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Review Article

Analytical Strategies for the Determination of Arsenic in Rice

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Arsenic is an element of concern given its toxicological significance, even at low concentrations. Food is a potential route of exposure to inorganic arsenic and in this regard arsenic in rice is associated with soil contamination, fertilizer application, and the use of arsenic-containing irrigation water. Therefore, there is a need to investigate the regional rice crops with a view to future discussions on the need for possible regulatory measures. Several studies have reported high concentrations of arsenic in rice grown in soils irrigated with contaminated water; however, procedures used, including sample pretreatment and preconcentration steps, have to be followed to ensure sensitivity, accuracy, and reproducibility. Arsenic is a difficult element to measure in complex matrices, such as foods, because the matrix must be destroyed at an elevated temperature without the loss of the analyte or contamination. This review summarizes the major methods for the determination of arsenic in rice samples. The main purpose of this review is to provide an update on the recent literature concerning the strategies for the determination of arsenic and to critically discuss their advantages and weaknesses. These difficulties are described along with recent developments aimed at overcoming these potential issues.

1. Introduction

Arsenic (As) is considered to be one of the most important toxic elements because of its potential risk to human health [1]. It is carcinogenic, the inorganic form being the most harmful, and thus it merits particular attention [2–4].

Sources of arsenic in the environment can be natural or anthropogenic, since this element occurs in trace amounts in most rocks as well as in soil, water, and atmospheric dust. Once released into the environment, arsenic compounds reach water sources, such as rivers and groundwater systems, and subsequently food sources. Arsenic-contaminated soil, sediment, and sludge are the major sources of arsenic in the food chain, surface water, groundwater, and drinking water [5]. Arsenic concentrations in noncontaminated soils are typically below 10 mg/kg while in contaminated soils they can be as high as 30,000 mg/kg [6].

In the soil environment, arsenic is present mostly as the inorganic species (arsenate As(V) and arsenite As(III)). Inorganic arsenic species can be methylated through microbial action to give monomethylarsonic acid (MMA) and dimethylarsinic acid (DMA). Organic and inorganic arsenic species are present in the solution phase of paddy soils and can also be assimilated by plant roots [7]. Under oxidized condition, since As(V) is the predominant form (the lesser toxic form in iAs) and can easily be sequestrated by iron oxyhydroxide, it acts as a favorable process limiting arsenic accumulation during rice cultivation [8]. On the other hand, under highly reduced conditions, As(V) is reduced to As(III), which precipitates out from the solution in sulfur minerals, primarily arsenopyrite. In paddy soils, due to flooding type irrigation, anoxic condition is generated which favors the release of arsenic from soils and sediments and thereby increases the bioavailability to rice plants. Arsenic can be found as a contaminant in drinking water and foods in the form of different

chemical species and this affects the assimilation pathway. Recently, published studies about the arsenic content of different food products (including drinking water), indexed in the ISI Web of Science for the period of 2010 to 2015, show that almost 32% of the papers on arsenic contamination via the diet relate to research on fish samples, while around 29% are associated with drinking water and 39% with other food samples, such as rice (which accounts for 52% of this category). Other foods researched were various cereals and vegetables, edible oils, wine, and beer.

Rice (*Oryza sativa*) is the most important grain crop worldwide, being consumed by half of the world's population. Studies indicate that rice is a major contributor of inorganic arsenic in human diets [9–16]. Although seafood is known to contain high levels of total arsenic, most of it is present as organic arsenic.

The use of arsenic-containing irrigation water can lead to both long-term soil contamination with arsenic and a supply of arsenic to the crop. Rice accumulates a higher amount of arsenic than any other grain crops, largely because of the high availability of arsenic to plants under reduced soil conditions [17]. Arsenic accumulates in different parts of the rice plants and the accumulation rate varies according to the variety. In one study, arsenic concentrations in rice plant parts were found to decrease in the following order: root > straw > husk > whole grain > husked rice [18]. A higher arsenic accumulation in the roots than in other parts of the plant has also been reported by other authors [19, 20]. Some authors have observed the translocation of arsenic in plant systems [21, 22]. The relatively high levels of arsenic in rice are due to several factors including (1) the mobilization and bioavailability of arsenic in the soil after the farmers flood the rice fields and (2) plant uptake of arsenic instead of silicon, which is used by the plant under normal conditions to strengthen the stems and husks. Arsenic and silicon are chemically similar under the soil conditions found in flooded rice paddies and thus arsenic can be transported by the silicon transporters. As the rice plant grows, the plant incorporates arsenic (instead of silicon) into the grain.

