Inorganic arsenic determination in food: A review on analytical proposals and quality assessment over the last six years

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ABSTRACT

Here we review recent developments in analytical proposals for the assessment of the inorganic arsenic (iAs) content in food products. Interest in the determination of iAs in products for human consumption such as food commodities, wine and seaweed among others is fueled by the wide recognition of its toxic effects on humans, even at low concentrations. Currently, the need for robust and reliable analytical methods is recognized by various international safety and health agencies, and by organizations in charge of establishing acceptable tolerance levels of iAs in food. This review summarizes the state of the art of analytical methods while highlighting tools for the assessment of quality assessment of the results, such as the production and evaluation of certified reference materials (CRMs) and the availability of specific proficiency testing (PT) programs.

Since the number of studies dedicated to the subject of this review has increased considerably over recent years, the sources consulted and cited here are limited to those from 2010 up to the end of 2015.

Index headings: Inorganic arsenic; Food analysis; Analytical techniques; Quality assessment; Proficiency testing; Certified Reference Materials.

1. INTRODUCTION

The determination of inorganic arsenic (iAs) in food is considered a subject of paramount importance. Of the great number of known arsenic species that have been identified in different types of food, arsenic health concerns are derived primarily from the inorganic forms of this element. Moreover, food is the main contributor to human arsenic intake (excluding occupational exposure and drinking contaminated water). This interest is supported by a huge number of publications in the literature over many years [1]. The causal effect of arsenic with regards to cancer has been well studied more twenty years ago. The most recent reviews highlight new research concerning both the toxic and carcinogenic character of iAs [2–5], and many proposals have been made on the possible arsenic-induced carcinogenic molecular mechanisms [6–9]. Two reviews use the meta-analysis of toxicity data[10,11] to obtain information concerning the assessment of iAs exposure risk or the possible dose–response relationship, among other approaches. Mechanisms involved in the pathogenesis of arsenic-induced toxicity have been reviewed[12]. Among the studies of the toxicity of iAs, vulnerable groups are especially considered, such as children[13–15] and pregnant women[16].

The toxic effects of inorganic arsenic forms led the Joint Commission FAO/WHO (Food and Agriculture Organization of the United Nations/ World Health Organization) in 1989 to set a provisional tolerable weekly intake (PTWI) for inorganic arsenic of 15 μg kg^{-1} of body weight (equivalent to 2.1 μg kg^{-1} bw per day)[17]. Recently, the European Food Safety Authority (EFSA)[18] and the JECFA (Joint FAO/WHO Expert Committee on Food Additives) [19] evaluated dietary exposure to iAs. Both concluded that the PTWI parameter is no longer appropriate and should no longer be used and it is thus withdrawn. The EFSA and JECFA evaluations provided estimates of toxic intake limits for iAs as a benchmark dose level (BMDL): 0.3–8 μgkg^{-1} b.w. per day for cancers of lung, skin and bladder as well as for skin lesions (EFSA $BMDL_{01}$[18]); and 3.0 μg kg^{-1} b.w. per day (2-7 μg kg^{-1} b.w. per day based on the estimated range of total dietary exposure) for lung cancer (JECFA $BMDL_{0,5}$ [19]). Also, both reports emphasized the need to produce speciation data, particularly iAs data, for different food products to estimate the health risk associated with dietary As exposure. EFSA and JECFA highlighted the need for a robust, validated analytical method for the determination of iAs in a range of food items; and the need for certified reference materials (CRMs) for iAs. In 2014, EFSA evaluated dietary exposure to iAs in the European population [20]. It concluded that for all ages except infants and toddlers, the main contributor to dietary exposure to iAs

is the food group: “grain-based processed products (non-rice-based)”. Other food groups that were important contributors to iAs exposure were rice, milk and dairy products (the main contributor in infants and toddlers), and drinking water. Furthermore, in order to reduce the uncertainty in the assessment of exposure to iAs, more analytical data on iAs are needed. This mainly refers to speciation data in fish and seafood, and for food groups that contribute substantially to dietary exposure to iAs (e.g., rice and wheat-based products). Many of the statements in the present paragraph are summarized recently in [21]. Rice and rice-based products are the type of food in which iAs toxicity is of most concern in many countries [22–28] especially in countries, such as those in Southeast Asia, where irrigation practices increasingly include flooding with water containing arsenic [29]. This can lead to an increase of the arsenic contents of rice and so control of such practices is frequently called for [30]. The other type of food product that merits special interest regarding iAs toxicity is those with a marine origin [31–34] and in lesser extent other food commodities such as apple juice[35] or mushrooms[36]. Furthermore, the assessment of iAs concentrations in food products aimed particularly at children deserves special interest [37–40]. Other studies also reveal that knowledge of iAs content is important in the control of processes of biotransformation in marine organisms that constitute a food source, after exposure to iAs compounds [41]. Lynch et al. [42] considered four food groups, in accordance with their iAs contents, reporting estimated mean values as: *seaweed/algae/seafood*, 11,000 μg kg^{-1} for seaweed/algae and 130 μg kg^{-1} for seafood; *rice*, 130 μg kg^{-1} ; *apple juice*, 5.8 μg kg^{-1} ; and *infant food*, rice, other cereals and related products, 92 μg kg^{-1} and vegetables, 20 μg kg^{-1} .

The establishment of maximum levels (MLs) regulating iAs are emphasized in Directives and Regulations[43–51]. Meharg and Raab[52] discusses several proposals and relates them with detection capacities and the availability of measurement techniques, highlighting the assessment of iAs contents. Among the regulations proposing MLs of arsenic tolerated in food, few establish specific levels for iAs. Table I summarizes the ML for inorganic arsenic or total arsenic in food established by several countries. The maximum tolerable level of total arsenic (tAs) in drinking water defined by the World Health Organization (WHO) is 10 μg L^{-1} [60]. Very recently, the European Union published Regulation (EU) 2015/1006 [58]amending Annex to Regulation (EC) No 1881/2006 [61]regarding the maximum levels of iAs in foodstuffs, especially rice and rice-based products. The new MLs of iAs range from 0.10 to 0.3 mg As kg^{-1} depending of the rice product. Furthermore, the EU established a maximum levels for iAs in

animal feeds, contents of below 2 mg kg^{-1} are recommended, especially those based on the seaweed species *Hizikiafusiforme*[62]. The Ministry of Health of China established a maximum level of iAs in food products depending on type of food[56]. The CODEX Alimentarius Commission in a draft report on contaminants in food accepts a ML of 0.2 mg kg^{-1} of iAs for polished rice and analysis of tAs as a screening method[63]; the same document states that no agreement was reached for a ML of iAs in husked rice, but a value of 0.4 mg kg^{-1} is ongoing discussed[63,64] and may be adopted at the next session of the Committee. The Australia New Zealand Food Standard Code(FSANZ) [54] established a limit of 1 mg kg^{-1} for seaweed and mollusks; while for crustacean and fish, iAs is not allowed to exceed 2 mg kg^{-1}. Meanwhile, the authorities in the UK have advised consumers to avoid consumption of hijiki seaweed [65]while the Canadian Food Inspection Agency (CFIA) advises consumers to avoid that seaweed [66]. Specific regulations for iAs in edible seaweed have been established in some countries: 3 mg kg^{-1} (dw) as the maximum permitted level in the USA [67] and France [57]. The content of iAs in apple juices is considered a matter of concern by the U.S Food Drug and Administration (FDA) [68] and by the FSANZ [54]. The FDA recommends 10 ppb (as in drinking water) as a ML for iAs adequate to protect public health. The Canadian government, thorough Health Canada, established 0.1 ppm as the maximum tolerated limit for arsenic in fruit juices, fruit nectar and ready-to-serve beverages[69]; furthermore, this organization is currently considering establishing a specific lower tolerance of 0.01 ppm for apple juice. Several national initiatives and authorities have advised against consumption of rice drinks for infants and toddlers because it can increase the intake of iAs. The UK Food Standards Agency [70]does not recommend substitution of breast milk, infant formula, or cows' milk by rice drinks for toddlers and young children up to 4.5 years, whereas the Swedish National Food Agency[71]recommends no rice-based drinks for children younger than 6 years and, in Denmark[72], children are advised against consuming rice drinks and biscuits.

The analytical technology to be applied for the assessment of arsenic species, highlighting iAs, is continuously updated and reviewed[43,73–84]. Nearing et al. [85] reviewed additional analytical methods suitable for obtaining data to complement the information on arsenic speciation obtained when applying the methods commonly used. Among such complementary methods, electrospray mass spectrometry (ESI-MS) is most useful for identifying or complementing information on several arsenic compounds with more

complex molecular structures than those corresponding to iAs species. Some articles report the use of some supplementary methods for iAs, among them Nearing et al. [86] report X-ray absorption near edge structure (XANES) for As speciation in solid samples to obtain information on which As species cannot extracted, provided that enough mass remain after extraction, as a complementary information of HPLC-ICPMS technique, and Whaley-Martin [87] in a study on arsenic species distribution in marine periwinkle tissues samples by HPLC-ICPMS, uses X-ray Spectroscopy (XAS) for the estimation of inorganic arsenic species and to reveal their high concentrations in contaminated samples. Some other general reviews of element speciation provide broad information on arsenic speciation, including analytical methodology and types of food [77,88–92]. Moreover the importance of maintaining the integrity of arsenic species during the overall analytical process, with final measurement by HPLC-ICPMS and HPLC-HG-AFS, is emphasized widely in a recent Review [93].

Efforts have also been made in the last decades by Research scientists, government agencies (FDA and EPA), and commercial laboratories to establish methodologies for the specific determination of iAs in food products. The validation of such methods is mandatory to demonstrate their suitability for routine analysis in control laboratories. Reliable analytical methods are currently available and it can be expected that they will be considered in future Regulations from Government Agencies. For this, the European Committee for Standardization (CEN) (CEN TC 327/WG 4) standardized a method (EN 16278:2012) for the determination of iAs in animal feeding stuffs by HG-AAS after microwave extraction and off-line separation of iAs by solid phase extraction (SPE) [94]. Other two standards are published, such as: Chinese Standard Method GB/T 5009.11-2003 [95]; and EN 15517:2008 [96]. Currently, there is an ongoing proposal for CEN method to determine iAs in foodstuffs by HPLC coupled to inductively coupled plasma mass spectrometry (HPLC-ICPMS) (CEN TC275/WG10). The AOAC, through the AOAC International, invited method authors and developers to submit methods for quantitation of arsenic species in selected foods and beverages, that propose to meet the AOAC Standard Method Performance Requirements SMPR's. 2015.006 for quantitation of arsenic species in selected foods and beverages, and the preferred analytical technique for quantitation is HPLC-ICPMS, this proposal is currently in its fourth draft version [97]. Furthermore, for future implementation of analytical methods for iAs determination in food control laboratories, the availability of validated methods as well as participation in proficiency testing (PT) and the analysis of

CRMs is mandatory, according to the ISO/IEC 17025 standard [98].Obviously, this is applicable to speciation of iAs in food; considering its toxicity and the need to develop methods that can be applied in routine analysis.

The present review summarizes recent analytical proposals, including the use of CRMs and the availability of specific PT for the determination of iAs in the most widely consumed food products, covering the period 2010-end of 2015. Increasing interest in the iAs contents of food products has led to a large number of studies being published on subjects such as: the evaluation of toxicity, bioaccessibility and bioavailability studies; the estimation of dietary intake; and estimations of iAs consumed by populations in different geographical areas. Such studies and the data they generate are beyond the scope of the present review; thus they are not included in it.

1.1. Overview of the literature

Due to the vast number of scientific publications on the subject of the present Manuscript, the authors have been selected the Web of Science database, widely accepted by the scientific community, as a basis to reflect the information. This database includes 50.2 million journal articles. A preliminary search provided us with more than 18,000 papers and reviews whose titles contain the term “arsen*” between 1985 and 2014. Refining the search and including the search terms “speci*”or “compo*” or “inorg*” in the titles, led to 3301 publications (Figure 1). The distinction between “species” and “compounds” is not entirely clear and several authors use the terms as though they were synonyms; so both terms could be found interchangeably in the titles, meaning the same. From the search reported above and the data obtained, Figure 1, representing the rate of publication related to As speciation, clearly shows a significant increase, making evident the interest in arsenic speciation within the scientific community over the last fifteen years. The blue plot in Figure 1 reveals a peak in interest in arsenic species over 2011-2014, which could be related to the increased focus on iAs in food by authorities and institutions [18,19].It seems that this call could have encouraged researchers to produce more data on arsenic species in different food products and hence the number of publications has increased from 2010 to the present.

Refining the initial search and including “arsenite” or “arsenate” or “food”, or food synonyms as well as types of food (rice, seaweeds, fish, etc.), in the title led to approximately 500 which are represented by the red plot in Figure 1. A tendency can be

observed in the literature related to arsenic and dealing with several subjects such as speciation, compounds, inorganic or food; this is an increase of the publication rate over recent years (2009-2014).

Finally, the terms "speci*" and "compo*" were excluded from the last search and a more specific search was performed. Hence, we searched for papers and reviews including "arsen*" and either "inorg*", "arsenite" or "arsenate" in the title as well as including several terms in the title such as "food" or "nutrit*" and several types of food. This provided us with 250 approximately (Figure 1). The green plot in Figure 1 shows the same tendency: a rise in the numbers of publications dealing with iAs in food, surely due to the increasing emphasis on iAs in food by the authorities and institutions mentioned above.

Focusing on the period 2010-2015, 115 publications were found in the Web of Science database that deal with iAs in foodstuffs. These papers were sorted according to the research area of the publication and the Web of Science classification criteria (Figure 2a). A wide variety of fields was obtained and as can be seen, areas such as "chemistry", "environmental sciences ecology", "food science technology", and "toxicology" are the most cited in these publications related to iAs in food. From the data consulted, a detailed distribution of these publications, according to type of food analyzed, was elaborated and is represented in Figure 2b.It can be seen that more than 50% are related to "cereal-based food" and specifically "rice and rice products", which accounted to 43%. This means that research on iAs in the last five years focused on rice and its products; which is not surprisingly since rice is the main food of over half the world's population, owing to its nutritive properties and its relatively low cost. It is estimated that in many countries, rice may contribute as much as 50% of the daily intake of protein, and in Asian countries it is a staple food. Furthermore, it is estimated that the As content of rice is over 10 times greater than that found in other cereals [99,100]. As stated above, cereal-based food and especially rice and its products are among the foods that contribute most to iAs exposure in the European population. It seems quite clear that speciation research focused on cereals and rice, motivated by the recommendations of the EFSA [18] and JECFA [19] reports. The second and the third groups are "fish and shellfish" and "seaweed and algae" which represent 17% and 10%, respectively (Figure 2b). Marine foods usually have higher tAs (in the range of mg As kg^{-1}) than rice or cereals (in the range of µg As $kg^{-1)}$; however, the proportion of iAs in such food is very low compared to that in terrestrial foodstuffs. The non-toxic

arsenobetaine is the major compound in fish and shellfish; while it is the so-called "potentially toxic" arsenosugars in "seaweed and algae" [101]. Other minor groups (3%) are "vegetables and tubers", "mushrooms" and "dietary supplements".

2. ANALYTICAL METHODS AND MEASUREMENT TECHNIQUES

In analytical element speciation the best way to ensure there are no alterations of the species across the overall analytical process, including sampling, in general consists of the use of techniques capable of performing the measurements *in situ*. Nevertheless, very few techniques are selective and sensitive enough to determine individual elemental species at trace levels. In practice, analytical speciation involves two main steps: extraction and measurement. Figure 3 summarizes an overall scheme including the most important steps in element speciation, and highlights specific information for iAs determination in food products. The steps need proper optimization to guarantee minimal changes to the original species, especially in complex matrices, such as different foodstuffs. The challenge is greater when a single group of species has to be determined, as in the case of iAs, from among other arsenic species that are present in the samples. Some reviews focus on specific analytical aspects, such as sampling and sample pre-treatment[82,102–106]. From the large number of proposals for arsenic speciation within the field of food analysis, we summarize here those developed with the aim of determining iAs contents. Two groups of methods are reported here, based on either direct measurement techniques (2.1) or on the use of coupling systems between separation and detection (2.2). In both cases, preliminary steps of extraction or selective separation are also reported.

2.1 Methods involving non-coupled techniques

The vast majority of these methods are based on selective separation of arsenic species and spectroscopic detection; they are designed to determine only iAs species, the most toxic, and many of them are presented as alternatives to the use of ICPMS, which is more costly than other element detection techniques. Methods and applications based on such techniques are reported here by separately summarizing those that use direct measurement (A) and those that useHG, as a previous derivatization technique (B).

