



# Comparison of strategies for sample preparation prior to spectrometric measurements for determination and speciation of arsenic in rice



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## ABSTRACT

Rice (*Oryza sativa* L.) is a bio-accumulative plant for arsenic (As), particularly the most toxic inorganic As species (i-As), and the main contributor to i-As intake among agricultural products. The analytical process for determination and speciation of As in rice is complex. Different aspects have to be considered, including detection method, calibration strategy, sample-treatment and preparation procedures, and quality assurance and quality control of results. It is well known that sample preparation is a critical step in the whole analytical chain, so this review surveys achievements in analysis of rice for the content of total As and the species of As reported in the past 15 years using spectrochemical techniques. We discuss different sample-preparation procedures, with their advantages and drawbacks. We highlight common strategies and alternative approaches to speciation analysis of As.

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## 1. Introduction

Rice (*Oryza sativa* L.) in its grain and flour forms constitutes a staple food for half the world's population due to its nutritive properties and low cost [1–8]. It is the main food in developing countries of Asia, contributing over 70% of energy provided by their daily food

intake. Nevertheless, it is also widely produced and consumed in Europe, South America, Africa and USA [3–5,7,8].

Rice is a complex matrix composed of carbohydrates, proteins, fats, fiber and numerous components (macro and micro), essential for human health [3,6,7,9]. Among different kinds, white and brown rice are by far the most commonly consumed. The main differences between these two forms of rice lie in the processing (polishing and milling) of paddy rice (unhusked). When only the outermost layer of a rice grain (the husk) is removed, brown rice (unpolished) is produced. If the next layers underneath the husk

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(the bran layer and the germ) are removed, leaving mostly the starchy endosperm, white rice (polished) is obtained [10]. White or brown rice can be sold as parboiled rice (i.e., soaked in water, steamed under pressure and dried before milling) [10]. Basmati and jasmine rice are common aromatic types [11], while Italian rice (Japonica cultivars) with high content of starch and the ability to absorb water is recommended for making risotto dishes [4]. Considering common available rice varieties, wild rice can also be found, but it is not regarded as true rice, but rather as seeds of a wild aquatic grass native to North America [12]. Interestingly, rice varieties with colored kernels (e.g., red, violet-black and green) are also favored. Besides consumption, colored rice can be used as a pigment or as a nutritional supplement to white rice [13].

Much interest in rice comes from not only a health point of view but also because a rice plant can easily accumulate arsenic (As) into grains [3,5,6,14,15]. The concentration of As in rice is generally an order of magnitude greater than in other cereal crops (e.g., wheat, barley, rye, corn, and rye) [2,4,5,15–18]. Four As species (i.e., arsenite [As(III)], arsenate [As(V)], dimethylarsenic acid (DMA) and monomethylarsonic acid (MMA)) are commonly reported to be present in rice [4,17,19–24], whereas inorganic As (i-As) (i.e., As(III), As(V) and DMA) are dominant species [2,5,13,25–29]. Other organic As compounds (e.g., arsenobetaine (AsB)) are occasionally determined [14,30].

Contamination of rice by As (basically i-As) may originate from natural processes, such as growth media (i.e., soils and water and their components [9,31–36]), geological impurities [4], country of origin (geographical location) [3,8,17,21,31,33,36] and human activities, including agriculture (cultivation) practices, such as application of crop-protection agents or chemical and organic fertilizers [4,9,14,21,33,34,36–38].

Contamination can also happen during different stages of rice manufacture (e.g., polishing of brown rice into white, milling or soaking and parboiling, especially when As-free water is not used) [38]. DMA in rice mainly comes from an uptake of DMA through soil, but methylation of i-As species within a plant as a detoxification pathway cannot be excluded [39]. However, there is emerging evidence that the rice plant lacks As-methylation ability [40].

Contamination can also result from man-made activity, since DMA was used in the past as a component of weed killers [26]. Because a traditional method for cultivating rice involves flooding fields, the total As content in rice grains depends generally on the concentration of As in soil and irrigation water used during the growth period [3,16,31,35]. Even if As-containing water is not used, the rice plant will take up As. In this way, As(III) and As(V) species are taken up by a rice plant due to their similarities to silica acid [As(III)] and phosphate [As(V)], while DMA or MMA can be transported through the silica pathway (see references [18,19,21] in [35]). There is additional information in a recent review by Rahman and Hasegawa [41].