Reported levels of As in rice [23–27] are <0.01–2.05 mg kg^{-1} for Bangladesh, 0.31–0.70 mg kg^{-1} for China, 0.03–0.044 mg kg^{-1} for India, <0.10–0.76 mg kg^{-1} for Taiwan, 0.11–0.66 mg kg^{-1} for the US, 0.03–0.47 mg kg^{-1} for Vietnam, and 0.08–0.38 mg kg^{-1} for Italy and Spain.

A survey of the research focused on regions with high levels of arsenic contamination in rice within the period covered by this review (2010–2015) returned 335 articles. The main aspects of this survey are highlighted in Figure 1. Most studies relate to the USA and Bangladesh while the other regions are China, the Indian state of West Bengal, India (as a whole), Mexico, Colombia, and Brazil.

According to WHO, the main sources of human exposure to arsenic are water and food [23]. Inorganic arsenic in water is regulated [24, 25]; however, there is no European Union (EU) or United States of America (USA) standard for inorganic arsenic in food products, despite the fact that food products represent the main route of exposure, especially rice and rice-based products [26, 27]. Recently, the JECFA proposed a maximum level of 0.2 mg/kg of inorganic arsenic in polished rice [28]. The European Food Safety Authority (EFSA) has reviewed the diet of the European Union population and has recommended that dietary exposure to inorganic arsenic should be reduced. The JECFA also carried out a review and stated that dietary exposure to inorganic arsenic is worthy of considerable attention and should be reduced. Therefore, there is a need to investigate the regional rice crops with a view to future discussions on the need for possible regulatory measures.

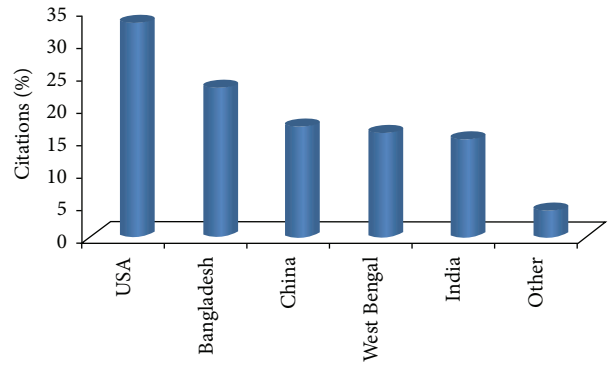

Figure 1: Regions with high levels of arsenic contamination in rice.

Several studies have reported high concentrations of arsenic in rice grown in soils irrigated with contaminated water [29–33]; however, procedures used, including sample pretreatment and preconcentration steps, have to be followed to ensure sensitivity, accuracy, and reproducibility.

Arsenic is a difficult element to measure in complex matrices, such as foods, because the matrix must be destroyed at an elevated temperature without the loss of the analyte or contamination. Determination of As species is generally carried out using hydride-generation (HG) [34, 35], liquid chromatography (LC) [36, 37], gas chromatography (GC) [38], and capillary electrophoresis (CE) [39, 40]. As speciation, particularly in solid samples, requires very careful sample preparation since this element is volatile, and it is important to avoid modification of the form and concentration of the species [41].

This review summarizes the major methods for the determination of arsenic in rice samples. The main purpose of this review is to provide an update on the recent literature concerning the strategies for the determination of arsenic and to critically discuss their advantages and weaknesses compared with the commonly accepted approach of combining nonchromatographic and spectroscopic techniques. The problems focused on involve sample preparation, as well as changes in "species information" that occur during the use of various separation technologies. These difficulties are described along with recent developments aimed at overcoming these potential issues.

2. Analytical Methodology

Analytical procedures for sample preparation are one of the most important steps in analytical methods. At this stage,

Table 1: Sample preparation methods for determination of inorganic arsenic in rice.