2.1.A Techniques involving direct measurement

Electrothermal atomic absorption spectrometry (ETAAS)

Electrothermal atomic absorption spectrometry (ETAAS), including its different atomization systems, is considered one of the most sensitive Atomic Absorption Spectrometric techniques, and several proposals have been made for As speciation in different matrices of interest, among them food samples. The determination of arsenic species can be considered a challenge when using ETAAS, since accurate optimization of the operational parameters, as well as the type of chemical modifiers, is required.

Lopez-Garcia et al. proposes arsenic speciation in fish-based baby foods using ETAAS[107]. According to those authors, iAs, MA (monomethylarsonate), DMA (dimethylarsinate) and AB (arsenobetaine) can be determined using sample suspensions in TMAH (tetramethyl ammonium hydroxide) and by means of several injections using three different chemically modified ETAAS atomizers: cerium (IV), palladium salts and a zirconium-coated tube. This approach is qualified by those authors as semi-quantitative due to the incomplete discrimination among arsenic species; but they claim it is suitable for food products where AB is the predominant compound, compared to methylated arsenic species. The same authors [108] applied dispersive liquid–liquid micro extraction for extracting the water-soluble arsenic species from organic phases (oils of animal or plant origin), achieving a pre-concentration and using ETAAS for final measurement; according to the authors although a reliable arsenic speciation is not achieved, the toxicity of water-soluble arsenic species: As(III), As(V) and MA present in edible oils can be assessed. Arsenic species and total iAs in rice is determined by using microwave-assisted dispersive liquid-liquid microextraction and measurement by ETAAS [109]. Dos Santos Costa et al. [110] determine arsenic species in rice by CPE (cloud point extraction) and ETAAS, using graphite tubes with different modifiers. Shah et al. [111]determines total As and iAs in samples of edible fish from the arsenic-contaminated Manchar Lake, Pakistan, and evaluated the estimated daily intake (EDI) of iAs. The method adopted allows the measurement of total As, after prior acidic digestion; whereas As(III) and As(V) are separated by two sequential steps with chloroform as the extracting agent and reducing As(V) to As(III).The corresponding extracts, as well as total As, are measured by ETAAS, using Mg $(NO_3)_2$ + Pd as a modifier. Pasias et al. [112] develops and fully validates a method to determine total As and iAs in rice. The method

is then applied to determine total As and its inorganic forms in several varieties of rice and rice flour samples from local markets in Lamia (Greece). The authors applies two selective extraction procedures: total iAs is extracted with EDTA in acidic media (1M HNO_3) whereas the determination of As(III) is performed by extraction with 1M HNO_3 and further addition of EDTA (as masking agent to prevent interferences of divalent cations) at pH 4.8, followed by addition of APDC at this pH, to form the complex with As(III), extracting it with MIBK and back extracting in HNO_3 ; Pd is chosen, among other chemical modifiers, for the ETAAS measurement of As in all extracts. Accuracy is assessed against the certified Reference Material IRMM 804 through the IMEP-107 PT (Proficiency Test).

In a study of As speciation in mono-varietal wines purchased in Mendoza (Argentina) Escudero et al.[113] determines total As and iAs in samples of Malbec and Sauvignon Blanc varieties using ionic liquid (IL) dispersive micro extraction as a pre-concentration technique, coupled with ETAAS. This system is applied to each separate fraction previously obtained of As(III), total iAs and total As. Zmozinski et al. [114] proposes direct solid sample analysis with a graphite furnace (SS-ETAAS) as a screening method for iAs determination in fish and seafood. A method for the determination of arsenate and total iAs in rice samples is proposed by Dos Santos Costa et al. [110]; after whole extraction with HNO_3, arsenate is determined by cloud point extraction (CPE) of the complex formed with molybdate and As(V) in a sulfuric acid medium; while total iAs is extracted by the same CPE method, after previous oxidation of As(III) to As(V). In both cases, the final measurement is performed by ETAAS using Ir as the modifier.

Interest in the use of nano materials as sorbents to separate and preconcentrate trace elements is currently increasing, among them and a recent review [115] summarizes some applications of these materials as sorbents for arsenic complexes, applied to arsenic species determination with final measurement by spectroscopic techniques, among them ETAAS. Hassanpoor et al. [116] describes a new sorbent based on aluminium oxide nanoparticles functionalized by a ligand, applied as preconcentration system for inorganic arsenic speciation in spiked food samples, with final measurement by GFAAS

Inductively coupled plasma mass spectrometry (ICPMS)

ICPMS has been widely used as a system for arsenic determination at very low levels and fundamental studies are frequently published.

D'Ilioet al. [117] reports and discusses the most common interferences found in As measurements, and proposals for correction. Rajakovic et al. [118] reports a study focused on estimating the limits of detection (LOD) for arsenic at trace levels, when using ICPMS. Those authors review current approaches and discuss them, supporting the conclusions with their experimental work. Bolea-Fernandez et al. [119]reports information concerning performance mechanisms, interferences and new proposals dealing with the use of such detection systems applied to arsenic determination.

Among the applications of ICPMS as a technique for iAs determination in food, differences arise in the pre-treatment of the sample and the extraction system applied. Kucuksezgin et al. [120], in a study on risk assessment based on the consumption of some edible marine organisms from Izmir Bay (eastern Aegean Sea),uses acidic digestion to determine total As; whereas separation of iAs is carried out in an alkaline medium with further oxidation of the arsenate. In both cases, final measurement of As is performed by ICPMS. Lewis et al. [121]develops a study of the stability of fish (megrim) samples over time, under different conditions, to ascertain whether some variability of arsenic species can occur. Within the study, iAs, obtained by applying the method using extraction with chloroform after acidification and further reduction, and final back-extraction, is measured by an HR-ICPMS detector with Ga as the internal standard.

2.1.B Techniques involving hydride generation (HG) as a derivatization step

The use of HG as a tool may improve selectivity and sensitivity in elemental analysis and different proposals are frequently reviewed[122–125].Such system can easily be combined with spectroscopic and ICPMS detectors. Regarding arsenic, volatile arsines generated by reduction can be transported to the detector, avoiding chemical interference, thus achieving a very low LOD. The boiling points of the volatile arsines generated by reduction of inorganic and methylated forms of arsenic are sufficiently different to allow their separation. Nevertheless, HG is not suitable for arsenic compounds which cannot generate volatile hydrides by reduction; among such compounds arsenobetaine and arsenocholine, both usually present in fish-based food products, require transformation into iAs, capable of generating arsines by reduction. Moreover, efficiency in the formation of volatile arsines strongly depends not only on the type of original arsenic compounds in the sample, but on the matrix composition. The mechanisms of arsine generation, the gas transport systems leading to the detector

and detection conditions are frequently discussed. Sodium tetrahydroborate, $NaBH_4$, in acidic media, which is probably the most commonly used reducing agent for the generation of volatile arsines, is required in substantial amounts; and some alternatives have been proposed. Several specific conditions have been proposed and reviewed.

Thus, Wu et al. [122] reviews applications of several reducing systems other than tetrahydroborate; while D'Ulivo et al. [126] discusses the mechanisms of hydrides forming from iAs and from methylated arsenic species, by using $NaBH_4$ and the formation of intermediate byproducts. Anawar[127]discussesthe advantages and disadvantages of the combined HG-ETAAS system, in a review focused on this combined technique applied to arsenic speciation. Lehmann et al. [128] proposes the determination of iAs by controlling the medium of reduction and detection by FI-HG-MF-AAS (flow injection–HG–metal furnace–atomic absorption spectrometry) as the final measurement technique. Leal et al.[129] and Chaparro et al.[130] in studies using flow systems as on-line pre-concentration systems, propose a multi-commutation flow system coupled to HG atomic fluorescence spectrometry (AFS) for the analysis of As. The method is applied to arsenic speciation and the determination of DMA and iAs using multi-syringe flow injection analysis (MSFIA) coupled to an HG-AFS system. Yang et al.[131] uses a low-temperature plasma-assisted chemical vapor generation method to avoid the use of large amounts of sodium tetrahydroborate for the generation of volatile arsines, with detection by HG-AFS. Chen et al. [132]proposes a method for selective separation of As(III) from As(V) based on adsorption on multi-wall carbon nanotubes functionalized with branched cationic polyethyleneimine (BPEI-MWNTs) and measurement by HG-AFS. Matousek et al. [133] develops a method for arsenic speciation based on selective HG-cryotrapping-ICPMS, based on cryotrapping of arsines and desorption at their boiling points. Dados et al. [134] proposes a system to trap *insitu* arsenic hydrides previously generated using a nano-sized ceria-coated silica-iron oxide and final measurement of the slurry by ICPOES.

The recent applications of HG-spectroscopic detection, focused on the determination of iAs in food samples, are briefly summarized in the next few paragraphs, grouped by techniques.

Hydride generation–atomic absorption spectrometry (HG-AAS)

Several studies propose previous sample extraction and concentration before measurement of iAs. Among them Uluzolu et al.[135] develops a method based on solid-

406 phase extraction (SPE) using *Streptococcus pyogenes* loaded on Sepabeads SP70 resin,
407 for the speciation of As(III) and As(V). The method is applied to food samples of
408 animal and plant origin. A method involving selective separation of As(III) and As(V)
409 is proposed by Tuzen et al. [136]. That method is based on the selective adsorption of
410 As(III) onto Diaion HP-2MG resin coated with *Alternaria solani*. The method is applied
411 to CRMs of plant origin. Rasmussen et al [137] develops a method to determine iAs in
412 food and feed samples of marine origin. The method involves off-line aqueous
413 extraction and separation by SPE followed by HG-AAS (silica cell) detection.
414 Optimized conditions during the extraction permit the selective separation of iAs from
415 organic arsenic species such as AB, MA and DMA; the method is validated in-house.
416 The same author[138]also develops and validates another method based on the same
417 extraction–pre-concentration system, optimized to obtain lower LOD and a higher
418 throughput of sample extraction, to determine iAs in rice and rice products. Cerveira et
419 al.[139] applies HG-AAS to measure iAs in several types of rice samples, after selective
420 extraction with HNO_3.Sun and Liu [140] develops a method for analysis of As(III) and
421 total iAs in dietary supplements by using a slurry in the presence of 8-hydroxiquinoline.
422 After generation of hydride, As(III) is determine with HG-AAS using a gas–liquid
423 separator and an electrothermal quartz atomizer. Total iAs is measured after reduction
424 of As(V) to As(III). The authors check the recovery in the determination of total iAs by
425 comparing it with the Chinese Standard Method [95] using HG-AFS for As measurement.
426 The same method was applied for speciation of iAs in wheat and rice flours [141].
427 Among the applications of methods that already exist, several studies report iAs
428 determination in food across different fields of interest. A method based on the
429 determination of total As via dry ashing mineralization and quantification by FI-HG-
430 AAS together with acidic digestion and chloroform extraction determines iAs from the
431 back extraction[142]. This method is applied in Diaz et al. [143] to determine total As and iAs
432 in several algae species, for both human consumption and production of phytocolloids,
433 harvested from different regions of the Chilean coast. Several research groups in
434 Thailand apply a similar analytical method in several studies with different objectives,
435 but all based on the assessment of total As and iAs in samples collected from different
436 regions of Thailand. Those studies include: marine fish, mollusks and crustaceans [144];
437 freshwater fish and prawns [145]; and a comparative study of total As in fresh water fish
438 sampled from natural water sources and aquaculture systems [146]. Three types of rice and
439 rice bran produced from them are also analyzed and the results compared[147].Ubonnuch

et al.[148]analyzesrhizomes of Zingiberaceae, a family of plants collected in Thailand, as a preliminary assessment of therisk of consuming natural products. Ruangwises et al. (2010) [149] and Ruangwises et al. (2011) [150] evaluate the intake of total As and iAs within populations from two contaminated areas of Thailand. Also, a study is developed to assess the risk of cancer due to exposure to iAs in Ronphibun, Thailand [151], by applying the guidelines in USEPA 2001. Mania [152] reports a method for the determination of tAs and iAs in fish products, seafood and seaweeds; iAs is determined by reduction with hydrobromic acid and hydrazine sulphate, followed by extraction with chloroform, back-extraction and ashing. Measurement of iAs in the dissolved ash is performed by HGAAS. A recent Review on recent progress on vapor-generation-atomic as pre concentration in spectrometric techniques from Gil [153] include arsenic speciation, among other elements.

Hydride generation–atomic fluorescence spectrometry (HG-AFS)

Several studies report using HG-AFS to measure total As and iAs in different food samples. In a study of the arsenic content of several commercial Spanish garlic samples, Sousa Ferreira et al. [154]proposes a method for screening of As(III) and As(V) based on extraction with H_2SO_4.In that study As is further measured in two aliquots in which the differences in the efficiency of HG with and without previous reduction is evaluated by means of two equations relating to the two oxidation states of As. G. Chen and T. Chen [155] proposes the quantification of iAs in rice via initial extraction with HNO_3 and H_2O_2 after which the resulting As(V) is selectively retained in a SPE cartridge (silica-based SAX) and iAs determined after elution and generation of arsine. The experimental conditions for acid-oxidizing extraction, absorption in an SPE cartridge and the generation of arsine are carefully optimized and discussed in depth. B.Chen et al. [156] describes a fast screening method for total As and iAs in a wide variety of rice grains of different geographic origins, with the different matrices having no significant influence on the final measurements. For total As, UV-HG-AFS is used since the oxidative photolysis ensures quantitative oxidation of all the As species to As(V).

Hydride generation–inductively coupled plasma mass spectrometry (HG-ICPMS)

Several methods are proposed to suitable screening of iAs in food samples using an oxidative acidic extraction. Musil et al.[157] reports a method based on the extraction of

iAs with HNO_3 and H_2O_2, and then on the use a selective HG coupled to ICPMS. To achieve this, HCl and $NaBH_4$ concentrations are optimized to volatilize almost exclusively arsines from the iAs, while minimizing possible volatile compounds generated from other organoarsenic compounds present in the samples. The method is applied to rice and seafood samples. The same method is further applied by Pétursdóttiret al. [158] for the analysis of a wide number of rice samples. Moreover, both methods are compared with the more widely used one involving HPLC-ICPMS for measurement and the results are shown to be comparable.

2.2 Methods using coupled techniques

Many proposals have been made for arsenic speciation by combining techniques that provide efficient separation of the species with suitable detection and quantification. These coupled techniques provide a high degree of automation, good reproducibility and offer application in different fields. Among them, here we mention some reviews that are specifically dedicated to arsenic speciation with coupled techniques [73,78,79,83,105,159]. In addition, some more general reviews of analytical techniques include arsenic speciation. Some of them describe food samples or summarize such aspects as pre-treatment, extraction and preservation of the arsenic species, pre-concentration, how to overcome matrix interference and specific instrumental conditions (such as types of nebulizers, the use of a dynamic reaction cell and internal standards) [76,77,82,88,90,91,160–162]. Some studies treat and discuss a specific subject in depth, as in the work of Pétursdóttiret al. [163] concerning the influence of the extraction step on the analysis of iAs in seafood, with measurement by coupled techniques. Next we summarize studies of applications of coupled techniques for iAs determination in several types of food, according to the separation technique.

2.2.A Coupled techniques that use HPLC as the separation technique

Most information corresponds to coupling techniques that use HPLC to separate As species. We consider applications based on HPLC-AAS, HPLC-HG-AFS and HPLC-ICPMS. No applications have been found of HPLC-ICPAES. Based on these coupling options, most studies use HPLC-ICPMS. Nevertheless, we also include studies using HPLC and detection systems other than ICPMS and that report iAs contents,

along with some other species, to highlight interest in its toxicity. The vast majority of studies based on HPLC use strong anion exchange columns (SAX) and $NH_4H_2PO_4$, NH_4NO_3 or $NaHCO_3$ as the mobile phase. Thus, in the following information, the type of chromatographic system is only reported in studies that use a system other than these.

The coupled technique HPLC-MS or HPLC-MS/MS, proposed for arsenic speciation in samples containing more complex compounds than those considered as iAs, has been applied to obtain molecular structure information on arsenic compounds of interest, although in general with no proved toxic effects, and has been shown not to be suitable for small molecules such as arsenate, arsenite and their methylated compounds.

