Journal of Food Composition and Analysis 54 (2016) 37–47

Contents lists available at ScienceDirect

Journal of Food Composition and Analysis

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

Original research article

Exposure assessment of arsenic speciation in different rice types depending on the cooking mode

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ARTICLE INFO

Article history:
Received 13 June 2016
Received in revised form 14 September 2016
Accepted 18 September 2016
Available online 20 September 2016

Keywords:
Food analysis
Food composition
Food safety
Risk evaluation of rice in France
Total and inorganic arsenic
DMA
Speciation analysis
HPLC
ICP-MS

ABSTRACT

Total (As_t), inorganic arsenic (As_i = As(III) + As(V)) and dimethylarsonic acid (DMA) were determined in 37 commercial rice samples collected in France. As_t was measured by inductively coupled plasma-mass spectrometry (ICP-MS) whereas anion-exchange chromatography – ICP-MS was used for As_i and DMA determination. As_t in raw rice varied from 0.041 to 0.535 mg kg^{-1} whereas As_i varied from 0.025 mg kg^{-1} (polished Basmati rice) up to 0.471 mg kg^{-1} (organic rice duo). The daily intake and associated health risk for different population groups as a function of age and gender was also assessed. The intake varied between 0.002 and 0.184 μg kg^{-1} body weight for As_t and 0.002 and 0.153 μg kg^{-1} body weight for As_i, which do not pose a chronic toxicity risk. Organic wholegrain rice may entail a risk for children in the case of sole consumption at the expense of polished rice. The impact of rice cooking/boiling in terms of the overall toxicological risk related to As species was also investigated. Pre-rinsing and boiling the raw rice by using an excess of water is the most efficient mode to obtain a significant As_i removal and further reduction of the toxicological risk for children, particularly for white rice varieties.

1. Introduction

Arsenic (As) is an ubiquitous metalloid that is widely dispersed at trace levels in the environment, particularly in air, water, and the Earth's crust; it enters the food chain mainly from contaminated drinking water (European Food Safety Authority, 2009) and several widely consumed foodstuffs, such as fish and rice, the latter being an important contributor to As intake in countries with traditionally rice-based diets (Feldmann and Krupp, 2011; Jiang et al., 2015). Arsenic levels in rice depend on the geographical location, growing/soil conditions and also on the level of contamination of the irrigation water (Batista et al., 2011; Ma et al., 2014; Das et al., 2016; Signes-Pastor et al., 2016a,b). Despite the relatively large variety of As species present in food, rice accumulates mostly monomethylarsonic acid (MMA), dimethylarsinic acid (DMA), arsenite (As(III)) and arsenate (As(V)), the latter two inorganic species being the most widespread (Feldmann and Krupp, 2011; Signes-Pastor et al., 2016a,b). Given their similar toxicological properties, the sum of As(III) and As(V) is in most cases referred to as inorganic arsenic (As_i). As_i is carcinogenic for humans (European Food Safety Authority, 2009) and acute exposure to high As_i levels can also cause vomiting, abdominal pain and diarrhea (FAO/WHO, 2010). Chronic exposure to As_i can cause skin lesions, diabetes, hypertension and cardiovascular diseases. MMA and DMA (the methylated metabolites of inorganic arsenic) are excreted in urine and are considered less toxic than As_i; nevertheless, MMA and DMA have also been identified as possible cancer promoters and further studies are underway regarding their actual toxicity (Batista et al., 2011). Several other arsenic species commonly present in rice, such as arsenobetaine (AsB), arsenocholine (AsC), trimethylarsine oxide (TMAO) and arseno-sugars are currently considered non-toxic (Feldmann and Krupp, 2011).

Taking into account the high health risk associated to arsenic poisoning, the European Food Safety Authority (EFSA) stated that an intake ranging from 0.3 to 8 μg kg^{-1} body weight (b.w.) per day should be used as a reference for characterizing As_i risk (European Food Safety Authority, 2014a,b). Similarly, the Agency for Toxic

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http://dx.doi.org/10.1016/j.jfca.2016.09.007
0889-1575/

Substances and Disease Registry (ATSDR) provided a Minimal Risk Level (MRL) of daily intake between 0.3 and 20 $\mu g\,kg^{-1}$ b.w. for individual As species (As_i, MMA and DMA), which is defined as the dose that is likely to lead to no appreciable risk of adverse non-cancer health effects over a specific duration of exposure (U.S. Department of health and human services, 2007). In 2014, the Joint Expert Committee on Food Additives (JECFA) (FAO/WHO, 2014) recommended a maximum level for As_i in milled and parboiled rice of 0.2 $mg\,kg^{-1}$ (no such limit is yet regulated for husked brown rice). Very recently, the European Commission regulated the maximum levels of As_i in different types of rice, with maximum levels (ML) ranging from 0.10 $mg\,kg^{-1}$ for rice destined for infant foods up to 0.30 $mg\,kg^{-1}$ for rice waffles, wafers, crackers and cakes (Official Journal of the European Union, 2015). Apart from the EU regulations, at an international level, the only existing regulatory limit for As in rice is applied in China (0.15 mg $As_i\,kg^{-1}$) (FAO/WHO, 2014).

The lack of international regulations in terms of health risk related to As exposure via food relates also to the difficulty of its accurate determination in biological matrices, especially at trace and ultra-trace levels. The most common analytical approach for As speciation analysis relies on the coupling of (anion exchange) high performance liquid chromatography (AE-HPLC) with inductively coupled plasma-quadrupole mass spectrometry (ICP-QMS) (Welna et al., 2015; Ma et al., 2016). Despite the well-recognized advantages of ICP-QMS as a detection technique for trace and ultra-trace elemental analysis, its application to As determination is still difficult because of several severe spectral interferences such as $^{40}Ar^{35}Cl$ and $^{40}Ca^{35}Cl$ (Wang and Forsyth, 2012; Nardi et al., 2009). In addition, since As is mono-isotopic, the use of a primary method for its quantification such as isotope dilution-ICP-MS is not possible. In such circumstances, one of the main approaches of method validation for As determination (including speciation analysis) is based on assessment of the accuracy profile (Comité Français d'Accréditation, 2016; Agence Francaise de Normalisation, 2010).

