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FOOD, HEALTH, AND THE ENVIRONMENT (KE NACHMAN, SECTION EDITOR)

Recent Advances in the Measurement of Arsenic, Cadmium, and Mercury in Rice and Other Foods

Brian P. Jackson · Tracy Punshon

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Abstract Trace element analysis of foods is of increasing importance because of raised consumer awareness and the need to evaluate and establish regulatory guidelines for toxic trace metals and metalloids. This paper reviews recent advances in the analysis of trace elements in food, including challenges, state-of-the-art methods, and use of spatially resolved techniques for localizing the distribution of arsenic and mercury within rice grains. Total elemental analysis of foods is relatively well-established, but the push for ever lower detection limits requires that methods be robust from potential matrix interferences, which can be particularly severe for food. Inductively coupled plasma mass spectrometry (ICP-MS) is the method of choice, allowing for multi-element and highly sensitive analyses. For arsenic, speciation analysis is necessary because the inorganic forms are more likely to be subject to regulatory limits. Chromatographic techniques coupled to ICP-MS are most often used for arsenic speciation, and a range of methods now exist for a variety of different arsenic species in different food matrices. Speciation and spatial analysis of foods, especially rice, can also be achieved with synchrotron techniques. Sensitive analytical techniques and methodological advances provide robust methods for the assessment of several metals in animal- and plant-based foods, particularly for arsenic, cadmium, and mercury in rice and arsenic speciation in foodstuffs.

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B. P. Jackson (✉)
Department of Earth Sciences, Dartmouth College,
Hanover, NH, USA
e-mail: Brian.P.Jackson@dartmouth.edu

T. Punshon
Department of Biological Sciences, Dartmouth College,
Hanover, NH, USA

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Introduction

Arsenic is a naturally occurring element present in water, soils, and rock; it is also a toxic element, and both inorganic and organic arsenic compounds have been used widely in agriculture and livestock throughout the 20th century as insecticides, pesticides, and antibiotics. Consequently, it is not surprising that arsenic is found at detectable levels in many food crops. Additionally, marine fish, marine algae (seaweed), and rice all concentrate arsenic from the environment. Methylmercury bioaccumulates in the food chain and is found at elevated levels in many higher trophic-level aquatic organisms. The US Food and Drug Administration (FDA) has a maximum concentration limit of 1 mg/kg for methylmercury in fish [1]. Mercury uptake in rice grown on contaminated soils is also of recent concern. Cadmium is another toxic non-essential element that is present in food; for non-smokers, food is the major source of exposure. The European Food Safety Authority (EFSA) has set maximum limits for cadmium in a variety of foodstuffs and, in 2013, released a draft that amended these regulations to include cocoa and chocolate products [2]. Clearly there is a continued need for robust analytical methods to determine the concentration and speciation of these toxic elements in food.

Total elemental analysis in food is, in principle, no different than elemental analysis in any other biological matrix. The solid sample first requires solubilization, most usually accomplished by acid digestion, followed by analysis of the resulting digestate by a suitable analytical technique, for instance inductively coupled plasma mass spectrometry (ICP-MS). A holistic overview for single laboratory-validated analysis of metals

in food has recently been outlined [3]. The general approach of acid digestion followed by ICP-MS analysis is probably the most routine method currently used for multi-element analysis of food products. A standardized method utilizing high-pressure digestion has been reported for arsenic, cadmium, mercury, and lead in foods [4].

Food is particularly challenging, because the matrix can be high in low-molecular-weight organics, which, if not completely decomposed during acid digestion, can cause severe matrix effects during analysis, as noted in the ICP-MS analysis of wines [5] and fish [6]. The presence of these low-molecular-weight carbon compounds has a pronounced effect on the analysis of high ionization potential elements, arsenic, selenium, and mercury, by ICP-MS that, if uncorrected, can lead to significant over-estimation of the concentration of these elements [7, 8]. Trace element concentrations in food are usually quite low, for instance and as will be discussed later, a potential guideline limit for arsenic in rice that has been discussed is 0.2 μg/g [9]; assuming the digestion procedure introduces a dilution of 100-fold, then the actual concentration in the solution to be analyzed is 2 μg/L. This effectively means that only very sensitive analytical instrumentation can be used for trace element analysis in food and that methods must be robust, precise, and accurate as even a small positive bias could cause a sample to appear above a maximum limit.