HPLC–atomic absorption spectrometry (HPLC-AAS)

Since very few applications of this technique were found, each is mentioned here. Tian et al. [164]develops a gas–liquid separator for gradient arsenic HG, interfaced between HPLC coupled to the AAS detector, using a reversed-phase column and using sodium 1-butanesulfonate, malonic acid, tetramethylammonium hydroxide, MeOH and ammonium tartrate as the mobile phase. After optimizing the transport of the hydrides to the detector, the method is applied to the determination of arsenic species in hijiki algae. Niedzielski et al. [165] aims to determine iAs and DMA in species of mushrooms collected from forests in Poland with different degrees of contamination, as well as some that are commercially available. The extraction of arsenic species is performed with phosphoric acid with Triton X100 and the species are measured by HPLC-HG-AAS with a quartz atomizer and Ar as the carrier gas. HPLC-HG-AAS is used by Mleczek et al.[166] for inorganic arsenic determination in edible mushrooms and cultivation substrates. Bergés-Tiznado et al. [167] analyzes cultured oyster samples from the SE Gulf of California in Mexico; although a non-coupled technique is used, since the corresponding fractions are collected from two HPLC columns (anionic and cationic) are finally measured by ETAAS. Only two samples are reported to have very low contents of iAs.

HPLC–Hydride generation–atomic fluorescence spectrometry (HPLC-HG-AFS)

A review by Y-W Chen et al.[168] describes relevant chemical and instrumental aspects, as well as applications, of this coupled technique for the speciation of some elements; among them arsenic. For this element, the literature on speciation in some

food materials is included, among a wide number of matrices. Extraction systems as well as the stability of the chemical species throughout the overall chemical process are also included. Jesus et al. [169] proposes a method for arsenic speciation by adding sequential injection analysis: SIA-HPLC-AFS. In such a system, while the chromatographic detection operates in the usual way, the SIA module is programmed to inject sequentially the standard additions of the arsenic species. The method is applied to the analysis of seafood extracts to quantify the most toxic species: As(III),As(V), MA and DMA. Garcia-Salgado et al. [170] applies HPLC-HG-AFS using both anionic and cationic columns, which includes a photo oxidation step, resulting in HPLC-(UV)-HG-AFS, to carry out arsenic speciation in edible algae extracts. The same authors in Garcia-Salgado et al. [171]use the same technique in a study of the stability of toxic arsenic species and arsenosugars in hijiki alga samples under several storage conditions. They highlight the predominance of As(V)in such food. Cano-Lamadrid et al. [172] applies HPLC-HG-AFS to determine iAs, together with MA and DMA, in rice samples collected from different provinces of Iran. Extraction of the arsenic species is carried out using TFA and the iAs levels are found to be below the maximum FAO residue limit of 200 $\mu g kg^{-1}$ for rice [63].

HPLC–inductively coupled plasma optical emission spectrometry (HPLC-ICPAES)

In a study of interference to the determination of iAs in seaweed by ion chromatography (IC)-ICPAES, Cui et al. [173] assays two extractants: HNO_3 and MeOH. That study concludes that suitable performance was not obtained with either system and the authors propose an alternative method for the determination of total iAs from seaweed. They add concentrated HCl and after separation, HBr and hydrazine sulfate are added to reduce As(V) to As(III); extraction of iAs with chloroform is finally carried out and measured by ICPAES.

HPLC–inductively coupled plasma mass spectrometry (HPLC-ICPMS)

As mentioned above, this technique has been the most commonly used over the last decade to determine arsenic species in several matrices. Here we summarize studies whose aim is the specific determination of iAs in food products. Furthermore, some studies to determine other arsenic species but that highlight the importance of obtaining information on iAs contents are also considered, reporting the suitability of this technique for arsenic speciation.

Thus, Prinkler et al. [174]compares different methods of signal treatment to improve the LOD of the different species, as an attempt to decrease the noise signal. The study obtained different signal-to-noise ratios according to the convolution of the signal treatment systems with Gaussian distribution curves, for the noise reduction via Fourier transform or wavelet transform. The study concludes that the last method was the most appropriate. Ammann[175]used a narrow-bore chromatographic system with low flow rates to optimize the efficiency of the nebulizers when using high resolving sector-field ICPMS as the detection system. Chromatographic performance for arsenic species separation and interference with the detection are discussed. Amaral et al [176] uses ICP-QMS in the coupled system and proposes the use of $^{83}Kr^{+}$ instead of Ar for the interference standard method (ISM) to overcome the most common sources of interference that occur in Ar plasma. The system improved both the accuracy and sensitivity of arsenic species determination. Some reviews and studies report sample preparation and extraction methods for arsenic speciation in food as a preliminary step before measurement [103]. Grotti et al.[177]discusse the influences of the arsenic species on the ICPMS signal when working at a low liquid flow rate (μHPLC-ICPMS). In general, different ICPMS responses are originated by differences in the volatility of the elemental species, as discussed by several authors. After assaying and comparing different nebulizers/spray chamber systems, this study supports this assumption and recommends species-specific calibration for the quantification of arsenic species. Jackson et al. [178] proposes a general approach for arsenic speciation by modifying the existing method and using carbonate eluents for a small particle size, short Hamilton PRP-X100 column which is interfaced with an ICPMS triple quadrupole, Agilent 8800 ICP-QQQ, using oxygen as the reaction gas and detection of AsO at m/z 91.

Among the types of food to which HPLC-ICPMS is applied for the determination of toxic iAs compounds, rice and rice-based products, and to a lesser extent other cereals, are the focus of increasing interest; as reported in studies this decade. Among the applications, the optimization of extraction systems to obtain selective extraction of iAs is one of the main objectives, but when applying a separation–detection coupled system, information on methylated arsenic species in those types of samples is also obtained and reported. Thus, the studies using this technique report results for iAs as well as DMA and MA, and they differ mainly in the extraction systems for arsenic species. The variety of extraction systems and measurement conditions are summarized next, according to the target food type.

610

611 *Rice and rice products*

612 Huang et al. [179] studies several extraction systems that ensure suitable extraction
613 of iAs compounds while preserving any possible transformation between As(III) and
614 As(V) during the process, and finally proposes extraction with 0.28 mol L^{-1} HNO_3 at
615 95ºC for 90 min. The method was applied to several types of rice samples. Narukawa
616 and Chiba [180] develops heat-assisted extraction with water for arsenic speciation in rice
617 flour at 90ºC for 3h. The authors discuss optimization of the extraction parameters in
618 depth, as well as the influence of sample particle size on the extraction conditions, by
619 considering information obtained from SEM (scanning electron microscopy) analysis of
620 the surface of samples. For separation of arsenic species, a C18ODS L-column was used
621 with sodium 1-butanesulfonate/malonic acid/tetramethylammonium hydroxide/MeOH
622 as the mobile phase. Nishimura et al. [181]develops a partial digestion method using 0.15
623 mol L^{-1} HNO_3. After assaying 80ºC and 100ºC, the latter temperature was adopted for
624 extraction, for 2 h, of iAs, MA and DMA from several varieties of rice from Japan. Paik
625 et al. [182] proposes and validates a method based on ultrasonic extraction with
626 MeOH:water (1:1) containing 1% HNO_3 in a study of arsenic speciation in eleven
627 polished rice samples cultivated near areas of South Korea polluted by mining and for
628 iAs finds a mean value of 25.5 μg kg^{-1} .Huang et al.[183] validates the method established
629 before for iAs determination [179] by applying it to rice CRMs and through participation
630 in the PT IMEP-107 [46,184], dedicated to the determination of iAs in rice. The validated
631 method is applied to twelve types of rice samples of different origins. The
632 concentrations of As(III) and As(V) increased with increasing total grain As
633 concentration, and As(III) was predominant in almost all the samples analyzed,
634 independent of the rice origin. Narukawa et al.[185] proposes specific monitoring test for
635 iAs in rice, based on a previously developed and validated method, using water as the
636 iAs extractant[180].The method is applied to 20 white rice flour samples. For separation, a
637 C18 column with sodium 1-butanesulfonate/malonic acid/tetramethylammonium
638 hydroxide/MeOH as the mobile phase was used and arsenobetaine was used as the
639 internal standard. Different percentages of iAs, with respect to total As, were found,
640 depending on the geographical origin of the samples. In a further publication [186] the
641 same research group develop a similar method after the study of several eluents and
642 elution conditions and adopting for separation a C18 column with sodium 1-
643 butanesulfonate/malonic acid/tetramethylammonium hydroxide/MeOH as the mobile

644 phase with the addition of an additional buffer containing $NH_4H_2PO_4$ and 0.05%
645 acetonitrile, with final pH 2.7. Under such conditions an improvement of the sensitivity
646 for As(III) and As(V), with respect to the previous method, is achieved. The method is
647 applied to the determination of As(III), As(V), MA, DMA and AB in three rice-based
648 CRMs. Llorente-Mirandes et al. [40] optimizes and validates a method for the
649 determination of arsenic species in rice. The arsenic species were extracted with a
650 mixture of 0.2% HNO_3 and 1% H_2O_2 in a microwave (MW) system, to completely
651 oxidize As(III) to As(V). Full validation is performed and the relative expanded
652 uncertainty is estimated, based on the top-down method. The validated method is
653 applied to the determination of arsenic species in 20 samples of rice and rice products.
654 Sommella et al. [187]determines total As and iAs in several Italian rice samples. Extraction
655 is performed with 1% HNO_3 and further addition of H_2O_2, while separation is by anion
656 exchange column and quadrople ICPMS is used for detection. The iAs contents varied
657 with the region of Italy the samples came from. Maher et al. [188] extracts arsenic species
658 using 2% HNO_3 before measurement by the coupled technique. Both cation and anion
659 exchange columns are used for separation. The analysis is also carried out by XANES
660 (X-ray absorption near edge structure) and the results of both measurement techniques
661 compared, showing general agreement.. The method is applied to rice samples from
662 different countries. Kim et al.[189] uses 1% HNO_3 at 80ºC for 30 min for the extraction of
663 arsenic species from 30 samples of rice grain collected from regions in South Korea
664 known to contain arsenic, as well as 34 polished rice samples from the USA. The
665 As(III) concentration in the American rice samples was slightly lower than that in the
666 samples collected in Korea. Baba et al.[190] performs iAs, MA and DMA analysis by
667 extracting them with 0.15 mol L^{-1} HNO_3 for 120 min at 100ºC. The authors summarize
668 the chromatographic separation modes used for arsenic speciation; among them anion
669 exchange columns are the most widely used although several other chromatographic
670 systems are mentioned and discussed. They adopt the use of PFP (pentafluorophenyl)
671 columns, after assaying and comparing some systems. The best results were obtained
672 with a Discovery HS F5 column in isocratic mode and, after optimization of the elution
673 conditions, 0.1% HCOOH and 1% MeOH, the latter as an organic modifier to enhance
674 the signal. AB is used as the internal standard. The method is applied to several samples
675 of rice purchased from markets in Japan. Narukawa et al. [191] assays various extraction
676 systems for arsenic speciation in rice flour and the efficiencies are discussed in depth.
677 Moreover, prevention of possible changes in the arsenic species during the processes, as

well as the effects of the most common sources of interference on the separation and on the detection are also reported and discussed. A proposal for both As(III) and As(V) extraction from rice flour is based on 0.15 mol L^{-1} HNO_3 containing Ag in a heat block, and if only iAs is required, the proposal is based on extraction with 0.5 mol L^{-1} HNO_3 and H_2O_2 in a heat block. For separation, a C_{18} column with sodium 1-butanesulfonate/malonic acid/tetramethylammonium hydroxide/MeOH as the mobile phase is used. Sinha [29] uses LC-ICPMS, after extraction of arsenic species with 2 mol L^{-1} TFA (trifluoroacetic acid) in a study to evaluate and compare contents of iAs in rice samples grown in a contaminated area and the relationship with the arsenic content in the irrigation waters.

Cereal-based food

As a part of a study of the distribution and speciation of arsenic in wheat grain from field-grown crops from European countries, Zhao et al.[192] determine iAs species in whole meal and white wheat flour samples. The extraction of the species is performed with HNO_3 and H_2O_2 under MW. Tsai and Jiang [193] proposes an extraction system based on that established by Mar et al.[194] (which uses MW-assisted enzymatic digestion with Protease XIV and amylase) optimizing the conditions by extending the digestion time with respect to the proposed by Mar et al. [194], and applies it to the analysis of cereals. The final measurement is performed by IC-DRC-ICPMS (IC–dynamic reaction cell–ICPMS). D'Amato et al. [195] focuses on the sample treatment to obtain a good yield of arsenic species without degradation. After assaying different methods, MW extraction with HNO_3 was the most effective. The conditions are detailed in depth, including lyophilization and elimination of the residual humidity, and the method is applied to wheat and wheat products. Llorente-Mirandes et al.[39] performs a fully validated method, based on [40], for the determination of arsenic species in a large number and variety of samples of cereal-based food products and infant cereals. The method is used by the Laboratory of the Public Health Agency of Barcelona under accreditation by ENAC/Spanish National Accreditation Entity, according the ISO/IEC 17025 standard, for its application in cereal-based food products.

Infant food

The method of Llorente-Mirandes et al. [39] mentioned above was applied to the determination of arsenic species in 9 samples of infant cereal products. Brockman and

712 Brown IV [196] proposes an initial extraction with water at 98ºC for 3 h and later addition
713 of hydrogen peroxide to the aqueous filtrate obtained. The resulting arsenate, MA and
714 DMA from infant rice cereals are analyzed by this coupled technique. The authors
715 conclude that iAs was found in all of the infant rice products in a large range between
716 33% and 77% of total As. Jackson et al. [37], in a broad study of iAs content in infant
717 formulas and first foods, used an extraction with 1% HNO_3 following a progressive
718 heating program with MW from 55ºC to 95ºC. For measurement, two chromatographic
719 systems were used: both based on two anionic exchange columns, and with either
720 phosphate at pH 6 as the mobile phase or with tetramethyl ammonium hydroxide. The
721 samples, purchased from supermarkets, included 15 infant formulas, 41 fruit purees, and
722 18 second- and third-stage foods. As concentrations< 23 ng/g were found. Juskelis et al.
723 [197], in a study for a survey of arsenic in rice cereals for infants, applied an extraction
724 method for iAs, MA and DMA based on the use of 0.28 M HNO_3 at 95ºC for 90 min in
725 a block digestion system. A total of 31 different samples of organic wholegrain rice,
726 mixed-grain flour, organic rice and rice flour were analyzed and the results showed that
727 the iAs levels varied among all the samples studied: values in the range of μg iAs per
728 serving, for all the samples are reported (considering 15 g per serving, according to the
729 reference amount customarily consumed (RACC) per 21 CFR 101.12). Recently
730 Signes-Pastor [38] in a study on rice-base products for children, uses IC-Q-ICPMS after
731 extraction with HNO_3 1% under MW, for the determination of iAs in a large number of
732 samples from the UK shops and supermarkets.
733
734 *Other types of food*
735 The coupled technique HPLC-ICPMS has also been applied for arsenic
736 speciation in types of food other than rice and cereals. In many cases, as for example in
737 several types of food of marine origin, the number of arsenic species could be high.
738 However, as mentioned above, in such samples there are drawbacks caused by the
739 presence of polyatomic sources of interference arising from chloride .Several correction
740 systems have been proposed such as high-resolution MS and quadrupole-based
741 instruments with a reaction cell or collision cell [160]; or the use of the interference
742 standard method (IFS)[176]. In complex food matrices, the selective extraction of iAs is
743 more difficult than it is from rice and cereal samples. When analyzing complex
744 matrices, a shift in the retention time of the iAs species (As(III) and As(V)) may be
745 observed, and consequently co-elution with organic arsenic species (arsenobetaine,

arsenosugars and others) may occur. Moreover, not all extractant reagents (MeOH/water, dilute HCl, HNO_3, TFA, NaOH, etc.) quantitatively extract iAs from the matrix. As a consequence, the analytical proposals reported in the literature are scarcer and here we summarize those applications in which the main goal is the selective determination of iAs.

