Journal of Food Composition and Analysis xxx (xxxx) xxx–xxx

Contents lists available at ScienceDirect

Journal of Food Composition and Analysis

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

Original research article

Ultra-trace determination of bromine and iodine in rice by ICP-MS after microwave-induced combustion

Filipe S. Rondan[a], Carla A. Hartwig[a], Diogo L.R. Novo[a], Diogo P. Moraes[b], Sandra M. Cruz[c], Paola A. Mello[c], Marcia F. Mesko[a,*]

[a] Centro de Ciências Químicas, Farmacêuticas e de Alimentos, Universidade Federal de Pelotas, 96160-000, Capão do Leão, RS, Brazil
[b] Instituto de Química, Universidade Federal do Rio Grande do Sul, 91501-970, Porto Alegre, RS, Brazil
[c] Departamento de Química, Universidade Federal de Santa Maria, 97105-900, Santa Maria, RS, Brazil

ARTICLE INFO

Keywords:
Food analysis
Food composition
Rice
Bromine
Iodine
Sample preparation
Microwave-induced combustion
Inductively coupled plasma mass spectrometry

ABSTRACT

In this study, a method for bromine and iodine determination in rice by inductively coupled plasma mass spectrometry (ICP-MS) after digestion by microwave-induced combustion (MIC) was developed. Samples (up to 1000 mg) were digested in closed system pressurized with oxygen. Ultrapure water and NH_4OH solutions were evaluated as absorbing solution. Recoveries from 98 to 108% were obtained for Br and I using 50 mmol L^{-1} NH_4OH, and the relative standard deviations (RSDs) were up to 9 and 11% for Br and I, respectively. Limits of detection (LODs) of 0.004 and 0.0008 mg kg^{-1} for Br and I, respectively, were obtained. These LODs were lower than those reported in the literature, and it was possible due to the high sample mass digested by MIC associated with the detection capability of ICP-MS. The proposed method was applied to 23 samples of rice from different countries and types. The results showed a wide variation for Br concentrations (0.304 to 55.7 mg kg^{-1}), whereas for I it was not observed (< 0.003 to 0.031 mg kg^{-1}). In this way, the proposed method presents several advantages for the routine analysis and indicate that it is an excellent alternative for Br and I determination in rice.

1. Introduction

Rice is one of the most widely consumed cereals worldwide, and it is present in the diet of more than half of the world's population (Nguyen et al., 2008). The annual average world consumption of rice is about 62 kg per person (Wailes and Chavez, 2012). Asian countries are the largest rice producers and the consumption in this continent is higher than the average consumption worldwide. Rice cultivation occurs mainly in regions with tropical, subtropical and temperate climates (Burlando and Cornara, 2014). The main producers of rice in the world are China, India, Indonesia, Bangladesh, Vietnam, Thailand, Myanmar, Philippines, Brazil and Japan (FAO, 2015). In this sense, Brazil is outstanding as the only non-Asiatic country present among the ten largest producers of rice in the world. In Brazil, Rio Grande do Sul state accounts for about 70% of the total rice production (CONAB, 2015).

Rice is a rich source of nutrients needed by the human body, such as proteins, lipids, carbohydrates, dietary fibers and minerals (Zhou et al., 2002), which are present in different amounts in each type of rice. Among the types of rice, white, parboiled and brown rice should be mentioned because they are commonly marketed in different countries. These types of rice are obtained through different processes after harvesting and this can also change the mineral content of the final product (Burlando and Cornara, 2014). In addition, the composition of the soil where rice cultivation occurs and also pesticides and fertilizers used during this stage can be directly related to the amount of nutrients and/or contaminants contained in this cereal.

Thus, the control of the essential and non-essential elements concentration in rice is extremely important, since the presence of these elements in inadequate concentrations can cause problems to human health. It is important to emphasize that this monitoring should not be restricted to elements that are toxic to the human body, but also to nutrients that ensure the maintenance of a balanced diet (Tarantino et al., 2017). In this sense, halogens are examples of elements to be investigated in food because they are important in several biological processes in the human body (Cressey, 2003; Mccall et al., 2014).