Arsenic species	Sample preparation	Arsenic found (mg Kg^{-1})	Detection	Reference
As total	Hot plate (HNO_3)	—	ICP-MS	[44]
As total	Microwave digestion (HNO_3/H_2O_2)	0.046–0.315	ICP-MS	[45]
As inorganic	Microwave digestion (HNO_3)	0.029–0.121	HPLC-ICP-MS	
As total	Ultraclave microwave (trifluoroacetic acid/H_2O_2)	0.036–0.218	HPLC–ICPMS	[46]
As inorganic		0.025–0.171		
As total	—	0.110–0.421	INAA	[47]
As inorganic	Hot plate (water)	0.050–0.172	LC-ICP-MS	
As total	Microwave digestion (HNO_3/H_2O_2)	0.07–0.47	ICP-MS	[48]
As inorganic	Microwave digestion (HNO_3)	0.001–0.17	HPLC-ICP-MS	
As total	Microwave digestion (HNO_3 concentrated)	<0.022–0.271	ETAAS	[49]
As inorganic	Vortexed and ultrasound (HNO_3 solution)	<0.030–0.147		
As(III)	Microwave digestion (HNO_3 solution)	<0.019–0.097		
As(V)	—	<0.030–0.076		
As total	Hot plate (HNO_3)	0.012–0.578	ICP-MS	[50]
As total	Ultrasound (HNO_3)	0.0125–0.1893	ETAAS	[51]
As(V)		0.0433–0.0625		
As total	Microwave digestion (HNO_3/H_2O_2)	0.026–0.464	ICP-MS	[52]
As total	Water bath (HNO_3 solution)	0.199–0.284	HPLC-ICP-MS	[53]
As inorganic	—	0.02–0.18	LC-AFS	[54]
As inorganic	Microwave digestion (HNO_3/H_2O_2)	0.045–0.235	HG-AFS	[55]
As total	Microwave digestion	0.013–0.150	HPLC-ICP-MS	[56]
As(III)	ELL (methanol-water (1 : 1)/HNO_3)	0.0036–0.0311		
As(V)		N.D–0.054		

several variables must be controlled and studied to ensure the quality and reliability of the results. In addition, the determination of arsenic and its species requires very careful sample preparation, since this element is volatile, and it is important to avoid the modification of the chemical form in order to maintain the integrity and concentration of the species of interest during the sample preparation process [42, 43].

Some recent studies reported in the literature in which total arsenic and/or inorganic arsenic species were determined are listed in Table 1 and also detailed in the text.

Dwivedi et al. [44] evaluated the effect of the presence of arsenic on the synthesis of essential and nonessential amino acids in rice grains. Rice seeds were obtained and grown with the cooperation of the Rice Research Station, Chinsurah, West Bengal, India, in a randomized block design, following conventional agronomic practices. Sixteen rice genotypes were selected, based on the overall contrast of the grains, from 90 rice germplasms grown in three As-contaminated areas of West Bengal. All field sites were fertilized with chemical fertilizers (N, P, and K) and a field trial was conducted over two years. The rice grain samples were pulverized and 0.5 g was digested in 3 mL of HNO_3 at 100°C for 2 h and 120°C for 4 h, then filtered in 10 mL of water, and stored at 4°C until the analysis. The total As in the grain samples was quantified using inductively coupled plasma-mass spectrometer (ICP-MS) while the As species were determined according to the protocol described by Zheng et al. [57]. The results of the field tests indicated that the accumulation of As in the soil led to its significant uptake by the rice grains and inhibited the synthesis of amino acids in some genotypes [44].

Carbonell-Barrachina et al. [45] analyzed Spanish rice gluten, cereals with gluten, and baby food and determined the total arsenic (t-As) and inorganic arsenic (i-As) using ICP-MS and high performance liquid chromatography (HPLC) with ICP-MS (HPLC-ICP-MS), respectively. Samples were dried in an oven at 80°C until constant weight and then homogenized by grinding in a ball mill and stored in a desiccator. For the determination of total arsenic, 0.2 g of dried product was placed overnight in contact with 2 mL of concentrated nitric acid. The samples were then digested in a microwave oven with hydrogen peroxide applying a temperature program reaching a maximum of 95°C. A certified reference material (CRM; rice flour NIST SRM 1568a) was used to assess the precision and accuracy of the chemical analysis. Arsenic species were extracted according to conditions previously described for t-As. However, HNO_3 (1% (w/v)) was used and the microwave digestion was conducted without the addition of hydrogen peroxide. The digested samples were centrifuged and 900 μL of the filtered supernatant was mixed with 100 μL of H_2O_2 and left overnight at 4°C. The content of inorganic arsenic was significantly higher in the Spanish rice gluten than in the cereals with gluten, placing children with celiac disease at high risk, since rice gluten is used as a replacement in gluten-free food products (note that rice gluten differs from "true gluten").

Raber et al. [46] proposed an analytical method for quantitatively determining inorganic arsenic in foods (including

rice). Rice samples were ground in a centrifugal mill to a particle size of <0.25 mm. The authors studied different sample preparation methods to improve the extraction efficiency and the compatibility between the extract and the chromatographic separation method. Among the different extractors studied, trifluoroacetic acid was found to be a potential reagent for the extraction of inorganic arsenic (iAs) from rice and no change in the retention time compared with aqueous standard solutions was noted. In the sample preparation procedure a portion of the powdered samples was placed in a quartz tube, to which 5 mL of 0.02 mol L^{-1} trifluoroacetic acid containing 50 μL of a 30% H_2O_2 solution was added and the suspension was sonicated for 15 min. The tubes were transferred to a Teflon rack of the Ultraclave microwave system which was closed. An argon pressure of $4{\cdot}10^6$ Pa was then applied and the mixture was heated to 95°C over a period of 10 min and this temperature was maintained for 60 min. After cooling to room temperature 1 mL aliquots of the extracts were transferred to vials and centrifuged. The supernatant was used directly for the HPLC-ICP-MS analysis.