Dufailly et al.[198] validates a method using IC-ICPMS for measurement, after ultrasound-assisted enzymatic extraction (UAEE) with protease XIV and α-amilase. The method is validated for a variety of food samples including rice, infant food and fish. Mao et al. [199]develops highly polar stir bar sorptive extraction (SBSE) for arsenic species, coated with TiO_2-PPHF (polypropylene hollow fiber), coupled to HPLC-ICPMS. A C_{18}chromatographic column with MeOH/water, and sodium butane sulfonate/malonic acid is used as the mobile phase. The method is applied to determine arsenic species, including iAs, in chicken samples. Raber et al.[200] proposes an extraction method based on 0.02 mol L^{-1} trifluoroacetic acid with 30% H_2O_2 under sonication. In a second step, 95ºC of heat is applied for 60 min in an Ultraclave MW system. The method is applied to rice, wheat and tuna fish samples. Julshamn et al.[201] applies an extraction method for iAs based on 0.07 mol L^{-1} HCl and 3% H_2O_2 at 90ºC for 20 min. The method is applied to determine iAs in 25 fish samples from Norwegian seas. Pétursdóttiret al. [202], in a study to establish a method to determine iAs in seafood, assayed three extraction methods based on 0.07 mol L^{-1} HCl in 3% H_2O_2; 2% HNO_3 or NaOH in 50% EtOH. The results are discussed; pointing out that some of them could influence the performance of the separation. HG was introduced for measurement in the coupled technique, resulting in HPLC-HG-ICPMS. This additional step, which uses $NaBH_4$ in an HCl medium as a reducing agent, enhances the sensitivity, since the volatile hydrides generated enter quantitatively into the plasma in a measurable fashion, and in this study LOD improved 10- to 100-fold, with respect to conventional nebulization systems. Narukawa et al. [203] studies extraction methods for As(III) and As(V) from several edible algae, including 15 samples of *Hizikia fusiforme*. They assay MeOH, HNO_3, THAH, pepsin and α-amylase, under three extraction conditions: ultrasonic, heat-assisted and MW-assisted, and conclude that extraction with water under ultrasonic conditions is the most useful for monitoring iAs in hijiki and the other algae studied. For separation, a C_{18} chromatographic column is used, with sodium 1-butanesulfonate/malonic acid/tetramethylammonium hydroxide/MeOH as the mobile phase. Contreras-Acuña [204] from a study of ultrasonic and microwave-based extraction

methods, the authors chose the last option for the extraction of arsenic species, among the inorganic forms, from anemones samples by final measurement by both HPLC-ICPMS and HPLC-MS techniques. Khan [205] validate a method for the determination of As(III), As(V), AB, AC, DMA and MA in a wide number of samples from five seaweed species after extraction with MeOH in 1% HNO_3 under sonication and measurement by LC-ICPMS. In a study about the contents of arsenic and arsenic species in Belgian food [206] species of marine and freshwaters fish are analyzed; water under MW assisted extraction followed by HPLC-ICPMS is used for arsenic speciation analysis; in the discussion about the extraction of arsenic species the authors stated that the method used is sufficiently suitable for the purpose of their study. Numerous studies have been reported on arsenic speciation in marine fish if compared with those on freshwater fish. To take some example Ciardullo et al. [207], in a study on several fish species collected from the Tiber river reports extraction of arsenic species with methanol:water (1:1) and measurement with HPLC-ICPMS. The study emphasizes on the optimization of the conditions to achieve the best recovery in the extraction efficiency.

In a study of the iAs content of dietary supplements, considering that no maximum levels for As are included in the recent EU regulations, Hedegaard [208] studies 16 different dietary supplements based on herbs, other botanicals and algae collected from stores in Denmark, with origins in China (9), Taiwan (1), Denmark (5) and the USA(1). Extraction with 0.006 mol $L^{-1}$and 3% H_2O_2 at 90ºC for 20 min is applied. For measurement, a polymer strong anion exchange column with 3% ammonium carbonate adjusted to pH 10.3 is used. To estimate the exposure, the corresponding daily dose is considered for each supplement. In work on the shiitake species *Lentinula edodes* [36], several types of edible shiitake mushrooms are extracted with 0.02% HNO_3 and 1% H_2O_2 in a MW system; the results show that iAs is the predominant As species. Piras et al. [209] determines tAs and iAs in samples of several marine organisms collected from the Boi Cerbus Lagoon in Sardinia (Italy): an important fishing area. The iAs is determined using HPLC-ICPMS after extraction with HCl0.07mol $L^{-1}$and 3% H_2O_2.

Some studies determine iAs in fruit juices, following the recommendations of the FDA[35].Wang et al.[210] proposes iron-pairing chromatography with a ODS column and malonic acid/TBA/MeOH as the mobile phase, to determine iAs, MA and DMA in fruit juice samples, and fruit-based beverages: iAs is the major arsenic compound found.

Liu et al. [211] in a contribution on the arsenic species determination in chicken meat treated and not treated with roxarsone, establishes and validates method based in enzyme-assisted extraction of the arsenic species: As(III), As(V), AB, DMA, MA, 3-nitro-4hydroxyphenylarsinic acid (Roxarsone) and N-acetyl-4-hydroxy-m-arsanilic acid (NAHAA). After assaying some proteolytic enzymes and extraction systems, the method using papain with ultrasonication is adopted due to the highest extraction efficiency. For final measurement two techniques: LC-ICPMS and LC-ESIMS are used, by splitting the eluent of the chromatographic column to the ICPMS and ESIMS detectors simultaneously.

As a summary of results for iAs by HPLC-ICPMS in various types of food**,** several chromatograms are shown in Figure 4 (a-f): a) rice, b) infant multicereals, c) hijiki seaweed (*Sargassum fusiforme*), d) mushroom supplement (*Grifola frondosa,* commercially known as Maitake) e) tuna fish, and f) mussel. The chromatograms are unpublished results of research by our working group.

2.2.B Coupled techniques that use capillary electrophoresis (EC) as the separation technique

Capillary electrophoresis (CE) has been proposed as a coupled technique for element speciation, but fewer contributions are reported than for than HPLC. Previous problems associated with the interface with the different detection systems have recently been overcome[212]. Very few contributions have been found that deal with arsenic speciation in general over the last five years [213,214]. We now summarize those reports with applications to arsenic speciation in food samples; some of them include iAs results, although with no specific determination of iAs species.

Hsieh et al. [215] couples CE with dynamic reaction cell ICPMS as the detector for arsenic speciation, with application to the CRM NRCC DOLT-3, in which the iAs value found was lower than the LOD, and to dietary supplements. Niegel et al. [216] develops a method based on CE-ESI-TOF-MS (CE coupled to electrospray ionization time-of-flight mass spectrometry) for arsenic speciation, with application to the analysis of some algae extracts; although no results for iAs compounds are obtained. Liu et al. [217] proposes a novel interface (the commercial CE-ESI-MS sprayer kit) for CE-ICPMS and applies it to arsenic speciation in the CRMs TORT-2 and DORM-3, as well as to herbal plants and chicken meat, the results from which include iAs compounds. More recently, Qu et al. [218] develops a method for arsenic speciation in rice and cereals. It is based on

the extraction of arsenic compounds by means of direct enzyme-assisted MW digestion, to reduce matrix effects in the final measurement by CE-ICPMS. The method is validated by applying it to the rice CRMs: NIST SRM 1568b and NMIJ CRM 7503-a.

2.3 Other analytical techniques

Some analytical techniques, other than those reported before have been reported for inorganic arsenic speciation, although few of them report applications to food samples. Here we summarize briefly few of them based on several analytical principles.

Among spectrophotometric analytical techniques Gürkan et al. [219] describes a method to determine iAs by means of a CPE (cloud point extraction) procedure based on the formation of a complex with neutral red as the ion-pair reagent and using UV-vis detection (CPE-UV-Vis). The method allows the determination of As(III), total As and As(V), and is applied to alcoholic and non-alcoholic beverage samples. The same authors [220] propose Acridine Orange, AOH^+ using Triton X-114 with tartaric acid pH 5.0 as a new ion pairing complex formation of As(V), for applying it to the method above described, which is applied to determine iAs in beverage and rice samples.

Some electrochemical techniques have been developed for the measurement of iAs. Liu and Huang [221] reviews recent contributions of voltammetric methods for the determination of iAs. That review considers types of electrode systems, including electrodes based on nanomaterials, and highlights the increased demand by researchers for sensors to measure *in situ*. The vast majority of applications of such systems have been applied to the analysis of iAs in water and waste water, or in some plant samples [222] and no applications to the measurement of iAs in food samples have been found. A new arsenate selective electrode have been recently developed by Somer et al. [223], prepared from solid salts: Ag_3AsO_4, Ag_2S, Cu_2S; the responses of some interfering anions are studied, and it is applied to the determination of arsenate in beer.

Several biosensors for the detection iAs have been developed. They involve the coupling of a biologically engineered system with a sensitive analytical technique; they can be based on fluorescence [224], luminescence, electrochemical [225] or other analytical response [226]. Different developments in this field are reviewed by [227,228]. A novel technique using Total-Reflection X-Ray Fluorescence Spectrometry (TXRF) have been proposed for the measurement of arsenic species, by combining a pre-concentration system based on dispersive microsolid phase extraction (DMSPE), by using a new synthesized novel adsorbent [229]. The literature warns that the application of these

techniques to complex matrices, such as environmental or food samples, is still a challenge.

In the preceding paragraphs the proposals for the determination of iAs in food were described, all of them based on instrumental analytical techniques, and therefore laboratory based. Anyway some proposal, as that recently reported by Bralatei et al. [230], based on the well-known Gutzeit method, is proposed as screening method for iAs in rice assuring quantification limits of about 50 μg kg^{-1}.

3. ASSESSMENTOF QUALITY CONTROL

Noticeable efforts have been made in recent years to develop strategies to support the quality of results in speciation analysis. The preparation of suitable CRMs of different types of food and the organization of PT form the basis of these efforts; the use and application of both are mandatory in food control laboratories, as regulated by ISO/IEC Standard 17025 [98]. A comprehensive scheme of QA in analytical chemistry laboratories would include the following elements: validation of analytical methods; use of CRMs; routine application of internal QC; and participation in PT[231].Method validation is an essential component of the measures that a laboratory should implement to allow it to produce reliable analytical data and demonstrate whether the method is fit for a particular analytical purpose. Typical performance characteristics of analytical methods are: applicability, selectivity, calibration, trueness, accuracy, precision, recovery, operating range, LOD and limits of quantification (LOQ), sensitivity, uncertainty, ruggedness and fitness-for-purpose [232].

The following subsections specifically focus on the evaluation of the accuracy of the method by means of use of certified reference materials (CRMs) (3.1), and on participation in PT (3.2) as external QC of method validation. Besides, section 3.1 is subdivided and the text focuses on: CRMs available foriAs (3.1.1);other CRMs available with a certified total arsenic value (3.1.2); other strategies to evaluate accuracy (3.1.3).

3.1. Use of certified reference materials (CRMs)

912 CRMs are useful to evaluate the accuracy of the analytical method; both for
913 validation and QC purposes. In any case the differences of matrix composition between
914 the sample and the CRM have to be carefully evaluated, since such differences may
915 prevent reach satisfactory results. Sample treatment (digestion, extraction, etc.),
916 separation and measurement processes are all subject to errors such as contamination,
917 degradation, matrix effects, instability and interconversion of arsenic species, and
918 calibration errors. Recovery, mass balance and QA/QC of the analytical method should
919 be determined in all the steps of the procedure (Figure 3). CRMs are traceable to
920 international standards with a known uncertainty and therefore can be used to address
921 all aspects of bias, assuming that there is no matrix mismatch. CRMs should be of
922 similar composition of real samples and have concentration levels similar to those of the
923 samples analyzed[232]. CRMs are provided by various organizations, such as: the Institute
924 for Reference Materials and Measurements (IRMM), the National Institute for
925 Environmental Studies (NIES), the National Institute of Standards and Technology
926 (NIST), the National Metrology Institute of Japan (NMIJ), the National Research
927 Council of Canada (NRC-CNRC), the Chinese Academy of Geological Sciences
928 (CAGS), the China National Analysis Center for Iron and Steel (CNCIS), the Korea
929 Research Institute of Standards and Science (KRISS) and the Antarctic Environmental
930 Specimen Bank (BCAA) all produce CRMs for different matrices.

931 The first food CRMs were certified for tAs content and were produced several
932 decades ago. Later, since the toxicological effects of arsenic species differ markedly
933 between them, some analytical methods were developed to quantify the mass fraction of
934 the species in various matrices. The start was made with environmentally and food
935 matrices of relevant species. Feasibility studies of some arsenic species (e.g. AB and
936 DMA) were performed in the 1990s and 2000s. In the last years, efforts on the
937 production of CRMs with inorganic arsenic value in food, especially rice, are
938 performed. Although considerable progress has been made regarding the establishment
939 of specific and sensitive analytical methodology for arsenic species, few CRMs are
940 available with certified values for arsenic species in food samples.

941 As far as the authors know, few CRMs are available with certified values for
942 some arsenic species (AB and/or DMA). Among them the CRM BCR-627 Tuna Fish
943 was one of the first materials certified for As species and it was produced by IRMM in
944 1999[233]. The material was certified for tAs, DMA and AB values. Years after

945 certification, the material is still available from the IRMM website[234], which means that
946 AB and DMA species are stable over time and no transformation or degradation is
947 produced[235]. More recently, three other marine food materials have been produced,
948 extending the availability of suitable fish and shellfish CRMs with certified AB value:
949 TORT-3 Lobster Hepatopancreas (NRC-CNRC), CRM 7402-a Cod Fish Tissue and
950 CRM 7403-a Swordfish Tissue(both from NMIJ).

951

952 ***3.1.1 CRMs available for inorganic arsenic***

953 The commercially available food matrix CRMs with a certified iAsvalue are
954 summarized in this section. Although some advances have been made in specific
955 analytical methods for iAs determination in recent years, very few CRMs have been
956 developed. Only rice and seaweed CRMs are available with a certified value for the iAs
957 content. Five CRMs for iAs have been produced since 2009 by different institutions
958 including NMIJ, NIST and IRMM. Four of them are rice matrices: NIST SRM 1568b,
959 ERM-BC211, NMIJ CRM 7503a and NMIJ CRM 7532a, which are also certified for
960 tAs and DMA. The other is hijiki seaweed (NMIJ CRM 7405a) which is also certified
961 for tAs, and other arsenic species have been reported[236]. Inorganic arsenic results
962 available from the literature for these CRMs in the period 2010-2015 are shown in
963 Table II. The type of food, supplier, certified values, tAs reported, method and
964 measurement technique for iAs determination are also shown. Based on the information
965 provided in Table II, the need to produce more CRMs with a certified iAs value in
966 different food matrices can be appreciated. Some aspects should be considered to select
967 and analyze a representative CRM: the origin and type of the matrix, the type of As
968 species and the level of concentration.

969 Some thermal process is generally applied before the pre-treatment of the
970 CRMs. For example, SRM 1568b was dried for 24 h at 101°C while NMIJ 7532a was
971 dried at 60°C for 8 h; in contrast, BC-211 was stored at -20°C before being processed.
972 All the rice CRMs were milled and sieved or pulverized and mixed to ensure
973 homogeneity. The hijiki CRM was washed, freeze-dried, freeze-pulverized, sieved and
974 mixed for homogenization. For all of the CRMs, a sterilization step was applied by γ-
975 irradiating the material at a range of doses in order to eliminate active bacteria as a
976 potential source of instability for arsenic species. The producers of CRMs usually

977 recommend storing the materials shielded from sunlight or UV-radiation, in a clean
978 place at room temperature or below. Only in the case of BC211 is it specified that the
979 material should be stored at -20^{0}C ± 5^{0}C, in the dark.

980 Different approaches have been adopted by the producers to express the iAs
981 mass fraction or concentration in the CRMs: three of the rice CRM (NIST 1568b, ERM-
982 BC211 and NMIJ 7532a) are certified with iAs values (the sum of As(III) + As(V)); the
983 other one is certified for As(III) and As(V) separately (NMIJ 7503a); and the seaweed
984 (NMIJ 7405a) as arsenate. The inorganic species present in these CRMs are of natural
985 origin, according to the certification reports, no spiking experiments were performed.
986 The iAs level in the four rice CRMs ranged from 0.084 to 0.298 mg As kg^{-1} ; the typical
987 range for rice samples[244]. Typically, the iAs content in the brown rice CRM is higher
988 than in the white rice CRMs, as commonly reported[245–247].