The aim of this study was to determine the concentration and toxicological relevance of As_t, As_i and organic As species in a variety of rice (types of grain, industrial processing and geographical origin) commonly consumed in France. The influence of four different cooking approaches was assessed regarding exposure to children (3–10 years old) and adults. For this task, fully validated methods based on the accuracy profile were employed (Leufroy et al., 2011). These results can be useful to understand as well as to mitigate arsenic exposure related to consumption of specific types of rice depending on the consumer profile.

2. Materials and methods

2.1. Reagents

Ultrapure water (18 MΩ cm) obtained by purifying distilled water using a Milli-Q™ PLUS system combined with an Elix 5 pre-purification system (Millipore SA, Saint-Quentin-en-Yvelines, France) was used throughout the study. The As concentration (As_t) of this ultra-pure water was $\leq$0.012 $\mu g\,L^{-1}$, which was considerably lower that the method limit of detection (MDL), hence it was considered As-free water.

Methanol (HPLC gradient grade), nitric acid (Suprapur, 67%) and hydrogen peroxide (Normapur, 30% m/m), used to oxidize As(III) to As(V) for As_i determination were purchased from VWR (Fontenay-sous-Bois, France).

For As_t measurements, an As(III) stock standard solution at 1000 $mg\,L^{-1}$ (Analytika, Prague, Czech Republic) was used. Standards solutions for external calibration were prepared daily in 6% (v/v) HNO_3. For speciation analysis, standard solutions of individual As species (1000 $mg\,L^{-1}$, as As) were prepared from the following substances: sodium arsenate dibasic heptahydrate (≥98.0%), DMA (≥99.0%), AsB (≥95.0%) (Sigma Aldrich, Saint-Quentin-Fallavier, France), methylarsonic acid (≥98.0%), AsC bromide (≥98.0%), TMAO (≥98.0%) (all from Tri Chemical Laboratories, Yamanashi, Japan). A multi-species solution of As(V), MMA, DMA, TMAO, AsC at 1.0 $mg\,L^{-1}$ and AsB at 3 $mg\,L^{-1}$ was used as an intermediate stock standard solution for external calibration; the working standard solutions were prepared daily from this multi-species standard solution by dilution in ultra-pure water. A standard solution of scandium (Sc) at 2.0 $\mu g\,L^{-1}$ was used as internal standard (IS) for As_t determination. A multi-element solution (10 $\mu g\,L^{-1}$) prepared from a stock tuning solution (Agilent Technologies, Courtaboeuf, France) was used for ICP-MS optimization. All standard solutions were stored in the dark at 5 °C until analysis in order to prevent their degradation.

2.2. Reference materials and samples

Two certified reference materials (CRMs), namely TORT 2 (lobster hepatopancreas, National Research Council Canada), certified for As_t and BC 211 (rice powder, Institute for Reference Materials and Measurements, Geel, Belgium) certified for DMA and As_i were used in this study for quality control.

Fifty-four raw rice samples were purchased (a standard package in each case) from urban supermarkets in Paris in April 2013, to obtain a representative sample of rice varieties available domestically. In addition, when possible, rice of different varieties (short, medium, long, extra-long), different origins (Europe, France, Italy, India, Himalaya, Surinam, Uruguay, Thailand, Japan, Burma, USA, etc.), various pretreatment (white, organic white, brown, wholegrain, polished, steamed, parboiled, etc.) and different blends was selected. After purchase, the samples were kept at room temperature in the dark until treatment (digestion or extraction).

The rice samples analysed in this study represent the rice types mostly consumed in France: *Basmati*, *Thai*, *White*, *White for risotto*, *Organic semi-wholegrain duo*, *Three-rice mix* and *Wholegrain rice*. Each sample/composite was milled prior to the preparation step (digestion or extraction).

2.3. Instrumentation

A Multiwave 3000 closed-vessel microwave digestion system (Anton-Paar, Courtaboeuf, France) equipped with 80 mL quartz vessels (80 bar operating pressure) was used for sample digestion prior to As_t determination. The analysis was carried out using an ICP-quadrupole MS (ICP-QMS) model 7700× from Agilent Technologies (Courtaboeuf, France) equipped with a third-generation Octopole Reaction System (ORS^3). Helium was used as collision gas to minimize spectral interferences. The ICP-QMS was equipped with an autosampler (ASX 500 model 510, CETAC, Omaha, Nebraska, USA) for automated sample introduction. Daily optimization was carried out to obtain maximum sensitivity while minimizing oxides (CeO^+/Ce^+) and doubly-charged (Ce^{2+}/Ce^+) levels (<2%). More details regarding the instrumental settings and data acquisition parameters are given in Table 1.

As_i and DMA speciation analysis was carried out by ionic exchange chromatography (IEC, Ultimate 3000) coupled to a X-Series^{II} ICP-QMS equipped with a concentric nebulizer and impact bead spray chamber (both instruments from Thermofisher Scientific, Courtaboeuf, France). The chromatographic separation was achieved using an IonPac AS7 ion exchange column (250 × 4 mm; 10 μm particles). An IonPac AG7 guard column and an automated injection valve (100 μL injection loop) were used throughout (see also Table 1). All the digest or extract samples