According to Sun et al. [58], rice can easily accumulate As and the bioavailability of As released from this food matrix was assessed using an *in vitro* gastrointestinal simulator. Water, monosodium arsenate (NaH_2AsO_4), and sodium arsenite ($NaAsO_2$) were used and the samples were taken from the stomach, intestines, and colon. The analysis was carried out by ICP-MS and speciation was performed by HPLC. Procedures such as rice washing and cooking did not affect the result of the rice speciation although the arsenic content decreased in the range of 7.1 to 20.6%.

Brockman and Brown IV [47] extracted arsenic species from infant rice cereals through a hot water extraction procedure. Deionized water was added to each tube and the samples were maintained at 98°C (using a hot block) for 3 h. After cooling to room temperature the samples were centrifuged for 1 h in a centrifuge filtration system. The resultant filtered extract was diluted 1 : 25 with eluent and 100 μL of 30% hydrogen peroxide to oxidize the arsenite. Rice samples were analyzed for total arsenic by instrumental neutron activation analysis (INAA) and inorganic arsenic by liquid chromatography (LC) with ICP-MS (LC-ICP-MS).

The variability observed among rice grains is another dietary research approach to assessing arsenic exposure. Sommella et al. [48] evaluated the total arsenic and iAs in Italian rice grains and found that they varied by geographic origin and type. Concentrated HNO_3 (2.5 mL) was added to the pulverized samples and the mixture was left overnight. In the next step, H_2O_2 was added and the samples were digested in a microwave oven with a specific program. The samples were then cooled to room temperature and diluted to 50 mL with ultrapure deionized water. In the extraction procedure to investigate the speciation, 10 mL of 1% (w/v) HNO_3 was used and the same microwave temperature program applied to determine the total arsenic was employed. At room temperature, the samples were centrifuged and 900 μL of supernatant was mixed with 100 μL of H_2O_2. The samples were left overnight at 4°C before analysis. Inorganic arsenic was quantified by HPLC coupled to ICP-MS.

Pasias et al. [49] developed three different methods for the determination of total arsenic, total inorganic arsenic, and As(III)-As(V) in rice and rice flour food products. For the determination of total arsenic, 0.5 g of the homogenized rice or rice flour samples was digested in a microwave oven with 5 mL of concentrated HNO_3. For the determination of inorganic arsenic, 0.5 g of sample and 5 mL of 1 mol L^{-1} HNO_3 were vortexed and ultrasonicated for 15 min and then centrifuged at 4000 rpm for 15 min. In the next step 15 mL of 0.1% (w/v) EDTA was added to the mixture which was then vortexed again and centrifuged at 4000 rpm for 15 min. The supernatant was analyzed by ETAAS. Finally, for the determination of As(III) and As(V), 0.5 g of the sample was digested in a microwave oven with 5 mL of 1 mol L^{-1} HNO_3 (the highest temperature reached was only 85°C), and the extract was treated with 5 mL 5% EDTA (w/v). As(III) was determined and As(V) was then determined from the difference between the total inorganic As and As(III).

Phan et al. [50] investigated the potential exposure of Cambodian villagers to arsenic from their daily food consumption. Samples of lowland soils, paddy rice (raw and cooked), fish, and vegetables were collected from the Kandal, Kratie, and Kampong Cham provinces in the Mekong River basin in Cambodia. After acid digestion, extracts were analyzed by ICP-MS. The results revealed that the total concentrations of arsenic in lowland soils and paddy rice were significant. The samples were treated with concentrated HNO_3 (65%), the mixture was heated to 96°C and maintained at this temperature for one hour, and after cooling 5 mL of water was added. The extract was centrifuged and filtered and then the total arsenic was quantified by ICP-MS.

An interesting approach to determining total arsenic and As(V) with detection by electrothermal atomic absorption spectrometry after cloud point extraction (ETAAS/CPE), using ultrasound for the sample preparation, was developed by Costa et al. [51]. This procedure is based on the formation of a complex of As(V) ions with molybdate in the presence of sulfuric acid and extraction into the surfactant-rich phase with Triton X-114. The powdered samples were sonicated for 136 min with a 0.5 mol L^{-1} solution of nitric acid. For the As(V) determination an aliquot of the extract was submitted to the CPE methodology and for the total As determination an aliquot of the extract passed through a prereduction step with 1.0 mL of 8×10^{-8} mol L^{-1} $KMnO_4$ and agitation for 30 min was applied before the CPE methodology.