For arsenic and mercury analysis, a measure of the total amount of these elements is not sufficient, because both occur in different ionic or molecular forms (species) in food and these different species have different toxicities [10]. Methodology for speciation analysis is relatively well established for both of these elements. Arsenic speciation is most often accomplished by liquid chromatography (usually anion exchange chromatography) coupled to an element-specific detector. Mercury speciation most often involves gas chromatography and element-specific detection. For arsenic, it is usual to measure the presence of at least five species, arsenite, arsenate, arsenobetaine, monomethylarsonate (MMA), and dimethylarsinate (DMA), although in some foodstuffs that contain seafood or seaweed there may be additional organoarsenic species present such as arsenosugars [11]. In any case, the need for analytical methods with low detection limits becomes even more pressing when quantifying the individual species present.

In this review, we summarize the recent advances for the measurement of total arsenic and arsenic species in food, and particularly in rice and rice products. We also review the occurrence and concentration of cadmium and mercury in rice. We focus mostly on methods utilizing ICP-MS as the detector, increasingly recognized as the analytical technique of choice for low-level multi-element analysis. However, optical emission spectroscopy (ICP-OES), atomic fluorescence spectroscopy (AFS), graphite furnace atomic absorption (and the coupling of cold vapor or hydride generation with any of these techniques) all remain viable analytical techniques and are also discussed where appropriate. We also briefly review synchrotron techniques, which offer unique insights into in situ elemental analysis of spatial location and oxidation state mapping of foods such as rice grain.

Determination of Total Trace Element Concentrations in Food

Collision/Reaction Cell Inductively Coupled Plasma Mass Spectrometry (ICP-MS) Approaches to Alleviate Interferences in Food Analysis

ICP-MS offers distinct advantages for trace element analysis, including the multi-element capabilities and the high sensitivity. However, matrix effects on precision and accuracy can be severe. Polyatomic interferences, where two or more atoms combine in the plasma with the same mass as the target analyte, have largely been overcome by the advent of collision cell [12] and reaction cell technology [13]. Reaction cell approaches use a specific cell gas either to remove an isobaric interferent or to shift the detection mass for the analyte [13]. Ammonia has been used to suppress argon dimers and bromine hydrides and was shown to be effective for accurate determination of selenium in the US National Institute of Standards and Technology (NIST) tomato leaves 1537a where selenium is at 0.12 μg/g and bromine at 11 μg/g [14]. Methane is also efficient for selenium analysis in selenium-enriched rice [15]. Argon chloride interference on arsenic at m/z 75 was suppressed by using methane or by mass shifting detection to m/z 91 by reaction with oxygen; detection of AsO at m/z 91 yielded the lowest detection limits, and the approach yielded accurate results for seaweed and yellow croaker reference materials, both of which are high in chlorine [16]. Such reaction cell methods are also particularly suited to avoiding doubly charged interferences of rare earth elements (REEs) on arsenic analysis by mass shifting arsenic to m/z 91 [17].

ICP-MS analysis of food digests must also compensate for matrix effects on analyte sensitivity. For instance, sensitivity for arsenic and selenium increases in the presence of organic solvents, a phenomenon already reported in 1994 [18]. In fact, the addition of an organic modifier, usually methanol, to chromatographic mobile phases to enhance sensitivity for arsenic speciation is now commonplace in most approaches. The effect of residual organics in solution on the enhanced sensitivity of certain elements was recently reviewed [8]. In summary, phosphorus, arsenic, selenium, antimony, tellurium, iodine, gold, and mercury signals were always higher in carbon-containing solutions. The impact of residual organics raises a challenge for food analysis because the residual carbon background (and hence degree of signal enhancement) can differ between samples. Perhaps the most robust approach

in this instance is calibration by the method of standard additions, because the calibration standards experience the same degree of signal enhancement as the unspiked sample. This is a viable alternative when all samples have a similar matrix and can all be run against one standard additions curve, but becomes very time consuming when it must be performed for every sample due to variable sample matrix. An alternative approach is to add a swamping organic solvent to the sample. For example, in the analysis of infant formula, it is now common to add a fixed volume of methanol to all digested samples and standards to normalize organic matrix within the sample batch and enhance selenium sensitivity [19–21], and this approach should also be applicable to arsenic, mercury, and cadmium. A similar effect can be achieved by adding butanol [22] or isopropanol on-line via the internal standard mixture, which is then introduced into the sample line via a mixing block. Appropriate use of internal standards, i.e. tellurium for arsenic and selenium, as suggested by results of Grindlay et al. [8], can also correct these matrix-based sensitivity increases to some extent.