989 The first CRM released with a certified iAs value was CRM 7503-a rice and it
990 was produced by NMIJ. The certificate is dated August 2009 and it is the most analyzed
991 CRM. Several authors use it to assess the accuracy of iAs methods
992 [39,40,180,183,190,191,218,237–242]. The mean value for iAs content of the values reported in
993 Table II is 0.0823 ± 0.0037mg As kg^{-1} (mean value ± standard deviation, n=16reported
994 results) which is in perfect agreement with the certified value of iAs: 0.0841 ±
995 0.0030mg As kg^{-1} (the sum of the certified As(III) and As(V) values ± the square root of
996 the sum of their squared uncertainties).Nine of the published values use different
997 extraction methods, such as MW-assisted extraction (MAE) or heating in a block with
998 several extractants such as HNO_3, HNO_3/H_2O_2, $HClO_4$, H_2O or enzymes; and with final
999 measurement via the coupled HPLC-ICPMS technique, which allows iAs to be
1000 separated from methylated species and the iAs species to be determined
1001 satisfactorily[39,40,180,183,190,191,237,239,241]. A study of bioaccessible extracts (0.07 mol L$^-$
1002 ^{1}HCl and 0.01 % pepsin) was performed using (HPLC-ICPMS) with a high-efficiency
1003 photooxidation (HEPO) and HG system[242].A bioaccessible iAs value close to the
1004 certified one was obtained: 0.0821 ± 0.0024 mg As kg^{-1} . Two authors selectively
1005 extract the iAs with HCl and subsequent extraction with chloroform of the iAs present
1006 in the acid medium[238,240], based on the method of Muñoz et al.[142]. The final
1007 determination is performed by ICPMS and results comparable to the certified value
1008 were obtained. Although CE-ICPMS is not usual in iAs determination, Qu et al. [218]

extract iAs with an enzyme-assisted water-phase MAE and quantify by CE–ICPMS, reporting a satisfactory iAs value for the NMIJ 7503-a rice material.

Very recently, EC-JRC-IRMM has produced a rice CRM (ERM-BC211)which is certified for DMA and iAs as well as for tAs. Six studies analyze thismaterial[36,139,155,156,172,243]and the mean value for the reported iAs results is 0.122 ± 0.004(mean ± standard deviation, n=6results)which is in agreement with the certified value: 0.124 ± 0.011 mg As kg^{-1} . Five studies use MAE with HNO_3 or HNO_3/H_2O_2 as the extractant solvent; two of them with determination of iAs by HPLC-ICPMS[36,243]and two by HG-AFS [155,156] and the other by HG-AAS [139]. Another study extracts iAs with TFA and determination is by HPLC-HG-AFS [172].

SRM 1568bwhite rice was recently released by NIST and it is certified for arsenic speciation (DMA, MA and iAs).To date, two studies analyzes it to evaluate the accuracy of their methods; one is based on As species in rice by CE-ICPMS[218] and the other is focused on rice-based products for infants and young children by HPLC-ICPMS[248]. Finally, only one study was found that analyzes the NMIJ 7405a hijiki and the reported iAs value is in agreement with the certified one[242]. The high content of iAs (10.1 ± 0.5 mg As kg^{-1}) in this seaweed is usually found in studies of hijiki (*Hizikia fusiforme*), which is known to bioaccumulate arsenic as iAs[33,249].

3.1.2 Other CRMs available with certified total arsenic value

Due to the lack of CRMs with a certified iAs value, many authors perform arsenic speciation analysis on CRMs in which the tAs content or other arsenic species are certified. For validation purposes, the data obtained is compared with data reported in the literature by different researchers. This is one of the most commonly used practices within the scientific community to evaluate accuracy without a certified iAs value. Furthermore, the sum of As species is usually compared with the certified total As content (a so-called mass-balance study) or with tAs determined in the sample extract (column recovery). Mass balances or column recoveries of 80%–110% of total As are considered acceptable. Values close to 100% indicate full quantification of the As species present in the sample and guarantee the correctness of the chromatographic separation.

1040 Therefore, the following paragraphs focuses only on reported iAs values in food
1041 matrix CRMs; so studies reporting tAs or arsenic species in a CRM but not iAs results
1042 are not included in this section. The reported values are summarized in Table III, which
1043 includes type of food, supplier, certified values, total arsenic reported, iAs method,
1044 measurement technique and iAs value.

1045 The authors wish to summarize the ability of the analytical community to
1046 perform iAs analysis in different food matrices CRMs. For this, we focus on reported
1047 iAs results in the most commonly CRMs analyzed: SRM 1568a rice, TORT-2 lobster
1048 and DOLT-4 fish. The reported results in these CRMs are shown in Figure 5and Figure
1049 6for SRM 1568a and TORT-2, respectively; and in Table III for DOLT-4. Furthermore,
1050 specific highlights of iAs analysis in these CRMs are summarized in the following
1051 paragraphs.

1052 In the case of SRM 1568a (Figure 5) and TORT-2 (Figure 6), reported results
1053 are tabulated according to the iAs value, from low to high, illustrating the capacity of
1054 the analytical community to measure the iAs content in these CRMs. There are different
1055 ways to express and publish iAs results for these CRMs in the original publications:
1056 total iAs; only arsenite or only arsenate; or both species separately. We express and
1057 summarize all the results as iAs, i.e.,the sum of arsenite plus arsenate, in order to
1058 facilitate comparison of the data. Therefore, in the Figures, the continuous lines
1059 represent the average concentration of iAs and the dashed lines delimit the target
1060 interval X ± SD in mg As kg^{-1}. The individual error bars represent the errors reported in
1061 the original publications. Where arsenite and arsenate were reported separately, the iAs
1062 value (the sum of arsenite and arsenate) and the error bar are calculated (the square root
1063 of the sum of their squared uncertainties or standard deviations). We note that
1064 researchers usually report results as mean value ± error, which is predominantly SD for
1065 a number of replicates and in a few cases it is referred to the associated U value.

1066

1067 ***Highlights of inorganic arsenic analysis in SRM 1568a rice***

1068 For several years, NIST SRM 1568a rice has been analyzed as part of the
1069 method validation for the determination of As(III), As(V), MA, and DMA in rice.
1070 Although it is only certified for tAs content (0.290 ± 0.030 mg As kg^{-1}) and not for

arsenic species, it is routinely used to assess the accuracy of As species by comparing measured results with the literature. Almost no studies report results for more than 4 species and there seems to be agreement that the material only contains iAs and the two methylated species, as these are what are detectable by the majority of the methods employed in the literature reviewed.

Several authors analyze the rice material and dataset includes 46iAs results, as shown in Figure 5. Plotting the results chronologically does not lead to any further conclusion: there is no obvious change in the reported values as a function of time, although the time covered is short (2010-2015). The dataset includes one result outside the ± 3 standard deviations range, 0.204 mg As kg^{-1}, so this is considered an outlier. If this value is excluded, the mean value for iAs is 0.098 ± 0.009 mg As kg^{-1} (X ± SD, n=46 results, corresponding to 34% of the certified As), where the ± term is the standard deviation (SD) of all the reported values. Although several methods and techniques are used by different researchers, it is worth noting that little dispersion of the iAs results was found. The iAs results range from 0.074 to 0.113 mg As kg^{-1}. Satisfactory agreement between the reported values and the calculated mean value is observed. If the reported values are expressed in terms of error, considering the mean value as a reference value, they would range from 76% to 116%.

Different measurement techniques are used to determine iAs content, with HPLC-ICPMS being the most common (with different HPLC columns, different eluents, etc.): 36 results were found from several authors[37,39,40,162,180–183,187,190,193,195,197,198,200,239,241,251,266–274]whereas only one researcher used the HPLC-HG-AFS coupled system[275].Several authors use non-coupled HG as a previous step to measuring iAs with different techniques. Five publications from the same group use FI-HG-AAS to determine iAs content[147–151]; while two authors apply an HG-AFS system, one of them with a prior SPE step[155] and the other without SPE[156]. Furthermore, a validated method using an SPE-HG-AAS system is applied[138]; and also a speciation method using selective HG conditions and measuring by ICPMS is reported[157]. In addition, a method for determination of inorganic arsenic by CPE-UV-Vis is used [220]. Meanwhile, Lopez-Garcia et al.[107]reports a value for As(III) + As(V) + MA=0.099 mg As kg^{-1} by ETAAS using suspensions prepared in 0.01 mol L^{-1} TMAH, which is in close to the mean calculated value.

Different extraction solvents are used, supported by sonication, shaking, MAE or heating in a waterbath, etc. Some of these cause redox changes in the inorganic species producing a high dispersion in the values reported for arsenite or arsenate, and high uncertainty over the reported concentrations. In spite of high interconversion between arsenite and arsenate, the total iAs content remains constant and unaltered with no loss of analytes observed. This can be seen in Figure 5, in which the results are tabulated as iAs, and the majority of the data are inside the target interval X ± SD. The most commonly used extraction solvent is dilute HNO_3[37,181,183,190,195,197,200,239,266–268,271–273]. Other studies combine the use of $HNO_3$with the addition of H_2O_2 to oxidize As(III) to As(V) and quantify the total iAs as As(V)[39,40,138,155–157,162,187,251]. Also, a specific extraction method such as selective extraction of iAs with HCl and subsequent extraction with $CHCl_3$ of the iAs present in the acid medium is applied by several authors [147–151]. Meanwhile, other extraction methods are also used to extract iAs from the rice material, including: enzymatic extraction[193,198,241]; H_2O [162,180]; MeOH/H_2O [182,269]; TFA [200,274,275]; and suspensions of TFA in H_2O_2[200], NH_3[200]orTMAH[107].

Despite the use of different extraction methods and measurement techniques, the values reported show no clusters related to the analytical approach. The concentration of iAs determined in this CRM does not seem to depend on the analytical methodology. The NIST website indicates SRM 1568a is not available at present (last access: May 2015): this material is currently “out of stock” and was superseded by SRM 1568b, which was certificated in October 2013. As specified in the certificate of analysis, the existing material from production of SRM 1568a was used to produce the new SRM 1568b. The certified mass fraction value for iAs in the new SRM is 0.092 ± 0.010 mg As kg^{-1} , which is in perfect agreement with the data previously reported for the analysis of the former NIST 1568a (iAs= 0.097 ± 0.009 mg As kg^{-1}). The expanded uncertainty for SRM 1568b (0.010mg As kg^{-1}) does include the mean of the values reported for SRM 1568a, and thus it is likely that the means are not significantly different. Therefore, we seem to be able to claim that the international analytical chemistry community is capable of measuring iAs content in rice.

Highlights of inorganic arsenic analysis in TORT-2 Lobster Hepatopancreas

1134 Among the marine food CRMs, TORT-2 Lobster Hepatopancreas is one that is
1135 commonly analyzed in the literature. The material was produced by NRC-CNRC and
1136 the certificate is dated December 1994.It is certified for tAs content (21.6 ± 1.8 mg As
1137 kg^{-1}, mean value ± uncertainty) but not for arsenic species. Several As species have
1138 been reported in this material, with AB being the major species and DMA, MA and
1139 TMAO minor components [243,256].

1140 Thirty-four published iAs contents[137,163,202,217,243,256,259,276,277]are tabulated and
1141 shown in Figure 6. The dataset includes an outlier: 4.46 mg As kg^{-1}, which is excluded
1142 from our further calculations. Reported values range from0.230 to 1.233 mg As kg^{-1} for
1143 iAs; and the calculated mean value is0.606 ± 0.215 mg As kg^{-1} (X ± SD, n=33 reported
1144 data), where the ± term is the standard deviation of all the reported values. High
1145 variability of results is found, the RSD of the reported values is 36%. As expected, iAs
1146 corresponds to a low proportion (2.8%) of the certified tAs content. Classifying the
1147 results chronologically does not lead to any further conclusion about the high dispersion
1148 of the published results. If we assume that the calculated mean value is the "true value",
1149 values ranges from 38% to 204% which not desirable from the analytical point of view.

1150 Several techniques are employed to determine iAs content, with HPLC-HG-
1151 ICPMS being the most commonly used with different HPLC columns, mobile phases,
1152 extraction solvents, etc. Sixteen values for iAs have been found, resulting in an iAs
1153 value of 0.551 ± 0.142 mg As kg^{-1} (mean ± SD, n=16)[163,202,242,259]. Fourteen results are
1154 obtained using a coupled HPLC-ICPMS system, resulting in an iAs value of 0.652 ±
1155 0.275 mg As kg^{-1} (mean ± SD, n=14)[137,163,202,243,256,259,276,277]. Differences were
1156 observed when comparing the mean HPLC-HG-ICPMS values with those obtained by
1157 HPLC-ICPMS; however, in both cases the standard deviation is quite high and the
1158 intervals (i.e., mean ± SD) overlap, which leads us to consider that no differences are
1159 observed between the means for the two techniques. Only one author used another
1160 coupled technique: HPLC-HG-AFS, with an iAs value of 0.369 ± 0.018 mg As kg^{-1}
1161 [259].A study analyzing iAs content by CE-ICPMS obtained the highest value for iAs:
1162 4.46 ± 0.03 mg As kg^{-1} [217].Few data using non-coupled techniques are reported: two
1163 results obtained by SPE-HG-AAS, iAs=0.90 ± 0.07mg As kg^{-1} [137] and iAs=0.544 ±
1164 0.162 mg As kg^{-1} , as a value obtained from an inter-laboratory comparison (IMEP-32)
1165 [277]. Furthermore, one researcher found an iAs value of 0.669 ± 0.034 mg As kg^{-1} by
1166 high resolution (HR)-ICPMS[163].

A wide range of solvents supported by sonication, shaking, MAE or heating in a waterbath are used to extract iAs from the CRM matrix. The most commonly used extraction solvents are: HCl with or without H_2O_2[137,163,202,277]; HNO_3 with or without H_2O_2[163,202,243];NaOH in 50% EtOH[163,202,259,276]; and H_2O [163,256]. According to the reported values, mean values for iAs are: 0.674 ± 0.126 (n=8), 0.682 ± 0.097 (n=7) and 0.670 ± 0.264 (n=6) mg As kg^{-1} (mean ± SD) for HCl, HNO_3 and H_2O extractions, respectively. No differences in iAs content are observed between the three extraction solvents. However, mean data for NaOH in 50% EtOH extractions result in a lower value: 0.390 ± 0.085 mg As kg^{-1} (mean ± SD, n=7). To a lesser extent, other solvents are used, such as 50% MeOH or TFA extractions. In some cases, there are large differences between data obtained using the same extractant, with the measurement technique possibly being responsible for such dispersion. For example, using 50% MeOH, the differences between reported values are notable: the iAs value is 0.676 by HPLC-HG-ICPMS[163] and 1.233 mg As kg^{-1} by IC-ICPMS [256]. Similarly with TFA extractions the iAs values are 0.315 (with the addition of H_2O_2) and 0.514 mg As kg^{-1} (without H_2O_2)[163]; with there being differences in the use of H_2O_2 and also in the measurement technique: the former using HPLC-HG-ICPMS and the latter HPLC-ICPMS. In another example, applying selective solubilization of iAs with HCl, subsequent extraction with $CHCl_3$ and further back-extraction with HCl, differences were also observed in the iAs content: 0.669 vs 0.331 mg As kg^{-1} [163]. The higher value is obtained by HR-ICPMS while the lower value corresponds to using HPLC-HG-ICPMS.

As an overview of iAs content in TORT-2, and in accordance with the values in Figure 6, we can say that highly variable iAs data have been published, which illustrates that it is difficult to obtain a consistent value for iAs in this seafood CRM. Comparing values in the literature according to the extraction method used leads us to state that NaOH extractions show lower concentrations than other solvents (i.e., HCl, H_2O or HNO_3). The large differences in the literature between concentrations of iAs in this seafood material reinforce the need to develop more and more reliable methods for its determination.

Highlights of inorganic arsenic analysis in DOLT-4 dogfish

The dogfish (*Squalus acanthias*) liver DOLT-4 is one of most analyzed of seafood CRMs. The material was produced by NRC-CNRC and the certificate is dated May 2008.It is certified for tAs content (9.66 ± 0.62 mg As kg^{-1}, mean value ± uncertainty) but not for iAs. AB is the major As compound followed by DMA, iAs, MA, TMAO, etc., as minor compounds [243].

Studies analyzing this dogfish liver material produce 17 published values for iAs in the literature (Table III). Some of the data correspond to values reported from PT, IMEP-109/30[47]. From the results reported, the values range from0.010 to 0.387 mg As kg^{-1} for iAs; and two of them could be considered as outliers (0.387 and 0.152 mg As kg^{-1}). Excluding those two values, the calculated mean is 0.024 ± 0.019 mg As kg^{-1} (X ± SD, n=15, ranging from 0.010 to 0.075), where the ± term is the standard deviation of all the reported values. Very high dispersion of results is reported and the RSD of the reported values is 76%. As usual in fish, the iAs content corresponds to a low proportion (0.3%) of the tAs content. There are few data in the literature, and a classification chronologically does not lead any conclusion about the high variability of the published iAs results. Range of values, considering the mean value as true value, ranged from 41% to 308%; again highlighting the considerable variability of the iAs results in the literature.