Shraim [52] evaluated the presence of various metals including arsenic in rice sold in Saudi Arabia. The sample preparation consisted of the microwave digestion of samples that were previously milled using an analytical hand mill. Digestion was carried out applying a specific temperature program and the digestion agents used were concentrated nitric acid, water, and hydrogen peroxide. After the solutions had been digested they were diluted with water and a portion was filtered and analyzed by ICP-MS.

A method for the determination of total arsenic and inorganic arsenic in rice using HPLC-ICP-MS has been developed. Prior to analysis the samples are treated with 0.28 mol L^{-1} HNO_3 and heated in a water bath (95°C) for

90 min. After cooling to room temperature, the extracts were centrifuged at 5000 rpm for 35 min at 18°C, filtered, and analyzed [53].

In order to relate the inorganic arsenic (iAs) content in the rice to the As present in the soil, considering properties such as pH, TOC, available P, and available Fe, rice and soil samples were collected in a region of south China (with a typical red soil for which arsenic contamination has not been reported) and analyzed. The rice grain samples were washed with deionized water, air dried at room temperature, and ground into fine particles. The inorganic As in the grains was determined by liquid chromatography-atomic fluorescence spectrometry (LC-AFS). The results showed that the soil pH and available phosphorus were the main factors influencing the uptake of As by rice grains. The presence of phosphorus suppresses As uptake by rice grains and competition between arsenic and phosphorus for transporters affects the transport from the soil to the roots in the rhizosphere [54].

G. Chen and T. Chen [55] carried out a study focused on iAs in rice samples. The samples were processed to a fine powder using a small mill. A microwave reaction system (rated at 1200 W) was used (95°C for 30 min) with an extraction solution comprised of 0.06 mol L^{-1} HNO_3 and 3% (w/v) H_2O_2. After cooling, the solutions were transferred to centrifuge tubes and centrifuged for 15 min at room temperature. During digestion, As(III) was oxidized to As(V) and silica-based strong anion exchange cartridges were used to separate the As(V) from organic As forms. Inorganic As was quantified by hydride-generation atomic fluorescence spectrometry (HG-AFS) after prereduction by iodide [55].

A simple procedure for the extraction of As species from polished rice samples has been described. For arsenic species determination, sample was ground to a fine powder in a homogenizer and 1 g was mixed with 10 mL of a methanol-water (1 : 1) mixture containing 1% HNO_3 in a centrifuge tube and the mixture was sonicated for 30 min. The extracts were centrifuged and stored at −4°C prior to analysis. As species were previously separated by HPLC and measured by ICP-MS [56]. Total arsenic was extracted in a microwave oven with 9 mL of 70% nitric acid and 1 mL of hydrogen peroxide and after the digestion the extracts were diluted with water. The total content of As was measured by ICP-MS [56].

Extraction methods involve the selective separation of a target species from its matrix (e.g., rice). The methodology employed should ensure quantitative and reproducible extraction without altering the species pattern by decomposition, chemical conversion, or insufficient extraction yield. This is especially important due to the complexity of rice sample matrices. In this context, conventional extraction, also known as heating by hot plate, is one of the traditional methods most widely used for sample treatment. Based on this sample preparation strategy, several approaches have been used for arsenic extraction from acidic samples [44, 47, 50]. The concentrated acids are the most used extractant. Water is the extractant most commonly recommended for the more polar or ionic species of arsenic, but few studies are reported in the literature regarding the extraction of these species from water due to the low yields obtained.

In contrast with conventional extraction methods, for example, liquid-liquid extraction (LLE), which are characterized by the use of high volumes of solvents and long extraction times [56], the use of microwave energy results in a significant reduction in the extraction time, because the microwaves accelerate the heating rate [45, 46, 48, 49, 52, 54, 55]. Other advantages of microwave-assisted extraction are high recoveries, good reproducibility, and minimal sample manipulation. The most critical parameters for method optimization using microwave extraction procedures are the extraction medium, applied microwave power, and extraction time [34]. Most of microwave extraction procedures involve the use of nitric acid [46, 59–61]. Nitric acid is a strong oxidizing agent; however, its use in digestion procedures constitutes an important source of interference due to the formation of nitrogen oxides.