Among the halogens, bromine and iodine are associated with several disorders and may cause adverse effects in humans. The presence of Br in the body can impair I transport to the thyroid gland, inhibiting the formation of some hormones (Vobecky et al., 1996). In bromate form, Br is considered carcinogenic (Vobecky et al., 1996; DeAngelo et al., 1998; Delker et al., 2006). On the other hand, when ingested in excess or in insufficient concentrations, I may cause dysfunction and

* Corresponding author.
E-mail address: marcia.mesko@pq.cnpq.br (M.F. Mesko).

https://doi.org/10.1016/j.jfca.2017.12.023
Received 3 December 2016; Received in revised form 4 October 2017; Accepted 9 December 2017

pathologies in the human body, related to the thyroid gland (Zimmermann et al., 2008). Therefore, the World Health Organization (WHO) recommends safe daily intakes of these elements for adults (Br: 4 mg per kilogram of body mass and I: 150 µg) (WHO, 1996, 2009). However, although rice is one of the most consumed foods in many countries, there is few information about the concentrations of both elements in this cereal. Additionally, there are no official methods of analysis aimed at determining these elements in rice.

In the literature, few studies have determined Br and I in rice (Soliman and Zikovsky, 1999; Antoine et al., 2012; Laharojanaphand et al., 2012; Kongsri et al., 2016). In these reports, the authors used the instrumental neutron activation analysis (INAA). Although INAA allows the – direct analysis of samples, it is available in few laboratories since requires a nuclear reactor. In this sense, Pinto et al. (2016) used inductively coupled plasma mass spectrometry (ICP-MS) to determine various elements, including Br. However, they used concentrated acid during the sample preparation step, in contrast to what is proposed in this study.

According to the literature, ICP-MS can be highlighted due to sensitivity and selectivity for Br and I determination in different matrices, including rice, as well as high throughput and lower cost compared with INAA (Vanhoe and Allemeersch, 1993; Knapp et al., 1998; Hartwig et al., 2014; Costa et al., 2015; Mesko et al., 2015; Pinto et al., 2016; Toralles et al., 2017). Nevertheless, routine applications of the ICP-MS technique generally involve the introduction of samples into the instrument as solutions. In this case, digestion methods using concentrated acids are necessary to avoid high concentration of carbon in solutions that could interfere in analyte ionization in the plasma (Barin et al., 2016). Accumulation of carbon in the equipment interface can occur, impairing the determination and requiring additional maintenance (Nobrega et al., 2006). However, the use of concentrated acid for sample digestion has not been considered suitable for further halogen determination in view of the contamination and losses of the analytes by volatilization (Mesko et al., 2016).

Microwave-induced combustion (MIC) method is an interesting alternative for sample preparation, since it is based on sample combustion, eliminating all organic material by oxidation. This process occurs in closed vessels, minimizing losses of the elements by volatilization. It allows choosing a suitable absorbing solution for the analytes, and monitoring the pressure and temperature during sample digestion. These features make the MIC method suitable for sample preparation of several types of organic matrices such as shrimp, edible seaweed, honey, milk powder, milk whey proteins, egg powder and edible flours (Hartwig et al., 2014; Mesko et al., 2014; Costa et al., 2015; Picoloto et al., 2015; Silva et al., 2016; Toralles et al., 2016, 2017; Silva et al., 2017), for subsequent determination of Br and I by ICP-MS.

In this context, this study proposes for the first time the use of MIC for the digestion of white, parboiled, brown, wild and black rice from several origins and subsequent determination of Br and I by ICP-MS. For this purpose, some parameters such as rice mass and the suitable absorbing solution for Br and I were investigated. Method accuracy was evaluated by digestion of reference material (RM, NIST 8433 corn bran) and by recovery tests.