Arsenic, Cadmium, and Mercury Concentrations in Food

Arsenic

Seafood The main source of total arsenic to diet is seafood, where total arsenic concentrations can reach >10 mg/kg. However, in seafood, arsenic is predominantly present as arsenobetaine [23], an organic arsenic compound that is non-toxic and readily excreted in urine. Recent studies have highlighted fat-soluble arsenolipids that have been reported at mg/kg levels in fish oils and in some fish muscle. In vitro cellular toxicity studies on bladder and liver cells suggest that these arsenolipids have equivalent toxicity to inorganic arsenic exposure [24•].

Poultry Arsenic exposure to the US population through poultry consumption is of concern because of the long-standing and widespread use of organoarsenic feed additives in poultry, turkey, and swine production. The most widely used arsenic feed additive was roxarsone (3-nitro 4-hydroxyphenylarsonic acid), which, counter to industry claims, has been shown to be microbially degraded, with one of the products being inorganic arsenic [25–28]. A 2011 FDA study found that significantly higher concentrations of inorganic arsenic were detectable in poultry meat from chickens fed with the roxarsone-added feed compared with a control group [29]. As a consequence, roxarsone and two other structurally similar arsenic-containing antibiotics, carbasone and p-arsanilic acid, have been withdrawn from use and are no longer fed to animals in the USA, although roxarsone is still used in China. Nitrasone, 4-nitrophenylarsonic acid, is still used in the USA for the control of blackhead disease in turkey production.

Rice Concentration ranges of arsenic in rice and rice products have been extensively tested [30–38]. Total arsenic concentrations in rice vary widely as a function of rice cultivar, geography, environment, and growing conditions [39••]. Arsenic can vary spatially within the grain, with inorganic arsenic being higher in the bran layers [40] (see below). In 2014, the World Health Organization (WHO)/Food and Agriculture Organization of the United Nations (FAO), through the CODEX Alimentarius has proposed a guideline level for inorganic arsenic in polished and husked rice of 0.2 mg/kg [9], but consensus was not reached for inorganic levels in brown rice. Another particular area of study has been the levels of total and inorganic arsenic in rice products specifically marketed for infants and children [41–45] whose low body weight compared with adults puts them disproportionally at risk from exposure to contaminants. Overall, future guideline levels for rice need to be evidence-based while considering feasibility and technical challenges.

Seaweed Marine algae (seaweed) contains mg/kg levels of arsenic, present mostly as arsenosugars, which are thought to be of potential toxicity due to metabolite formation and tissue accumulation [46]. Seaweed-based snacks and foods are common in Korea and Japan and are of increasing popularity in the USA. Seaweed is used as a feed additive in dairy farming in the USA and as a soil fertilizer [47]. Seaweeds usually contain low concentration of inorganic arsenic, although one species, hijiki, had concentrations of approximately 100 mg/kg of total arsenic, with 71 % being inorganic [48]. Clearly this is an unsafe level of inorganic arsenic, and food safety authorities in many countries advise against consumption of this particular species.

Cadmium in Rice

Cadmium accumulates in rice when it is grown aerobically, whereas arsenic concentrations are highest when rice is grown under flooded conditions [49, 50]. A summary of ICP-MS analysis of rice grain cadmium from market basket studies in 12 countries showed mean concentration ranges from 0.006 to 0.099 mg/kg. For populations with high rice cadmium and high rice consumption, such as Bangladesh or Japan, cadmium-contaminated rice is a major health concern [51, 52]. ICP-MS [50–52], graphite furnace atomic absorption spectrometry (AAS) [53] and also AAS with solid-phase extraction [54] have all been used as sensitive detectors for cadmium analysis.