Many factors are important in the process of sample preparation, such as the physical state of the sample, the analyte that is determined, and the type of detection. In general, the analysis of solid samples such as rice is more difficult since most detection methods require that the analytes of interest are transferred to a liquid phase. In this context the ultrasound-assisted extraction of the analyte emerged as an efficient alternative which requires a short time and the use of acids in low concentration and operation conditions involving atmospheric pressure and room temperature [51, 62, 63]. The use of ultrasound involves the solid-liquid extraction. Sonication by ultrasound occurs in the acoustic cavitation process resulting in points with extremely high temperature and pressure gradients. This phenomenon occurs near the particle surface or in the surface itself and improves the analyte solubility and diffusivity of solvent inside the solid particles. The chemical effect of ultrasound improves the reactivity of some chemicals, allowing the occurrence and also acceleration of some reactions involved in sample digestion.

3. Arsenic Speciation

Rice is a crop plant which can absorb more arsenic than other cereals, such as barley and wheat, as shown in a study by Meharg and Rahman [64]. Thus, it is important to monitor the contamination of rice with arsenic and in order to estimate the risk to human health variations in the toxicity, mobility and bioavailability, factors which are strongly dependent on the chemical form in which the arsenic is present, must be taken into account.

For the effective diagnosis of the degree of toxicity through contamination by inorganic species of arsenic in rice, it is necessary to develop analytical methodologies to aid the differentiation of these forms. Separation and detection techniques can be used to study the chemical speciation; however, the majority of these techniques are limited because they do not tend to combine an efficient separation capacity with the sensitivity and selectivity required for detection. Hyphenated chromatographic methods, such as HPLC-ICP-MS, have become the preferred and most commonly used approach for this purpose. The main advantages are the high

Table 2: Speciation of arsenic in rice using HPLC-ICP-MS.

Arsenic species	Sample preparation	Figures of merit	Reference
As(III), As(V), DMA, MMA, AsC, and AsB	Microwave digestion with 1% (v/v) HNO_3	LOD: 0.1–0.3 μg/Kg LOQ: 0.5–1.5 μg/Kg Recovery: 91.4–114.3%	[59]
Total As, As(III), As(V), DMA, MMA, and AsB	Pressurized liquid extraction sonication	Recovery: 71.8–104.5%	[62]
As(III), As(V), DMA, and MMA	Microwave digestion with 10 mL of 2% (v/v) HNO_3	LOD: 0.03 μg/L for total As	[60]
As(III), As(V), MMA, and DMA	Sonication by ultrasound probe	LOD: 0.05–0.2 μg/Kg Recovery: 82–99%	[63]
As(III), As(V), MMA, and DMA	Extraction with 1% HNO_3	LOD: 0.01–0.07 μg/L Recovery: 95–100%	[61]
MMA, DMA, As(III), and As(V)	Digestion of the samples using pressurized microwave system	LOD: 0.5–1.0 μg/Kg Recovery: 94–98%	[46]

LOD: limit of detection; LOQ: limit of quantification.

sensitivity, multielement capacity, wide linear range, and possibility for isotope determination.

Studies reported in the literature in which arsenic species were determined mainly by HPLC-ICP-MS are listed in Table 2.

Kim et al. [59] determined As(III), As(V), DMA, MMA, AsB, and AsC in rice grains in samples grown in Korea and USA using HPLC-ICP-MS. As(III) was the species predominantly found in the samples. The results indicated high toxic effect and need for further attention.

Sanz et al. [62] held arsenic speciation analysis in samples of rice, straw, soil, hair, and nail in regions affected by arsenic contamination in the eastern and western plains of the Ganga down and Bangladesh. Arsenic species (As(III), As(V), DMA, MMA, and AsB) were determined by HPLC-ICP-MS. For the samples of rice, the content of inorganic arsenic corresponds to 70–98% of the total arsenic content (up to 636.7 mg/kg in the samples). The authors indicate that the speciation analysis reveals itself as a powerful tool for full analytical assessment in epidemiological studies.

Maher et al. [60] determined As(III), As(V), DMA, and MMA in rice varieties from Australia. Total arsenic was determined by electrothermal atomic absorption spectrometry (ETAAS) after extraction with concentrated nitric acid. Inorganic arsenic and methylated species were determined by HPLC-ICP-MS. The method was validated by comparing the results with X-ray absorption near edge spectroscopy (XANES). The determination by XANES allows direct analysis, dispensing steps prior extraction and preventing problems from changes in arsenic species [60].

Sanz et al. [63] studied a procedure for the extraction of As(III), As(V), MMA, and DMA in rice samples from Spain and India. The speciation was also performed by HPLC-ICP-MS. The total arsenic was determined by ICP-MS after digestion of the rice samples with hydrogen peroxide and concentrated nitric acid assisted by microwave. For speciation analysis, the extraction of arsenic species occurred through the enzymatic action of α-amylase and ultrasonic probe sonication in a short period of time (3 min). The extraction procedure has shown more efficiency than conventional methods, avoiding the use of highly dangerous organic solvents. As(III) was predominantly the arsenic form found in rice samples analyzed. These results show that rice is a bioaccumulative plant for the more toxic form of arsenic.