Tabulating the results by measurement techniques shows that the iAs mean values are: 0.014 ± 0.008 (n=9) and 0.031 ± 0.010 (n=6) mg As kg^{-1} (mean ± SD) for the coupled techniques HPLC-HG-ICPMS [163,202] and HPLC-ICPMS [47,202,243,253], respectively. Only two results obtained using non-coupled techniques have been published: iAs= 0.075 ± 0.005 mg As kg^{-1} by FI-HG-AAS[47]; and iAs= 0.152 ± 0.010 mg As kg^{-1} by HR-ICPMS [47].

Sorting the results by extraction method shows that several different solvents supported by sonication, shaking, MAE or heating in a waterbath, are used to extract iAs from the fish matrix. For example, the following extractants were used: H_2O (n=3) [163,253]; NaOH in 50% EtOH (n=2) [202]; MeOH (n=1) [163]; HCl with H_2O_2 (n=2) [202]; and TFA (n=2) [47,163]. Extractions based on HNO_3 provide a mean value of 0.019 ± 0.007 mg As kg^{-1} (mean ± SD, n=4). There is high variability between selective extractions of iAs based on the method of Muñoz et al.[142], depending on the measurement technique

employed; the iAs values are 0.036, 0.075 and 0.152 mg As kg^{-1} using HPLC-HG-ICPMS [163], FI-HG-AAS and HR-ICPMS [47], respectively.

It should be noted that a low iAs concentration is found in DOLT-4: 0.024 ± 0.018 mg As kg^{-1} (excluding the two outliers), with high dispersion between the reported values (Table III). It is not possible to show whether the extraction method or the measurement technique are significant influential factors; however, most reported methods show a low concentration of iAs in the material (<0.080 mg As kg^{-1}). Further developments and improvements of the analytical methods to determine iAs in seafood are needed in order to provide reliable iAs results.

3.1.3 Other strategies to evaluate accuracy

Although some CRMs with a certified iAs value have been produced in recent years, this does not seem to cover the wide range of the foodstuffs usually consumed in common diets. Some alternative approaches to estimate accuracy without the appropriate and representative CRMs are reported in the literature consulted, as follows: performing spiking experiments; compare the method with a reference method and comparing different sample preparations with each other. In the following paragraphs we summarize some alternatives found in the literature to assess accuracy without a certified reference value.

Spiking experiments

An alternative, to assess accuracy in the absence of CRMs, is to perform spiking experiments and then calculate the recovery. Typically, a test material is analyzed by the method under validation both in its original state and after the addition (spiking) of a known mass of iAs to the test sample. Spiking (also known as fortification) procedures must be carefully planned in order to select the most suitable strategy to introduce a single iAs species or mixture of both (i.e., arsenite and arsenate) into the matrix. Some other variables that should be checked in order to prepare a spiked sample with a similar matrix to the original sample are: the maximum volume or weight to be added to the matrix; the contact time and conditions; and further pre-treatment steps (e.g. drying,

sieving, milling, etc.). Furthermore, the homogeneity of the distribution of the species within the matrix should be addressed. In the case of the incorporation of a spiking solution into a liquid homogeneity is relatively easy to achieve; whereas, the process can be much more difficult when working with a solid matrix. Spiked samples, or sometimes a blank sample, are subjected to the respective sampling procedures and the contents measured [36,39,40,112,137,138,155,157,179,183,187,189,198,200,238,241,243,259]. The recoveries obtained are usually compared to CODEX criteria: 60%–115% for 10 μg kg^{-1} and 80%–110% for 0.1–10 mg kg^{-1} [278]. Recoveries in these ranges are considered acceptable and demonstrate the reliability of the sample preparation method. Sometimes spiking experiments are carried out by adding standards of As species to CRMs before analysis. Although the iAs content is not certified, the spiking of iAs has been performed on SRM 1568 rice [162,198] and also BCR-627 tuna fish [198].

Methods comparison

Another approach to evaluating accuracy is to compare the results achieved with a fully validated method to test for bias in the proposed method. This is a useful option when checking an alternative to an established standard method already validated and in use in the laboratory. Some studies of iAs determination compare methods in rice samples: SPE HG-AAS with HPLC-ICPMS [138]; HG-ICPMS with HPLC-HG-ICPMS [157]; HG-AFS with HPLC-ICPMS [156]; a slurry sampling-HG-AAS method [141] with the Chinese standard HG-AFS method[95]. Few studies comparing iAs results in on seafood samples were found, but one example of such a study compares SPE HG-AAS with HPLC-ICPMS [137].Another study used MAE extraction with NaOH (1.5 mg/mL) in 50% ethanol to extract iAs from seafood samples and CRMs; the results were compared using different techniques: HPLC-ICPMS vs HPLC-HG-ICPMS vs HPLC-HG-AFS [259].

Another strategy to check the reliability of results is to compare different sample preparation procedures followed by measurements using the same detection technique. For example, three extraction methods are compared in seafood samples and CRMs, and the results are discussed according to the use of HPLC-ICPMS with and without HG[202]. The same authors extend the study to nine extraction methods for iAs determination in seafood (i.e., the most commonly used in the literature) followed by measurements using HPLC-HG-ICPMS and the results are extensively discussed [163].

Different extraction methods are also applied, followed by measurements using HPLC-ICPMS, to compare the results in cereal-based food[195] and in rice[162,250].

3.2. Proficiency testing (PT)

As external QC, PT or inter-laboratory comparisons, is a valuable tool to test the reliability of a method by comparing results with an assigned reference value. Some institutions, organizations and laboratories regularly organize PT to evaluate the performance capabilities of analytical laboratories. In the following section we summarized PT focused on the determination of iAs in food matrices.

3.2.1 EC-JRC-IRMM proficiency testing (PT)

The Institute for Reference Materials and Measurements (IRMM) of the Joint Research Centre (JRC), a Directorate General of the European Commission, operates the International Measurement Evaluation Program (IMEP).It organizes inter-laboratory comparisons in support of European Union policies. The Directorate General for Health and Consumers (DG SANCO) of the European Commission (EC) has requested the European Union Reference Laboratory for Heavy Metals in Feed and Food (EU-RL-HM) to evaluate the performance of European laboratories with regards to total Asand iAs analysis in food, with a view to future discussions on the need for regulatory measures. With that brief, several PT protocols have been organized in recent years by the IMEP on behalf of the EU-RL-HM. In the following paragraph we focus on PT organized within the IMEP, as summarized in Table IV.

In general, the aim of the selected IMEPs is to: “judge the state of the art of analytical capability for the determination of total and inorganic arsenic in several foodstuffs with a view to future discussions on the need for possible regulatory measures and future discussions on risk management and the possibility of introducing maximum levels for iAs in the European Union”. In general terms, the IMEP protocol consists of the distribution of the test material within the participating laboratories (national reference laboratories (NRLs), official control laboratories (OCLs) or open to all laboratories) which are requested to determine total As and iAs by their routine

procedures. The participants are asked to report individual results, the mean value and its associated uncertainty. Sometimes, the test material is certified for tAs (a CRM is used in some PT) but unfortunately not for iAs, so it is sent to some expert laboratories in the field to assign a reference iAs value. Expert laboratories are asked to analyze the material using methods of their choice and no further requirements are imposed regarding methodology. They are also asked to report their results together with the measurement uncertainty. The mean of the independent values provided by the expert laboratories for total As and iAs are used as the "assigned value" (X_{ref}, also called the "reference value") and the associated "standard uncertainty" is also calculated. All of this is in accordance with the International Standards Organization guide 35[285]. Then, the organizers calculate the z and ζ parameters for each laboratory in accordance with ISO 13528[286]. The ζ-score and z-score are interpreted as follows (according to ISO/IEC 17043[287]: "satisfactory performance" (≤2), "questionable performance" (>2 ζ /z ≤3), or "unsatisfactory performance" (>3).

Further details, specific information for each IMEP, such as the PT code, type of food, objective, analyte, assigned values, results of participants (z-score) and comments, are shown in Table IV.

IMEP-107: Determination of total and inorganic As in rice

The first PT to include iAs as an analyte was organized in 2009 and focused on the determination of total As and iAs in rice (IMEP-107) [46,184]. Reference values for total As and iAs were satisfactory assigned by several expert laboratories. A wide range of sample pre-treatment methods, and instrumental set-ups were applied by participants and the expert laboratories. Despite the use of these different methods, the results were not observed to cluster in relation to the analytical approach. The organizers comment that no particular problem related to the determination of iAs in rice was detected in the PT, and the performance of the participating laboratories was satisfactory. Finally, they conclude that the concentration of iAs determined in rice does not depend on the analytical method applied and that introduction of a maximum level for iAs in rice should not be postponed due to analytical concerns [46].In addition, the IMEP-107 rice test material has been used as RMs in several studies and was analyzed to assess the accuracy of iAs results obtained using the specific method [40,112,138,183].

IMEP-109/30: Analysis of total Cd, Pb, As and Hg, as well as MeHg and iAs in seafood

Encouraged by the satisfactory results for iAs in rice, two inter-laboratory comparisons, IMEP-109 and IMEP-30, were performed in 2010 of the measurement of some trace elements, in addition to iAs, in seafood [47]. Only the EU NRL took part in IMEP-109 [280], while IMEP-30 was open to all laboratories [279]. The commercially available CRM DOLT-4 from NRC-CNRC was used as the test material for all this PT. Five expert laboratories, analyzed the test material to establish the reference value for iAs. The expert laboratories were not able to agree on a value for the iAs within a reasonable degree of uncertainty. For this reason, it was not possible to establish an assigned value for iAs and therefore the results from the laboratories for iAs could not be scored. The organizers concluded that the results were spread over a wide range, but 75% of the laboratories agreed that the iAs content of the test material did not exceed 0.25 mg kg^{-1}. Despite the spread, they stated that there seems to be no clear clustering of results according to the methods used. According to the results, the determination of iAs in seafood presented serious analytical problems and iAs is clearly more difficult to analyze in this seafood matrix than in rice (IMEP-107). Further information and possible causes for the dispersion of the results, attributed to the extraction and/or detection steps as the most likely cause, are widely discussed in the IRMM reports[279,280]and summarized in Baer et al. [47]. Additionally, it was concluded that more research is needed in the future to find appropriate and effective extraction procedures, as well as chromatographic conditions for reliable separation and quantification of iAs.

IMEP-112: Determination of total and inorganic in wheat, vegetable food and algae

IMEP-112 focused on the determination of total and inorganic arsenic in wheat, vegetable food and algae [48,281].The assigned values (total As and iAs in wheat, and iAs in vegetable food and algae) were satisfactorily provided by a group of expert laboratories in the field. The organizers concluded that the concentration of iAs determined in any of the matrices does not depend on the analytical method applied, as proven by the results submitted by the seven expert laboratories and by the participants. A wide range of sample pre-treatment methods and instrumental setups were applied

and despite this, clustering of results related to the analytical approach was not observed. Furthermore, the participating laboratories performed, in general, satisfactorily for the determination of iAs in wheat and vegetable food; however, only a few laboratories obtained a satisfactory score for iAs in algae. Finally, it was also highlighted that, purely from the analytical point of view, there is no reason not to consider the option of introducing maximum levels for iAs in wheat, vegetable food and algae in further discussions of risk management [48]. Besides, the wheat test material used in IMEP-112 was also analyzed as external QC [39].

IMEP-116/39: Total Cd, Pb, As, Hg and inorganic As in mushrooms

Since mushroom consumption has increased considerably in recent years due to promotion of their nutritional properties, two PT programs were organized using the same test item (shiitake mushroom) [49]: IMEP-116 (for NRLs) [282] and IMEP-39 (for OCLs and other laboratories) [283]. Reference values were satisfactory assigned by five expert laboratories which analyzed the test item. In general, the performance of the participating labs was satisfactory for iAs: in IMEP-116 (NRLs), a high percentage of satisfactory results was obtained (z=81%, n=13) which is considerably higher than in IMEP-107 (rice). The organizers also pointed out that in IMEP-39, five out of the seven laboratories which obtained a satisfactory z-score for iAs used AAS-based techniques, showing that sound determinations of iAs can be made without the need for expensive sophisticated instrumentation [49]. Furthermore, the IMEP-116/39 PT item, shiitake mushroom, has also been used as external QC for iAs analysis [36].

IMEP-118: Determination of total As, Cd, Pb, Hg, Sn and iAs in canned food

In 2014, a PT program was produced focused on the determination of total As, Cd, Pb, Hg, Sn and iAs in canned food (peas in brine) (IMEP-118) [51,284]. Participation in the PT was mandatory for nominated NRLs, and open to other OCLs and interested laboratories. Unlike other IMEPs, the test material was spiked with arsenic during preparation. Expert and participant laboratories were asked to analyze total As and iAs in the canned vegetables, in both the drained product and the solid/liquid composite. Good agreement between the theoretical and the assigned value for total As in the

solid/liquid composite was obtained; but not in the case of iAs. The brine was spiked with arsenate and the iAs mass fraction in the solid/liquid composite was found to be lower than the respective total As mass fraction: 35% lower than the theoretical one. Some possible causes are discussed and summarized in the IRMM report[51]. In spite this, the results from the two expert laboratories were in agreement and a reference value for the iAs mass fraction was assigned. From the PT results, it was concluded that the performance of the participating laboratories at determining iAs was satisfactory for both sample preparation approaches. However, few laboratories carried out analysis for iAs determination (only 33% reported values). Furthermore, the outcome of the PT clearly indicated that guidelines are needed on the sample preparation protocol to be used when analyzing canned food drained products and solid/liquid composites.

IMEP-41: Determination of inorganic arsenic in food

An inter-laboratory comparison was performed on a method evaluation by means of a collaborative trial for the determination of iAs in seven food products (IMEP-41) [50]. The method under evaluation was previously developed and in-house validated and final measurement was performed by FI-HG-AAS [142]. The organizers clearly stated that the standard operating procedure (SOP) was to be strictly followed and any deviation from the method should be reported. The seven test food items used in this exercise were RMs covering a broad range of matrices and concentrations (Table IV). Five experts analyzed the test items using a method of their choice, different from the one being assayed. From the results, the organizers concluded that the method evaluated is robust and does not require any adaptation according to the matrix to be analyzed. Furthermore, the proposed method is considered fit-for-purpose, i.e., determination of iAs in different food products[50].

4.2.2 Other inter-laboratory comparisons

Other inter-laboratory comparisons focused on the determination of iAs in food have been organized in recent years. Institutions, organizations and laboratories regularly organize PTs to evaluate competency in the analysis of iAs species in food matrices. The Food Analysis Performance Assessment Scheme (FAPAS) of the Food

and Environment Research Agency (FERA) has organized PTfor several years, focused on several analytes in foodstuffs, with a wide range of tests available throughout the year. PTs on the determination of total and iAs in several food matrices is regularly organized[288]. A rice test material from the FAPAS interlaboratory tests [289] was analyzed in several studies as QC for iAs [39,40,238]. Brooks Rand Labs organized an inter-laboratory comparison study for arsenic speciation in white rice flour, brown rice flour, kelp powder, and apple juice in 2013. A large group of participating laboratories from around the world, forty-six laboratories from fifteen countries, registered to participate[290].

Specific PTs focused on iAs in rice has recently been organized. The Ministry of Agriculture, Forestry and Fisheries (MAFF) of Japan organized a collaborative study of speciation and determination of iAs in rice using HPLC-ICPMS. For it, an SOP of the method was developed and the proposed method was validated through the collaborative study of eastern and southeastern Asian countries[291]. Further PT based on the iAs content of rice was organized by the Inorganic Analysis Working Group (IAWG) of the Consultative Committee for Amount of Substance (CCQM). The CCQM-K108 key comparison was organized to test the capacities of the national metrology institutes or the designated institutes to measure the mass fractions of arsenic species and tAs in brown rice flour; while the National Metrology Institute of Japan (NMIJ) acted as the coordinating laboratory. The participants used different measurement methods to determine the iAs content of a rice sample [292].