Mercury in Rice

Rice has also been shown to bioaccumulate methylmercury [55] in the grain. Published studies have largely focused on Chinese rice grown in mercury-contaminated soils [56–58]. Growing rice aerobically reduced methylmercury content by

reducing the activity of mercury methylating bacteria in the soil [59]. Concentrations of total mercury and methylmercury are on the order of 0.1 and 0.01 mg/kg, respectively [60, 61]. For individuals eating primarily rice-based diets, then these levels are of concern, especially as methylmercury, the most toxic mercury species, concentrates in the rice grain [62]. Methods for total mercury analysis of rice have been compared, and acid digestion ICP-MS or cold vapor AAS (CVAAS) have been found to be comparable to solid sampling mercury analysis, and satisfactory accuracy for rice reference material NIST 1558a was obtained [63].

Arsenic Speciation in Rice

The main arsenic species in rice are inorganic arsenic and DMA with trace amounts of MMA also occasionally detected. The proportions of DMA and inorganic arsenic vary with rice cultivar and environmental conditions [39••], with the former appearing to be the major driver. Rice grown from Asian countries has a linear relationship between total arsenic and inorganic arsenic, with an average 78 % of total being inorganic arsenic, whereas US rice exhibits a hyperbolic relationship between inorganic arsenic and total arsenic, with inorganic arsenic having maximum values of 0.15 mg/kg and total arsenic having maximum values >0.4 mg/kg [64]. It has been suggested that the widespread use of MMA and DMA as pesticides and defoliants in cotton production in South Central USA may be the cause of high levels of DMA in US rice now cultivated in that area; however, no data exist to substantiate this assertion, and DMA and MMA are thought to have relatively short half-lives in soil. Rice does not methylate arsenic [65], but does preferentially translocate DMA to rice grain. Elevated soil arsenic and soil conditions that favor net microbial methylation of inorganic arsenic appear to control the ultimate DMA concentration in the grain [64].

Speciation analysis generally employs some form of chromatography to separate the arsenic compounds coupled to element-specific detection. For fish, rice, and seaweed, where the expected arsenic species are mostly anionic, anion exchange chromatography using phosphate- or carbonate-based eluents are most frequently used [11]. The element-specific detector is often ICP-MS but can also be AFS when coupled to HG [66]. Accurate, precise, and meaningful speciation data depend on quantitative extraction efficiency from the solid, species fidelity during extraction (i.e. the extraction method does not change the distribution of species in the sample), and a sensitive and accurate analytical technique. One of the first reports on arsenic speciation in rice used 2 M trifluoroacetic (TFA) acid extraction [38]; the method gave good arsenic species recoveries of 64–99 % of total arsenic. The TFA extraction method was used by Williams et al. [36] in their paper on levels and speciation of arsenic across rice varieties of different international origin. A simpler extraction method using 1–2 % HNO_3 at temperatures of approximately 95 °C was demonstrated to be effective for extraction and speciation of arsenic from marine and animal tissue [67], and this general approach has been adopted by many groups for arsenic extraction from foodstuffs [42, 43, 68–70]. Because extraction can cause a species interchange between arsenic(III) and arsenic(V), and a combined measure of inorganic arsenic is often employed for reporting purposes, it is common to also add H_2O_2 to the HNO_3 extraction to oxidize all inorganic arsenic to arsenic(V) [44]. Other extraction methods, such as enzymatic extraction with amylase, have also been shown to yield quantitative recovery of arsenic species from rice [71].

In 2011, an international laboratory proficiency test (IMEP 107), where identical unknown test samples are sent to individual laboratories with the goal of assessing the robustness of methodologies, was organized by the EU Reference Laboratory for Heavy Metals in Feed and Food for the determination of inorganic arsenic in rice; seven expert laboratories and 98 participant laboratories were included [72]. The results of this test showed that the determination of total and inorganic arsenic from rice was not a function of the extraction or analysis method. Only 32 of the 98 participating laboratories performed speciation analysis and reported a value for inorganic arsenic; 75 % of the reported results had satisfactory z-scores. The authors of the study suggested that concerns that determination of inorganic arsenic in rice is method dependent are unfounded, and legislation should not be held up based solely on this concern.