Sun et al. [61] performed an arsenic speciation study on products derived from rice, such as cereals commonly eaten at breakfast, rice crackers, and condiments used to prepare Japanese rice. Arsenic species (As(III), As(V), MMA, and DMA) were extracted from samples with 1% (v/v) HNO_3 and quantified by HPLC-ICP-MS. The inorganic forms were prevalent (75.2 to 90.1%). The study provided useful information which leads to a better understanding of the distribution of arsenic species in rice products. These are important considerations in the formulation of new rice-based foods.

Hyphenated chromatographic methods contribute significantly to enhancing the study of arsenic speciation, but they are still costly and thus the development of nonchromatographic methods is a more accessible and promising approach. A major challenge in speciation analysis is to maintain the integrity of the chemical species of interest from the sampling to the detection stages. In nonchromatographic methods, selective extraction procedures using a small volume of extractor are often required, based on the analyte partitioning into a phase with compatible polarity. This type of extraction procedure has the advantage of preconcentration and the minimization of matrix effects. However, if the partitioning is not quantitative, low recoveries can be observed.

Nonchromatographic methods offer several advantages over the chromatographic techniques and represent a fast and inexpensive option for application in laboratories, particularly when applied to food and environmental samples. However, many of these methods provide limited information on the samples since most approaches have centered on a single element or a specific type of chemical form (i.e., free ions or organic compounds).

In addition to the challenge of preventing interconversion of species during the extraction steps, most procedures

Table 3: Nonchromatographic methods for speciation of arsenic in rice.

Arsenic species	Sample preparation	Detection	Figures of merit	Reference
As(III) and As(V)	Assisted digestion microwave with 0.14 mol/L HNO_3	HG-AAS	LOD: 1.96–3.85 ng/g	[65]
As(III) and As(V)	Vortex with 25 mL of solution 0.05 mol/L $(NH_4)_2CO_3$	HG-AFS	LOD: 1.3–4.4 ng/g Recovery: 94-95%	[55]
As(III) and As(V)	Cloud point extraction	UV-Vis	LOD: 1.14 μg/L Enrichment factor: 65 Recovery: 95–102%	[66]
Total As and As(V)	Sonication with 0.5 mol/L HNO_3	ETAAS	LOD: 10–33 ng/L Enrichment factor: 78.3 Recovery: 90.8–113.1%	[51]
Inorganic As, MMA, DMA, and AsB	0.01 mol/L TMAH (tetramethylammonium hydroxide)	ETAAS	LOD: 15–50 ng/g	[67]
Total As, As(III), and As(V)	Assisted digestion microwave with 1.0 mol/L HNO_3	ETAAS	LOD: 19–30 μg/Kg LOQ: 57–90.3 μg/Kg Recovery: 92–105%	[49]

LOD: limit of detection; LOQ: limit of quantification.

end up being restricted to inorganic species, and there are few studies using nonchromatographic procedures for determination of organic arsenic species. This challenge makes nonchromatographic speciation procedures more promising, opening an opportunity for research aimed at improving this focus. Table 3 listed some studies reported in the literature using nonchromatographic procedures for arsenic speciation in rice samples.

Speciation is relatively easy to investigate when a property of a particular compound can be measured directly in the sample without interference from the other matrix components. Direct speciation analysis is generally considered to be less challenging although this is not always the case.

Studies on direct and *in situ* analysis are increasing due to interest in simplifying the process of rapid substance identification for monitoring and quality control in the food industry. There are very few methods available for the determination of the speciation in solid food samples through direct analysis. The use of mass spectrometry (MS), with only a few sample preparation steps, allows the speciation of organic arsenic to be determined, with limited analyte loss. In contrast, matrix-assisted laser desorption/ionization (MALDI), electrospray ionization (ESI), and desorption electrospray ionization (DESI), despite being associated with greater losses, have greater tolerance in the presence of impurities, proving to be valuable for metal complexes [68].

Lin et al. [69] demonstrated that DESI-MS can be used as desorption/ionization technique for the determination of arsenic speciation (inorganic arsenic, monomethyl arsenic acid, dimethylarsinic acid, and arsenobetaine) in biological samples under environmental conditions. The results were effective in the identification of inorganic and organic arsenic compounds. Furthermore, the DESI method does not require sample preparation and its use has proved to be promising for *in situ* speciation studies [69].

