of 80 mL, maximum temperature and pressure of 280 °C and 80 bar, respectively) was used for MIC and MW-AE. A commercial quartz holder was used to insert the samples inside the quartz vessels for MIC. The software version was v1.27-Synt, and the microwave system was previously modified to run with a maximum pressure rate of 3 bar s^{-1} (and not 0.8 bar s^{-1} as in the original software) for MIC digestion.

Bromine and iodine determination was performed using an inductively coupled plasma mass spectrometer (Model Elan DRC II, Perkin Elmer-SCIEX, Thornhill, Canada) and also using an inductively coupled plasma optical emission spectrometer with axial view configuration (Model Spectro Ciros CCD simultaneous spectrometer, Spectro Analytical Instruments, Kleve, Germany). This equipment (ICP-OES) was also used for C determination in digests. Instrumental parameters, including nebulizer gas flow-rate, RF power and ion lens voltage for both instruments are described in Table 1 and were selected according to previous works [8,14]. Argon of 99.996% purity (White Martins, Praxair, São Paulo, Brazil) was used for plasma generation, nebulization and as auxiliary gas.

Carbon content measurements were performed using the same inductively coupled plasma optical emission spectrometer used for bromine and iodine determination. Operational conditions are shown in Table 1. Yttrium (1 mg L^{-1}) was used as an internal standard only for carbon determination by ICP-OES and carbonaceous gases dissolved into digests were previously removed using an Ar flow (0.1 L min^{-1} for 2 min) [32].

2.2. Samples, reagents and standards

In this study, three commercial samples of whole, semi-skimmed and skimmed milk powder and ten samples for infant nutrition (whole milk powder, five samples for the age of 0 to 6 months and other five samples for the age after 6 months) were used. All samples were purchased in a local market (recipients containing 400 g of milk powder). According to the manufacturer, fat content was about 6.8, 1.4 and below 1% for whole, semi-skimmed and skimmed milk powder, respectively. Samples were dried in an oven at 105 °C for 120 min and were pressed as pellets (13 mm of diameter) using a hydraulic press (Specac, Orpington, UK) set at 1 t for 1 min.

Accuracy of proposed method was checked using a CRM and a reference material (RM) provided by National Institute of Standards & Technology (NIST SRM 1549, non-fat milk powder and NIST RM 8435, whole milk powder). Before MIC digestion, CRMs were prepared in the same way as samples.

All the reagents used in this work were of analytical grade (Merck, Darmstadt, Germany). Water obtained from a Milli-Q (18.2 MΩ cm) system was used to prepare all reagents and standard solutions. A stock standard solution of bromine and iodine (1000 mg L^{-1}) was prepared by the dissolution of potassium bromide and potassium iodide salts, respectively in water. Calibration solutions (1 to 10 μg L^{-1} for bromine and 0.1 to 1 μg L^{-1} for iodine, for analysis by ICP-MS; and, 100 to 1000 μg L^{-1} for bromine and 50 to 500 μg L^{-1} for iodine, for analysis by

Table 1
Operational parameters for bromine and iodine determination by ICP-MS and ICP-OES.

Parameter	ICP-MS	ICP-OES
RF power (W)	1400	1600
Plasma gas flow-rate (L min^{-1})	15.0	14.0
Auxiliary gas flow-rate (L min^{-1})	1.20	1.00
Nebulizer gas flow-rate (L min^{-1})	1.09	1.00
Spray chamber	Cyclonic	Double path, Scott type
Nebulizer	Concentric	Cross flow
Sampler and skimmer cones	Pt	–
Ion lens (V)	Auto lens "on"	–
Dwell time (ms)	50	–
Isotopes (*m/z*)	^{79}Br and ^{127}I	
Emission lines (nm)		Br (154.065)
		I (183.038)
		C (193.091)
		Y (371.030)[a]

[a] Yttrium was used as internal standard only for carbon determination by ICP-OES.