4. CONCLUSIONS AND FUTURE TRENDS

Food control laboratories, consumers, authorities, institutions, health agencies and legislators have recently become more interested in iAs contents in food. This has led to several initiatives that move towards the development of robust and reliable analytical methods for selective determination of iAs in a range of food products. Although several techniques have been used in iAs determination, spectroscopic methods are the most commonly applied. Several such methods and techniques have been developed, but mild chemical extraction of iAs species and further determination by HPLC-ICPMS is undoubtedly the most popular approach used in iAs analysis in food. However, some non-chromatographic approaches that determine iAs accurately

even in presence of other organoarsenic compounds have been reported as being less time-consuming and more cost-effective alternatives than those based on HPLC-ICPMS.

Although numerous CRMs have been analyzed to evaluate the accuracy of the methods for total arsenic, few of them are certified for iAs content. The differences found in the literature between the concentration of iAs in seafood CRMs illustrates that it is difficult to obtain a consistent value and reinforce the need to develop reliable methods for its determination, especially when matrices with a complex distribution of arsenic species are analyzed, as in the case of food of a marine origin. Further production of seafood CRMs would help in the validation of iAs methods and in providing reliable iAs data. Furthermore, more PTs for iAs determination in seafood are needed to assess the reliability of the proposed methods, since to date, they have shown unsatisfactory performance.

Concerning food safety, the distinction between iAs and total As content or other species in foodstuffs should be addressed in future maximum levels of arsenic in food. Moreover, more reliable data on iAs content in foodstuffs, especially less studied food products, are needed for reliable risk assessment and to estimate the health risk associated with dietary As exposure.

Finally, more efforts should be made to transfer the knowledge obtained by the analytical community concerning the development of selective methodologies for the determination of iAs to the future implementation of that knowledge as routine methods in food control laboratories. To this end, the validation of methods as well as participation in PT and the analysis of CRMs should be performed, as mandated by the ISO/IEC 17025 standard for laboratory accreditation purposes.

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2444 **Table I.** Worldwide regulations on iAs and tAs in food. Table adapted and expanded from Petursdottir et
2445 al. [53]

Country	Food	iAs (mg kg^{-1})	tAs (mg kg^{-1})	Year	Reference
Australia and New Zealand	Crustacea	2.0		2011	**ANZFA 2011** [54]
	Fish	2.0			
	Molluscs	1.0			
	Seaweed (edible kelp)	1.0			
	Cereals		1		
Canada	Fish protein	3.5		2006	**CFIA (2014)** [55]
	Edible bone meal	1.0			
	Fruit juices, fruit nectar or other beverages (not mineral water)	0.1			
	Muscle of swine, chickens and turkeys; eggs	0.5 [a]			
	Liver of swine, chickens and turkeys	2.0 [a]			
China	Grains (excluding paddy rice)		0.5	2012	**MHC (2012)** [56]
	Processed milled grain products (excluding brown and white rice)		0.5		
	Paddy rice, brown rice, white rice	0.2			
	Aquatic animals and products (excluding fish and fish products)	0.5			
	Fish and fish products	0.1			
	Fresh vegetables, edible fungi		0.5		
	Meat and meat products		0.5		
	Raw, pasteurised, sterilised, modified, or fermented milk		0.1		
	Milk powder		0.5		
	Fats and their products		0.1		
	Seasonings (excluding aquatic or algae seasonings and spices)		0.5		
	Aquatic seasonings	0.5			
	Fish seasonings	0.1			
	Sugars and sweeteners		0.5		
	Packed drinking water		0.01 (mg/L)		
	Chocolate and cocoa and chocolate products		0.5		
	Supplementary food for infants and young children (with added algae)	0.2 (0.3)			
	Canned supplementary foods for infants and children	0.1 (0.3)			

France	Algae condiments	3	2010	**CEVA (2010)** [57]
European Union	Non-parboiled milled rice (polished or white rice)	0.20	2015	**EU (2015)** [58]
	Parboiled rice and husked rice	0.25		
	Rice waffles, rice wafers, rice crackers and rice cakes	0.30		
	Rice destined for the production of food for infants and young children	0.10		
USA	Chicken/turkey (uncooked muscle tissue)	0.5	2001	**FDA 2001** [59]
	Chicken/turkey (uncooked by-products)	2		
	Chicken/turkey (eggs)	0.5		
	Swine (uncooked liver kidneys)	2		
	Swine (uncooked muscle tissue and by-products)	0.5		

[a] ML for arsanilic acid

Table II. Available food CRMs with an inorganic arsenic certified value. Results obtained from literature (2010-2015) and expressed as mg As kg^{-1}.

CRMs Code	Type of food	Supplier	Certified value	tAs reported	iAs method	iAs technique	iAs reported value	References
CRM 7503-a	Rice	NMIJ	tAs= 0.098 ± 0.007 As(III)= 0.0711 ± 0.0029 DMA= 0.0133 ± 0.0009 As(V)= 0.013 ± 0.0009	0.098 ± 0.005	MAE/(HNO_3/H_2O_2)	HPLC-ICPMS	iAs= 0.0849 ± 0.0007	Llorente-Mirandes et al. [40]
				0.095 ± 0.005	MAE/(HNO_3/H_2O_2)	HPLC-ICPMS	iAs= 0.0837 ± 0.0016	Llorente-Mirandes et al. [39]
				0.095 ± 0.001	HEAT (block)/(HNO_3)	HPLC-ICPMS	As(III)= 0.067 ± 0.001 As(V)= 0.015 ± 0.002	Huang et al. [183]
				0.101 ± 0.005	HEAT (block)/(H_2O)	HPLC-ICPMS	As(III)= 0.0740 ± 0.0023 As(V)= 0.0140 ± 0.0005	Narukawa et al. [180]
				0.096 ± 0.002	MAE/(H_2O)	HPLC-ICPMS	As(III)= 0.0130 ± 0.0005 As(V)= 0.0711 ± 0.0008	Narukawa et al. [191]
				0.096 ± 0.002	HEAT (block)/(HNO_3)	HPLC-ICPMS	As(III)= 0.0133 ± 0.0005 As(V)= 0.0717 ± 0.0007	
				0.096 ± 0.002	HEAT (block)/(HNO_3/A	HPLC-ICPMS	As(III)= 0.0712	

	g)			
0.096 ± 0.002	HEAT (block)/($HClO_4$)	HPLC-ICPMS	As(V)= 0.0135 As(III)= 0.0714 As(V)= 0.0138	
0.099 ± 0.001	HEAT (block)/(HNO_3)	HPLC-ICPMS	As(III)= 0.0714 ± 0.0004 As(V)= 0.0134 ± 0.0002	Narukawa et al. [237]
No reported	Shaking/(HCl) /extraction ($CHCl_3$/back extr. 1 M HCl)/	ICPMS	iAs= 0.080 ± 0.008	Fontcuberta et al. [238]
0.096 ± 0.002	HEAT (block)/(HNO_3)	HPLC-ICPMS	As(III)= 0.057 ± 0.002 As(V)= 0.017 ± 0.003	Kuramata et al. [239]
No reported	Shaking/(HCl) /extraction ($CHCl_3$/back extr. 1 M HCl)/)	ICPMS	iAs= 0.0815 ± 0.0085	Wu et al. [240]
No reported	Heat block/HNO_3	HPLC–ICPMS	As (V)= 0.013 ± 0.001 As (III)= 0.068 ± 0.003	Baba et al. [190]
No reported	Heat with water/Enzymatic ext.(amylase)	HPLC-ICPMS	As(III)= 0.0602 ± 0.0025 As(V)= 0.0145 ± 0.0017	Nookabkaew et al. [241]
No reported	Shaking/HCl/pepsin (bioaccessible extracts)	HPLC-HEPO-HG-ICPMS	As(III)= 0.0594 ± 0.0028 As(V)= 0.0226 ± 0.0004	Oguri et al. [242]
No reported	MAE/ Enzymatic ext.(amylase)	CE-ICPMS	As(III)= 0.0621 ± 0.00173 As(V)= 0.01927 ± 0.0011	Qu et al. [218]
No reported	MAE/ Dispersive liquid–liquid micro-extraction integrated with the solidification of a floating organic drop	ETAAS	As(III)= 68.2 ± 5.3 As(V)= 13.5 ± 1.2 iAs= 85.5 ± 6.1	Ahmadi-Jouibari and Fattahi [109]

					(DLLME-SFO)			
ERM-BC211	Rice	IRMM	tAs= 0.260± 0.013 DMA= 0.119 ± 0.013 iAs= 0.124 ± 0.011	0.256 ± 0.009	MAE/(HNO_3/H_2O_2)	HPLC-ICPMS	iAs= 0.122 ± 0.006	Llorente-Mirandes et al. [36]
				0.263 ± 0.011	MAE/(HNO_3/H_2O_2)	HPLC-ICPMS	iAs= 0.119 ± 0.005	Zmozinski et al. [243]
				No reported	MAE/(HNO_3/H_2O_2)	SPE-HG-AFS	iAs= 0.124 ± 0.002	Chen. G et al. [155]
				No reported	MAE/(HNO_3/H_2O_2)	HG-AFS	iAs= 0.1214 ± 0.0048	Chen. B et al. [156]
				0.256 ± 0.008	HEAT/(TFA)	HPLC-HG-AFS	iAs= 0.129 ± 0.012	Cano-Lamadrid et al. [172]
				0.257 ± 0.015	MAE/(HNO_3)	HG-AAS	iAs= 0.116 ± 0.003	Cerveira et al. [139]
				No reported	HAE/(HNO_3)	HPLC-ICPMS	iAs= 0.127 ± 0.001	Narukawa et al 2015 [186]
SRM 1568b	Rice	NIST	tAs= 0.285 ± 0.014 DMA= 0.180 ± 0.012 MA= 0.0116 ± 0.0035 iAs= 0.092 ± 0.010	No reported	MAE/ Enzymatic ext.(amylase)	CE-ICPMS	As (III)= 0.05542 ± 0.0019 As(V)= 0.04092 ± 0.00678	Qu et al. [218]
				No reported	MAE/(HNO_3/H_2O_2)	HPLC-ICPMS	iAs= 94.5 ± 2% *	Signes-Pastor et al. [38]
				No reported	HAE/(HNO_3)	HPLC-ICPMS	iAs= 0.092 ± 0.004	Narukawa et al 2015 [186]
CRM 7532-a	Rice	NMIJ	tAs=0.320 ± 0.010 iAs=0.298 ± 0.008 DMA= 0.0186 ± 0.0008	No reported	HAE/(HNO_3)	HPLC-ICPMS	iAs= 0.298 ± 0.003	Narukawa et al 2015 [186]
CRM 7405-a	*Hizikia fusiformme*	NMIJ	tAs= 35.8 ± 0.9 As(V)= 10.1 ± 0.5	No reported	Shaking/HCl/pepsin (bioaccessible extracts)	HPLC-HEPO-HG-ICPMS	As(V)= 10.2 ± 0.1	Oguri et al. [242]
				34.6 ± 0.7	Sonication/ 50% methanol solvent in 1% HNO_3/ Anion-exchange cartridge	HPLC-ICPMS	As(V)= 9.8 ± 0.8	Khan et al 2015 [205]

Notes. The ± terms are as provided by the original publications. They are predominantly standard deviations for some number of replicates or in some cases uncertainties. MAE: microwave assisted extraction. HAE: heat assisted extracted technique.

2452 * Expressed as the original publication as % of recovery compared to the certified value.

2453

2454 **Table III.** Food CRMs with published results of an inorganic arsenic content. Results
2455 obtained from literature (2010-2015) and expressed as mg As/kg.

CRMs Code	Type of food	Supplier	Certified tAs value	tAs reported	iAs method	iAs technique	iAs reported value	References
NCS ZC73008	Rice	CNCIS	0.102 ± 0.008	0.105 ± 0.006	MAE/(HNO_3/H_2O_2)	HPLC-ICPMS	iAs= 0.080 ± 0.003	Llorente-Mirandes et al. [40]
				No reported	MAE/(HNO_3/H_2O_2)	HPLC-ICPMS	iAs= 0.084 ± 0.001	
GBW 10010	Rice	CAGS	0.102 ± 0.008	0.1099 ± 0.0072	Incubation 80ºC/Ultra-pure water	HPLC-ICPMS	As(III)= 0.0461 ± 0.0024	
							As(V)= 0.156 ± 0.0016	
					Incubation 80ºC/(Acetic acid (1%)	HPLC-ICPMS	As(III)= 0.0477 ± 0.0009	
							As(V)= 0.0152 ± 0.0004	
					Incubation 80ºC/(Nitric acid (1%)	HPLC-ICPMS	As(III)= 0.0616 ± 0.0045	
							As(V)= 0.0079 ± 0.0051	
					Incubation 80ºC/(TFA (0.2 M)	HPLC-ICPMS	As(III)= 0.0645 ± 0.0009	Liang et al. [250]
							As(V)= 0.0110 ± 0.0003	
					Incubation 80ºC/(TFA (2 M)	HPLC-ICPMS	As(III)= 0.0619 ± 0.004	
							As(V)= 0.017.4 ± 0.003	
					Incubation 80ºC/(Methanol (50%)	HPLC-ICPMS	As(III)= 0.0536 ± 0.0077	
							As(V)= 0.0128 ± 0.002	
					Incubation 80ºC/Methanol (50%)/TFA (0.2M)	HPLC-ICPMS	As(III)= 0.0626 ± 0.0056	
							As(V)= 0.0118 ± 0.0029	
SRM	Whea	NIS	0.00	0.0065	MAE/(enzymatic	HPLC-	As(III)= 0.0032 ±	Tsai et

1567a	t flour	T	6	± 0.0006	extraction)	ICPMS	0.00004 As(V)= 0.0027 ± 0.00005	al. [193]
SRM 8436	Durum Wheat Flour	NIST		0.013 ± 0.001	SON/(MeOH/H_2O)	HPLC-ICPMS	As(III)= 0.0012 ± 0.0002 As(V)= 0.00723 ± 0.00008	
				0.013 ± 0.001	Ultrasonic probe/(H_2O)	HPLC-ICPMS	As(III)= 0.00318 ± 0.00009 As(V)= 0.0027 ± 0.00025	D'Amato el al. [195]
				0.013 ± 0.001	MAE/(HNO_3)	HPLC-ICPMS	As(V)= 0.0109 ± 0.0006	
				0.013 ± 0.001	MAE/(enzymatic extraction)	HPLC-ICPMS	As(III)= 0.00216 ± 0.00044 As(V)= 0.00169 ± 0.0003	
SRM 1570a	Spinach leaves	NIST	0.068 ± 0.012	No reported	Shaking/(HCl) /extraction ($CHCl_3$/back extr. 1 M HCl)/	FI-HG-AAS	iAs= 0.038 ± 0.005	
					MAE/(HNO_3/H_2O_2)	HPLC-ICPMS	iAs= 0.075 ± 0.004	
					Shaking/(HCl) /extraction ($CHCl_3$/back extr. 1 M HCl)/	ICPMS	iAs= 0.074 ± 0.010	de la Calle et al. [48]
					MAE/(HNO_3/H_2O_2)	HPLC-ICPMS	iAs= 0.060 ± 0.002	
					MAE/(HNO_3 + H_2O_2)	HPLC-ICPMS	iAs= 0.055 ± 0.003	
					MAE/(HCl /H_2O_2)	HPLC-ICPMS	iAs= 0.034 ± 0.005	
					MAE/(TFA /H_2O_2)	HPLC-ICPMS	iAs= 0.045 ± 0.003	
				0.069 ± 0.005	MAE/(HNO_3/H_2O_2)	HPLC-ICPMS	iAs= 0.059 ± 0.005	Llorente-Mirandes et al. [36]
SRM 1573a	Tomato leaves	NIST	0.112 ± 0.004	No reported	UAE/(H_2SO_4/EDTA)	HG-AFS	As(V)= 0.0879 ± 0.0021 As(III)= 0.0226 ± 0.0003	Sousa-Ferreira et al.[154]
NCS ZC73012	Cabbage	CNCIS	0.062 ± 0.014	0.0603 ± 0.0007	MAE/(HNO_3/H_2O_2)	HPLC-ICPMS	iAs= 0.0519 ± 0.0035	Norton et al. [251]
SRM 1577	Bovine	NIST	0.055 ±	0.053 ± 0.002	SON/ HNO_3/MeOH	HPLC-ICPMS	As(V)= 0.012 ± 0.001	Batista et al. [103]