Finally, more recently, the development of speciation techniques has been highly focused on physical methods, such as X-ray diffraction (XRD), X-ray powder diffraction (XPD), and X-ray absorption spectroscopy (XAS) [70, 71]. However, it is clear that the cost of the instrumentation and the attainable sensitivity are not sufficient for routine speciation analysis of food samples [72]. For speciation, X-ray absorption near edge structure (XANES) spectroscopy is a powerful tool, because it is a direct method by which we can avoid the change of the chemical state of target elements. XANES is a nondestructive technique for identifying inorganic and organic arsenic species in complex environmental samples [73].

Manning described a procedure to evaluate the solid phase oxidation state and mineral surface binding sites in three agricultural soil samples by fitting linear combinations of XANES spectra derived from several synthetic and well characterized As(III)- and As(V)-treated model compounds. The data showed that As(III) is either partially or completely oxidized to As(V) when reacting with soil [74].

There is a trend toward reducing the sample preparation steps in order to limit the interconversion of species, providing more accurate results on the quantity of each species in the sample. However, based on this review it is clear that there are still considerable difficulties associated with reducing the number of sample preparation steps involved in speciation studies. Thus, in this regard, many approaches are focused on total arsenic without considering the specific chemical forms (free ions or organic compounds) and the information provided on the samples is consequently very limited. It is expected that procedures for direct speciation studies or a reduction in the number of preparation steps will be developed in the near future, based on the use of MALDI, ESI, DESI-MS, and X-ray, with chromatographic or nonchromatographic detection techniques. This approach could provide the best aspects of screening methods, particularly in relation to reduced handling, and involves the direct characterization of chemical forms, contributing to improving our understanding of the behavior of the different chemical forms of arsenic in food samples such as rice.

4. Conclusions

High levels of arsenic in rice grains are a potential concern in relation to human health. More information on arsenic speciation in rice and rice-based products for consumption is needed in order to carry out risk assessment studies on inorganic arsenic. The largest gap in our knowledge with regard to assessing inorganic arsenic consumption rates from rice is related to the levels of arsenic species in rice and rice products and appropriate analytical methods for speciation of arsenic ensure the integrity of the species.

A comprehensive risk assessment must be based on information on the dietary status and consumption of rice, along with the calculation of the daily intake of arsenic from the various routes of human exposure. The most commonly reported concern is arsenic entering the food chain, affecting food safety. Management options for health risk prevention and agricultural sustainability should therefore focus on minimizing As inputs to soils and limiting human exposure.

This review is not exhaustive, but it highlights some of the important and unique aspects related to the presence of arsenic in rice, addressed within the context of human nutrition. Due to the increasing consumption of rice, the available analytical methods need to be able to provide more detailed information on the chemical species present, overcoming the barrier created by the complexity of food matrices and the low concentrations of the analyte present. Unfortunately, the procedures for arsenic speciation studies are not yet suitable for routine analysis and clearly the development of such methods offers a great challenge for analysts around the world. Thus, the search for simple strategies suitable for obtaining quantitative information regarding arsenic species should be encouraged. However, these strategies require an interdisciplinary approach in order to cover the various aspects involved and represent a considerable challenge in the areas of toxicology and analytical chemistry.

Abbreviations

As: Arsenic
AsB: Arsenobetaine
AsC: Arsenocholine
As(V): Arsenate
As(III): Arsenite
CE: Capillary electrophoresis
CPE: Cloud point extraction
CRM: Certified reference material
DMA: Dimethylarsinic acid
DESI-MS: Desorption electrospray ionization-mass spectrometry
EDTA: Ethylenediaminetetraacetic acid
EFSA: European Food Safety Authority
ESI-MS: Electrospray-mass spectrometry
ETAAS: Electrothermal atomic absorption spectrometry
EU: European Union
GC: Gas chromatography
HG: Hydride-generation
HG-AFS: Hydride-generation atomic fluorescence spectrometry
HPLC: High performance liquid chromatography
iAs: Inorganic arsenic
INAA: Instrumental neutron activation analysis
ICP-MS: Inductively coupled plasma-mass spectrometer
JECFA: Food and Agriculture Organization/World Health Organization
LC: Liquid chromatography
LC-AFS: Liquid chromatography-atomic fluorescence spectrometry
LC-ICP-MS: Liquid chromatography-inductively coupled plasma-mass spectrometry
MMA: Monomethylarsonic acid
MS: Mass spectrometry
MALDI: Matrix-assisted laser desorption/ionization
USA: United States of America
XRD: X-ray diffraction
XPD: X-ray powder diffraction
XAS: X-ray absorption spectroscopy
WHO: World Health Organization.

Competing Interests

The authors declare that there are no competing interests regarding the publication of this paper.

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