Arsenic speciation methods have also been applied to rice-containing foods and have shown that inorganic arsenic is disproportionately higher in rice bran than in bulk grain [32]. As might be expected, rice-based food products have been shown to have total and inorganic arsenic concentrations that fall within the range of values reported for rice grain. Particular attention has focused on rice-based products for young children because their exposure in terms of μg arsenic/kg body weight is higher than for adults. Arsenic speciation methods have shown low concentrations of inorganic arsenic in infant formulas but no increase in arsenic levels as a result of rice starch fortification [43, 73], high levels of total arsenic and inorganic arsenic in toddler formulas using rice syrup as the sugar [42], higher levels of inorganic and total arsenic in infant second foods (jarred solid food meals) where rice is an ingredient [43], and high levels of total and inorganic arsenic in rice-based infant and toddler cereals [34, 41, 74, 75].

Arsenic Speciation in Other Foods

There have been many studies on arsenic speciation from marine fish (where the major species is invariably arsenobetaine [76–79]) and shellfish (where arsenobetaine

again predominates but studies occasionally report high levels of inorganic arsenic [80]). Arsenic species are typically very soluble from marine fish and are relatively easily extracted by water and water/methanol extracts [78]. A recent study of 13 different extractants for inorganic arsenic (a minor constituent) of fish tissue showed that dilute acids had the highest extractant efficiency whilst dilute base had the lowest, but most extractants were not significantly different from each other [81]. There is also currently much interest in arsenolipids from marine organisms, and methods using reversed-phase high-performance liquid chromatography (HPLC) coupled to ICP-MS have been developed for their detection and quantification [82–84]. Fish liver and some fish muscle, e.g. tuna, can contain mg/kg levels of these arsenolipids, and recent in vitro and in vivo toxicology studies show equivalent toxicity for arsenolipids compared with arsenic(III) [24•, 85]. Marine algae (seaweed) can also contain high (1–100 mg/kg) total arsenic concentration, and here the main arsenic species are arsenosugars. Arsenosugars generally require long chromatographic run-times to fully resolve all arsenic species, and some sugars can be degraded by acid extraction [86].

In 2012, another recent EU proficiency test (IMEP 112), including 74 laboratories, focused on the determination of total and inorganic arsenic in wheat, vegetable (NIST 157a, spinach leaves), and algae; only 20 % of the laboratories reported satisfactory inorganic arsenic results for algae (compared with 85 % for vegetable and 60 % for wheat), suggesting that robust methods are still lacking for samples containing arsenosugars [87•].

As stated above, poultry is another food that has attracted attention as a potential source of arsenic to diet. In the USA, arsenic-based drugs, such as 4-hydroxy-3-nitrophenylarsonic acid or roxarsone, were commonly used as antimicrobials in poultry production until 2013, when arsenic-based drugs were banned by the FDA, with the exception of nitarsone. HPLC-ICP-MS-based methods have been developed to analyze the parent arsenic drugs and degradation products in poultry litter [88] and soils [89], and in chicken liver [90] and meat [91].

Non-Chromatographic Methods for Inorganic arsenic Determination

Finally, while most speciation methods use chromatography coupled to ICP-MS or other detectors, a pragmatic approach to quantifying inorganic arsenic, the important form from a regulatory standpoint, has been to use the selective hydride generation of these species. The volatile hydrides can then be passed in a gas stream directly to the detector separated from the other arsenic species and any samples matrix effects. This approach has been used for rice and fish [76]. Hydride generation coupled to ICP-MS was also used for inorganic arsenic in rice after oxidation of the extract and off-line solid-phase extraction by anion exchange [92]. Hydride generation AAS has been used to determine inorganic arsenic in rice samples after initial acid extraction, H_2O_2 addition, and solid-phase extraction and concentration of inorganic arsenic [92]. The latter method had similar performance to chromatography-ICP-MS methods, with much lower capital costs for instrumentation.