2. Materials and methods

2.1. Instrumentation

The MIC method was performed in a microwave oven (Multiwave 3000, Anton Paar, Graz, Austria) equipped with eight high pressure quartz vessels (internal volume of 80 mL, maximum pressure and temperature 80 bar and 280 °C, respectively). The rice masses were measured on an analytical balance (AY220, Shimadzu, Rosario, Philippines), with a maximum load of 220 g and a resolution of 0.0001 g.

Bromine and I determination were performed using an inductively coupled plasma mass spectrometer (NexION 300X, Perkin-Elmer, Ontario, Canada), equipped with a concentric nebulizer (Meinhard Associates, Golden, USA), a cyclonic spray chamber (Glass Expansion Inc., West Melbourne, Australia), and a quartz torch with a quartz injector tube (2 mm i.d.). The parameters for Br and I determination by ICP-MS are shown in Table 1.

Table 1
Operational parameters for Br and I determination by ICP-MS.

Parameter	Condition
RF power (W)	1300
Argon flow rate (L min^{-1})	
Plasma	18.00
Auxiliary	1.20
Nebulizer	0.95
Spray chamber	Cyclonic
Nebulizer	Concentric
Sampler and skimmer cones	Pt
Ion lens	Auto lens “on”
Analytes	Isotope (m/z)
Br	79
I	127

2.2. Samples and reference material

Samples of white rice (WR), parboiled rice (PR), brown rice (BR), wild rice (WiR) and black rice (BkR) used in this study were purchased in Brazil, Chile, Germany (one sample was cultivated in the Himalayas), United States of America, and Uruguay. Initial studies were performed using an arbitrarily selected sample of white rice (WR1) from Brazil. Prior to digestion, all samples were ground in a knife mill (226/2, Lucadema Científica, Campinas, Brazil), dried in an oven (400/2ND, DeLeo, Porto Alegre, Brazil) at about 60 °C for 4 h, and stored in polypropylene vessels.

A reference material of corn bran from the National Institute of Standards and Technology (NIST 8433) was used for accuracy evaluation. Alternatively, the RM was also digested mixed with rice, like a recovery test (300 mg of RM and 700 mg of rice), and submitted to the same treatment and digestion as the samples.

2.3. Reagents and chemicals

Solutions used in this study were prepared in ultrapure water with a resistivity of 18.3 MΩ cm obtained from a suitable purification system (MegaUP, MegaPurity, Seoul, South Korea). All reagents used were of analytical grade or higher purity. Six mL of concentrated HNO_3 (Synth, Diadema, Brazil) were used to decontaminate the MIC system under a microwave heating program of 1000 W for 10 min and 0 W for 20 min. This procedure was then repeated using 6 mL of ultrapure water to assure low blank values for halogens.

Small filter paper discs (12 mg, 15 mm of diameter, Unifil, Hannover, Germany) with low ash content (0.00009 g) were used as aids in the combustion process. They were previously decontaminated by immersion in 10% (v/v) HNO_3 (Synth) for 10 min and subsequently immersed in ethanol 96°GL (Synth) for 10 min. These steps were performed in an ultrasonic bath (USC-2800A, Unique, Indaiatuba, Brazil), and at the end, the papers were washed with ultrapure water and dried in a class 100 laminar flow hood (CSLH-12, Veco, Campinas, Brazil). This same procedure was applied to the polyethylene films used to wrap the samples during the digestion by MIC.

The solution of 25% NH_4OH (Merck, Darmstadt, Germany) was used to prepare the absorbing solutions evaluated in the MIC method. Ammonium nitrate solution (6 mol L^{-1}) used as igniter was prepared by dissolution of solid NH_4NO_3 (Merck) in water. Oxygen with a purity of 99.5% (Oxigeo Gases, Curitiba, Brazil) was used to pressurize quartz vessels in the MIC system. Argon with a purity of 99.998% (White