The concentration of As in rice varies extensively, depending on the geographical location [3,21,31,36,42,43] and the rice type [5,13,15,21,22,42]. The highest amounts of As are found in paddy rice, followed by brown rice, while the lowest amounts are in white rice, proving that As is accumulated in bran and an outer layer of rice and removed during the processing of white rice [44,45]. However, As content is not related to the color of the rice kernel [13].

Table 1 shows that, with concentration ranges of total As and i-As percentage contributions in commercially available popular rice types, 0.4–100% (~50% on average) of total As in rice is inorganic, while As(III) is usually the predominant form among others [14,21–23,25,49]. Inorganic As is recognized a Class 1 non-threshold carcinogen and considered much more toxic than organic compounds of As [5,8,18,20,21,27,48], so rice (together with water) is assumed as the highest contributor to i-As intake among all other

products of vegetable origin [20,21,26,36]. Interestingly, i-As is typically found in rice in Asia, while DMA dominates in rice from USA [8,17,20,39,43]. We can therefore categorize rice into DMA types (DMA > i-As) [8,17,39,45,51] and i-As types (i-As > DMA) [2,5,8,17,22,51]. It was suggested that the DMA type is of lower risk to health than i-As type [39].

As toxicity of various As compounds differs greatly, knowledge regarding As species in rice, besides the total As content, is crucial to understand the potential harmful effects of As-contaminated rice to humans [23,28,49]. From toxicology, the health risk related to rice consumption mostly depends on i-As content. Accordingly, robust methodologies for the selective, quantitative determination of i-As (called toxic As) that distinguish between total As and i-As in rice are of special interest, especially in the light of legislation for i-As concentrations in foodstuffs [5,10,19,20,24,26,28,36,51–54].

Over the years, various coupled systems have been reported for As speciation and, in the majority of cases, a separation technique (e.g., liquid chromatography (LC) was combined with atomic spectrometry or mass spectrometry (MS) detection]. However, determination and speciation of As are still challenging, particularly in analysis of food samples with a complex organic matrix, including rice. The most difficult step of the whole analysis is proper sample preparation (i.e., digestion and extraction procedures for the total As determination and speciation of As species, respectively). In As speciation, the key parameter is quantitative extraction of As species without changing their original characteristics [22,27,28,48]. The main problems can be associated with low recovery of As species and oxidation or reduction between As(III) and As(V) species, and conversion of organic species to i-As species [12,25,28–30,49]. Speciation of As requires extraction under mild conditions in order to maintain integrity of all As species [1,27,49]. Significant difficulties concern quantitative extraction of As(III), which is known to be strongly bound to -SH groups of cytosolic proteins and macromolecular constituents of rice; strong conditions are needed to extract it [16,22,27,29,45]. In contrast, organic forms of As (e.g., DMA) are not chemically bound to large structures in rice, so they depend less on the extraction media used [29]. Another crucial point is to ensure stability of As species at the stages of sample storage and pre-treatment by using appropriately selected sample conservation, since several factors may promote inter-conversion of As species (e.g., microbial activity, temperature, and light).

The number of works concerning the determination and speciation of As in rice is limited. Two relevant reviews were published recently. The first covered As speciation in terrestrial plants [55], while the second focused on new techniques to speciate and to locate As in rice grains [56]. Since awareness and concern about As in rice is great, the present review covers determination and speciation of As in rice using spectrometric methods with special attention to the sample-preparation step. It illustrates the main aspects of proper sample preparation and indicates the importance of sample treatment before analysis. Analytical approaches and strategies for the determination of total As and its speciation in rice are systematized and compared. We summarize and discuss detail different extraction and digestion procedures, and methods of species separation and detection reported in the literature in past 15 years.

## 2. Instrumental methods for determination and speciation of arsenic in rice

Concentrations of total As and As species in rice are primarily measured using spectrochemical methods, particularly inductively-coupled plasma MS (ICP-MS) due to its extremely high sensitivity and wide dynamic range, adequate for determination of (ultra)trace quantities of As [2–5,10,12–14,17–19,21–27,29–31,35–37,43,48,49,51,57–64]. Regarding speciation analysis, chromatographic

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