Reference Materials for arsenic Speciation

The increased interest in arsenic speciation of food, driven in great part by impending WHO guideline limits for inorganic arsenic in rice and FDA guidelines for inorganic arsenic in juice, has outpaced the availability of relevant certified reference materials for arsenic species. This is not the case for mercury, where many certified reference materials have values for total mercury and methylmercury, and illustrates that speciation analysis for arsenic is still not as widely practiced as for mercury. Tort-3, lobster hepatopancreas, produced by the National Research Council of Canada (NRC), has certified values for total arsenic and arsenobetaine. DORM-2, (since superseded by DORM-3 and -4), a dogfish muscle standard produced by the NRC, reported certified values for total arsenic, arsenobetaine, and tetramethylarsonium. NIST released the rice flour Standard Reference Material (SRM) 1568b in 2013 with certified values for DMA, MMA, and inorganic arsenic; this was a recertification of the rice flour 1568a, which had been used by many researchers as a de facto SRM because robust consensus values for DMA and inorganic arsenic could be gained from the scientific literature. NIST also supplies SRM 2669, a human urine certified for arsenic(III), arsenic(V), DMA, MMA, trimethylarsine oxide (TMAO), arsenobetaine, and arsenocholine; while this is not a food SRM, it can at least serve as a reference for retention time and quantification of seven arsenic species. The European proficiency test IMEP 112 we referred to above used NIST 1570a, spinach leaves, as the vegetable sample; therefore, consensus reference inorganic arsenic values for this SRM are available. For arsenosugars and arsenolipids, neither pure reference compounds nor reference materials are readily available.

Spatially Resolved Trace Element Techniques

Recent developments in spatially-resolved metal analysis techniques, including synchrotron-based X-ray fluorescence (SXRF) microanalysis [62, 93, 94], nano secondary ion mass spectroscopy (nano-SIMS) [95, 96], and laser ablation ICP-MS [40] (see Lombi et al., [97] for technique comparison), provide the opportunity to evaluate trace element concentrations in different sections of the food item of investigation. In this section, we focus on arsenic and mercury in rice. SXRF uses focused, high-energy X-rays to cause elements to fluoresce, at an energy and amplitude that correspond to the

identity and quantity of the element. Samples are moved in the *x, y,* and *z* direction relative to the beam in 2D mapping, or additionally rotated through 360° in the case of 3D imaging. Detection limits vary between individual synchrotron beamlines, but arsenic and mercury concentrations <1 μg/g have been measured in rice [62, 93, 98]. Elemental mapping studies have shown that chemical species is a strong determinant in whether arsenic is present in the grain (endosperm) or whether it remains trapped in the vasculature that supplies the grain with nutrients from the parent plant (ovular vascular trace [OVT]) [40, 95, 98]. DMA is efficiently transported into the endosperm, whereas inorganic arsenite remains trapped in the OVT and bran layers (aleurone) that encase the grain [93] (Fig. 1). Rice grains grown in flooded conditions contained high concentrations of DMA, and nano-SIMS showed that arsenic was localized to the subaleurone tissue region; a particularly protein-rich layer of cells beneath the bran layer. Co-localization with S suggests strong binding to thiol groups [95]. In the case of mercury, elemental maps of Chinese rice show that mercury is also localized to the outer layers of the grain and OVT. Elemental mapping studies of mercury in rice have appeared relatively recently, and have not used a resolution that allows individual cell layers to be distinguished.

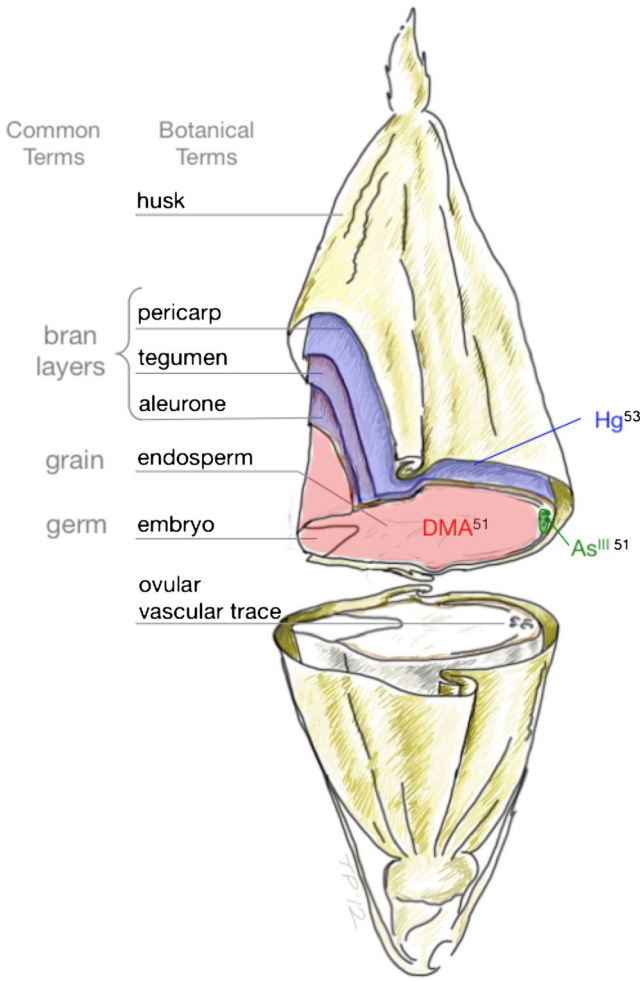

Fig. 1 Spatial location of mercury and arsenic species in rice grain as identified by synchrotron XRF

Analysis of arsenic and mercury via synchrotron is hindered by the low abundances typical for these elements in biological tissue in comparison with instrument detection limits. This has led to the use of extended count times of up to 1 minute per pixel in some studies [62], and studies that expose tissue to high concentrations of the target analyte during growth [94]. Spectral overlap is an issue when lead is present in samples for which arsenic is the target analyte, due to the proximity of the lead $L_{\alpha 1}$ emission line (10.55 keV) to the arsenic K_{α} line (10.54 keV) (assuming a minimum spectral width of 0.15 keV typical of silicon drift detectors) [99]. Hard X-ray microanalysis of mercury conducted at 15 keV, e.g. Meng et al. [100], uses the $L_{\alpha 1}$ emission line at 9.9, avoiding the $L_{\beta 1}$ at 11.8 keV that overlaps with arsenic K_{β}. The presence of an overlapping emission line can generate false-positive results or inflate count rates, and an additional method of elemental quantification, such as ICP-MS should be routinely used to validate the spatially resolved SXRF results, at least in a subsample.

Spatially-resolved speciation information for arsenic and mercury must also be determined via synchrotron-based X-ray absorption spectroscopy (XAS) [62, 93], a short-range probe of the coordination chemistry, oxidation state, and interatomic distances of the absorbing atom. The XAS spectrum has two main distinguishable regions, the near edge region (X-ray absorption near edge structure [XANES]) and the fine structure region (extended X-ray fine structure spectroscopy [EXAFS]). XANES can provide information about coordination environment and valence, whereas interatomic distance and nearest neighbor identity are determined using the EXAFS region of the spectrum. XANES was used to show that inorganic mercury is retained in the outer husk and bran layer of rice, whereas methylmercury was detected in the endosperm [62]. Although widely used, XAS is not without its technical limitations. This includes the critical influence of the initial choice of standard reference materials, from which the spectra for the unknown sample is derived using linear recombination fitting; the accuracy of XAS is enhanced when information from other techniques informs the standard choice. For arsenic in particular, beam-induced speciation changes can also occur in certain sample types when using XAS. Photoreduction of arsenic(V) to arsenic(III) has been observed during speciation analysis of arsenic in rice grains [97]. It has also been noted that the typical application of XAS – investigating the speciation of localized elemental features characterized by significantly higher abundances – has a tendency to misrepresent the prevalent speciation of that element in the sample as a whole [93, 97], which leads to recommendations that bulk XAS be used in addition to spatial resolution.

Conclusions

Sensitive analytical techniques exist for the detection and speciation of trace elements in foods. Advances in instrumental methods, such as collision and reaction cell ICP-MS, have made this technique more robust to interferences, but challenges still exist due to the complex and variable matrix of foods. In this regard, there is a clear need for more SRMs across a range of food types, analytes, and concentrations to allow for validated method development. Advanced instrumentation such as synchrotron and mass spectrometry nanoprobes are providing greater insight in the speciation and spatial distribution of trace elements in plants, while developments in hyphenated chromatographic-MS techniques continue to increase our knowledge on the extent and transformations of arsenic compounds in plants and animals.

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Compliance with Ethics Guidelines

Conflict of Interest Brian Jackson and Tracy Punshon declare that they have no conflict of interest.

Human and Animal Rights and Informed Consent This article does not contain any studies with human or animal subjects performed by any of the authors.

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