	Liver		0.005					
SRM 1566a	Oyster tissue	NIST	14.0 ± 1.2	No reported	Shaking/(HCl) /extraction ($CHCl_3$/back extr. 1 M HCl)/	FI-HG-AAS	iAs= 0.586 ± 0.049	Ruangwises et al. [146]
				No reported	Shaking/(HCl) /extraction ($CHCl_3$/back extr. 1 M HCl)/	FI-HG-AAS	iAs= 0.601 ± 0.037	Ruangwises et al. [149]
				No reported	Shaking/(HCl) /extraction ($CHCl_3$/back extr. 1 M HCl)/	FI-HG-AAS	iAs= 0.598 ± 0.035	Ruangwises et al. [144]
				No reported	Shaking/(HCl) /extraction ($CHCl_3$/back extr. 1 M HCl)/	FI-HG-AAS	iAs= 0.581 ± 0.050	Saipan et al. [145]
				No reported	Shaking/(HCl) /extraction ($CHCl_3$/back extr. 1 M HCl)/	FI-HG-AAS	iAs= 0.601 ± 0.037	Ruangwises et al. [150]
				No reported	Shaking/(HCl) /extraction ($CHCl_3$/back extr. 1 M HCl)/	FI-HG-AAS	iAs= 0.601 ± 0.037	Saipan et al. [151]
SRM 1566b	Oyster tissue	NIST	7.65 ± 0.65	6.94 ± 0.2 and 7.2 ± 0.3	MAE/($MeOH/H_2O$)	HPLC-ICPMS	As(V)= 1.16 ± 0.01	Santos et al. [252]
				7.67 ± 0.13	MAE/(HNO_3/H_2O_2)	HPLC-ICPMS	iAs= 0.05 ± 0.001	Zmozinski et al. [243]
				No reported	MAE/(H_2O)	IEC-ICPMS	As(III)= 0.357 ± 0.057 As(V)= 0.427 ± 0.038	Leufroy et al. [253]
				8.06 ± 0.08	MAE/($MeOH/H_2O$)	IC-ICPMS	As(V)= 0.05 ± 0.01	Nam et al. [254]
CRM 108-04-001	Oyster tissue	KRISS	13.51 ± 0.30	14.19 ± 0.09	MAE/($MeOH/H_2O$)	IC-ICPMS	As(V)= 0.03 ± 0.01	Nam et al. [254]
MURST-ISS-A2	Antarctic Krill	BCAA	5.02 ± 0.44	5.29 ± 0.4	Shaking/($MeOH/H_2O$)	HPLC-ICPMS	As(V)= 0.03 ± 0.01	Grotti et al. [255]
SRM 2976	Mussel tissue	NIST	13.30 ± 1.8	13.7 ± 0.25	MAE/(HNO_3/H_2O_2)	HPLC-ICPMS	iAs= 0.11 ± 0.013	Zmozinski et al. [243]
ERM-CE278	Mussel tissue	IRMM	6.07 ± 0.13	6.09 ± 0.21	MAE/(HNO_3/H_2O_2)	HPLC-ICPMS	iAs= 0.07 ± 0.003	Zmozinski et al. [243]
				5 ± 0.6	SON/	HPLC-	As(III)= 0.2 ± 0.02	Batista

					(HNO_3/MeOH)	ICPMS	As(V)= 0.4 ± 0.04	et al. [103]
BCR 627	Tuna fish tissue	IRMM	4.8 ± 0.3	5.2 ± 0.5	MAE/(H_2O)	IEC/ICP-MS	As(III)= 0.054 ± 0.014	Leufroy et al.[256]
				4.8 ± 0.3	MAE/(MeOH/H_2O)	IEC/ICP-MS	As(III)= 0.172 ± 0.071	
				4.68 ± 0.03	MAE/(MeOH/H_2O)	HPLC-ICPMS	As(III)= 0.29 ± 0.04 As(V)= 0.035 ± 0.001	Santos et al. [252]
				4.1	SON/(Enzymatic solution)	IC-ICPMS	iAs= 0.036	Dufailly et al. [198]
				4.84 ± 0.13	MAE/(HNO_3/H_2O_2)	HPLC-ICPMS	iAs= 0.02 ± 0.002	Zmozinski et al. [243]
				No reported	MAE/(H_2O)	IEC-ICPMS	As(III)= 0.068 ± 0.003 As(V)= 0.041 ± 0.001	Leufroy et al.[253]
				4.20 ± 0.03	Shaking (two-step sequential extraction)/acetone and MeOH/water	HPLC-HR-ICPMS	As(III)= below LOD As(V)= below LOD	Ruiz-Chancho et al. [257]
				No reported	Cell clean-up – PAEH	HPLC-ICPMS	As(III)= 0.075 ± 0.0006	Moreda-Piñeiro et al. [258]
				4.82 ± 0.41	Shaking/(HCl) /extraction ($CHCl_3$/back extr. 1 M HCl)/	HR-ICPMS	iAs= 0.82 ± 0.049	Lewis et al. [121]
DOLT-3	Dogfish Muscle	NRC-CNRC	10.2 ± 0.5	10.0 ± 0.4	MAE/(H_2O)	IEC-ICPMS	As(III)= 0.074 ± 0.011 As(V)= 0.073 ± 0.007	Leufroy et al. [256]
				9.6 ± 1.1	MAE/(MeOH/H_2O)	IEC-ICPMS	As(III)= 0.136 ± 0.004	
				No reported	MAE/(Enzymatic extraction)	CE-ICPMS	iAs below LOD	Hsieh et al. [215]
				10 ± 0.4	SON/(HNO_3/MeOH)	HPLC-ICPMS	As(III)= 0.3 ± 0.1 As(V)= 0.4 ± 0.2	Batista et al. [103]
DOLT-4	Dogfish Muscle	NRC-CNRC	9.66 ± 0.62	No reported	MAE/(HCl/H_2O_2)	HPLC-ICPMS	iAs= 0.039 ± 0.001	Pétursdóttir et al. [202]
					MAE/(HCl/H_2O_2)	HPLC-HG-ICPMS	iAs= 0.011± 0.002	
					MAE/(HNO_3)	HPLC-ICPMS	iAs= 0.028 ± 0.003	
					MAE/(HNO_3)	HPLC-HG-	iAs= 0.011 ± 0.002	

					MAE/(NaOH/EtOH)	ICPMS HPLC-ICPMS	iAs= 0.027 ± 0.003	
					MAE/(NaOH/EtOH)	HPLC-HG-ICPMS	iAs= 0.010 ± 0.003	
				No reported	MAE/(HCl/H_2O_2)	HPLC-ICPMS	iAs=<0.040	
					MAE/(MeOH/H_2O)	HPLC-ICPMS	iAs=ND	
					SON/(TFA/H_2O_2)	HPLC-ICPMS	iAs= 0.047 ± 0.006	
					Shaking/(HCl) /extraction ($CHCl_3$/back extr. 1 M HCl)/	FI-HG-AAS	iAs= 0.075 ± 0.005	Baer et al. [47]
					Shaking/(HCl) /extraction ($CHCl_3$/back extr. 1 M HCl)/	HR-ICPMS	iAs= 0.152 ± 0.010	
				No reported	MAE/(HCl/H_2O_2)	HPLC-HG-ICPMS	iAs= 0.011 ± 0.002	
					MAE/(H_2O/MeOH)	HPLC-HG-ICPMS	iAs= 0.012 ± 0.003	
					SON and MAE/(TFA/H_2O_2)	HPLC-HG-ICPMS	iAs= 0.011 ± 0.004	
					Shaking/(HCl) /extraction ($CHCl_3$/back extr. 1 M HCl)/	HPLC-HG-ICPMS	iAs= 0.036 ± 0.007	
					MAE/(HNO_3)	HPLC-HG-ICPMS	iAs= 0.011 ± 0.002	Pétursdóttir et al. [163]
					MAE/(HNO_3/H_2O_2)	HPLC-HG-ICPMS	iAs= 0.017 ± 0.003	
					MAE/(H_2O)	HPLC-HG-ICPMS	iAs= 0.011 ± 0.003	
					SON/(H_2O)	HPLC-HG-ICPMS	iAs= 0.010 ± 0.001	
					MAE/(NaOH/EtOH)	HPLC-HG-ICPMS	iAs= 0.010 ± 0.003	
				9.64 ± 0.11	MAE/(HNO_3/H_2O_2)	HPLC-ICPMS	iAs= 0.02 ± 0.003	Zmozinski et al. [243]
				No reported	MAE/(H_2O)	IEC-ICPMS	As(III)= 0.253 ± 0.019 As(V)= 0.134 ± 0.006	Leufroy et al. [253]
DORM-2	Dogfish Muscle	NRC-CNRC	18.0 ± 1.1	18.75 ± 0.66	MAE/(MeOH/H_2O)	HPLC-ICPMS	As(III)= 0.61 ± 0.04	Santos et al. [252]

				17.9 ± 0.9	MAE/(H_2O)	IEC-ICPMS	As(III)= 0.031 ± 0.014 As(V)= 0.029 ± 0.018	Leufroy et al. [256]
				19.7 ± 0.4	MAE/(MeOH/H_2O)	IEC-ICPMS	As(III)= 0.064 ± 0.011 As(V)= 0.026 ± 0.002	
				17.0 ± 0.7	Shaking (two-step sequential extraction)/acetone and MeOH/water	HPLC-HR-ICP-MS	As(III)= below LOD As(V)= below LOD	Ruiz-Chancho et al. [257]
				17.9 ± 0.98	Step 1: MAE/($HClO_4$/$Fe_2(SO_4)_3$/HCl Step 2: (As(III)):SON/HCl /$CHCl_3$/HCl	ETTAS	As(III)= 0.053 ± 0.001 As(V)= 0.051 ± 0.002	Shah et al. [111]
				16.9 ± 0.3 (as sum of As species)	Cell clean-up – PAEH	HPLC-ICPMS	As(III)= 0.081 ± 0.0005	Moreda-Piñeiro et al. [258]
				19.5 ± 1.3	Shaking/(HCl) /extraction ($CHCl_3$/back extr. 1 M HCl)/	HR-ICPMS	iAs= 0.131 ± 0.010	Lewis et al., 2012 [121]
				No reported	Ultrasonic bath/H_2O	SIA-HPLC-AFS	As(III)= 0.037 ± 0.02	Jesus et al. [169]
DORM-3	Dogfish Muscle	NRC-CNRC	6.88 ± 0.30	5.8 ± 0.4	MAE/(H_2O)	IEC-ICPMS	As(III)= 0.085 ± 0.014 As(V)= 0.243 ± 0.023	Leufroy et al. [256]
				7.1 ± 0.4	MAE/(MeOH/H_2O)	IEC-ICPMS	As(III)= 0.129 ± 0.018 As(V)= 0.276 ± 0.036	
				No reported	MAE/(EtOH/NaOH)	HPLC-ICPMS	iAs= 0.073 ± 0.008	Pétursdóttir et al. [259]
				No reported	MAE/(H_2O)	HPLC-HG-ICPMS	iAs= 0.11 ± 0.01	Pétursdóttir et al. [163]
					MAE/(H_2O/H_2O_2)	HPLC-HG-ICPMS	iAs= 0.12 ± 0.01	
					MAE/(HNO_3/H_2O_2)	HPLC-HG-ICPMS	iAs= 0.16 ± 0.01	
				No reported	MAE/(HCl/H_2O_2)	HPLC-ICPMS	iAs= 0.19 ± 0.01	Rasmussen et al. [137]
					MAE/(HCl/H_2O_2)	SPE-HG-AAS	iAs= 0.18 ± 0.02	
				No	MAE/(H_2O)	IEC-	As(III)= 0.134 ±	Leufroy

				reported		ICPMS	0.008 As(V)= 0.263 ± 0.009	et al. [253]
				7 ± 0.8	SON/(HNO_3/MeOH)	HPLC-ICPMS	As(V)= 0.4 ± 0.06	Batista et al. [103]
				No reported	Shaking/SON/(H_2O)	CE-ICPMS	As(V)= 1.40 ± 0.04	Liu et al. [217]
CRM n 9	*Sargassumfulvellum*	NIES	115 ± 9	110.3 ± 0.7	Shaking/(Water)	HPLC-ICPMS	As (V) = 69.9 ± 1	Llorente-Mirandes et al. [260,261]
				117 ± 2	Shaking/(Water)	HPLC-ICPMS	As(V)= 68.5 ± 6.6	Ruiz-Chancho et al. [262]
				109 ± 2	MAE/(Water)	HPLC-(UV)-HG-AFS	As(V)= 70 ± 1	Garcia-Salgado et al. [170]
BCR-279	*Ulva lactuca*	IRMM	3.09 ± 0.21	2.9 ± 0.3	Shaking/(Water)	HPLC-ICPMS	As(III)= 0.06 ± 0.03 As(V)= 0.53 ± 0.04	Pell et al. [263,264]
				3.4 ± 0.1	SON/(Water)	HPLC-ICPMS	As(V)= 0.7	Caumette et al.[265]

Notes. The ± terms are as provided by the original publications. They are predominantly standard deviations for some number of replicates or in some cases uncertainties. MAE; Microwave Assisted Extraction; SON: Sonication; PAEH: Pressurized Assisted Enzymatic Hydrolysis Extraction; UAE: Ultrasound-Assisted Extraction.

Table IV. Proficiency tests and method validation focused on the determination of iAs in foodstuffs organized by EC-JRC-IRMM.

Proficiency test	**Type of food**	**Objective**	**Analyte**	**Assigned values (mg As kg^{-1}) [a]**	**Results of participants [b]**	**Con**
IMEP-107 (2010)	**Rice** (produced by IRMM)	Judge the state of the art of analytical capability for the determination of total and iAs	tAs and iAs	tAs= 0.172 ± 0.018 and iAs= 0.107 ± 0.014	tAs, z= 77% (n=71) and iAs, z= 75% (n=21)	· Sa iAs. · Th that · A unce
IMEP-30/109 (2010)	**Dogfish liver** (NRC DOLT-4) CRM	· To evaluate the analytical capabilities of nominated NRL and other laboratories	Cd, Pb, As, Hg, iAs and MeHg	tAs= 9.66 ± 0.62 and iAs= not assigned	· IMEP-30: tAs, z= 89% (n=42) and no scored for iAs · IMEP-109: tAs, z= 85% (n=28) and no scored for iAs	· Fe resu · Un

IMEP-112 (2011)	**Wheat** (produced by IRMM)	To judge the state of the art of the determination of total and iAs in food	tAs and iAs	tAs= 0.177 ± 0.012 and iAs= 0.169 ± 0.025	tAs, z= 84% (n=51) and iAs, z= 58% (n=23)	· Sa
	Vegetable food (NIST SRM 1570a spinach leaves)			tAs= 0.068 ± 0.012 and iAs= 0.054 ± 0.012	tAs, z= 74% (n=35) and iAs, z= 77% (n=23)	· Sa
	Algae (produced by IRMM)			tAs= 58.3 ± 7.0 and iAs= 0.188 ± 0.025	tAs, z= 82% (n=41) and iAs, z= 16% (n=6)	· Lo scor · Tw bias · Ur dige
IMEP-39/116 (2013)	**Mushroom** (produced by IRMM)	To test the analytical capabilities of laboratories to determine heavy metals and tAs and iAs in mushrooms.	Cd, Pb, As, Hg and iAs	tAs= 0.646 ± 0.048 and iAs= 0.321 ± 0.026	· IMEP-116: tAs, z= 91% (n=29) and iAs, z= 81% (n=13) · IMEP-39: tAs, z= 65% (n=35) and iAs, z= 64% (n=7)	· In satis · In for i · F repo ICP · A were
IMEP-118 (2014)	**Canned food (peas in brine)** (produced by IRMM)	· To assess the analytical capabilities of participating laboratories · To evaluate the various sample preparation approaches when analyzing canned vegetables using the drained product or the the solid/liquid composite	As, Cd, Pb, Hg, Sn and iAs	Drained product: tAs= 0.117 ± 0.018 and iAs= 0.098 ± 0.020	tAs, z= 92% (n=47) and iAs, z=84% (n=16).	· iA agre · over
				Solid/liquid composite: tAs= 0.121 ± 0.014 and iAs= 0.082 ± 0.008	tAs, z= 82% (n=42) and iAs, z=74% (n=17).	· tA drai soli · A t · A unce · Si repo meth
IMEP-41 (2014)	**Rice** (IMEP-107)	· To determine the performance characteristics of an analytical method for the quantification of inorganic arsenic in food by FI-HG-AAS	· Inorganic arsenic	iAs= 0.108 ± 0.011	· RSD_r= 7.8% · RSD_R= 15.6 · Overall mean= 0.096 ± 0.030 · Rec= 88.9 ± 29.4	
	Wheat (IMEP-112)			iAs= 0.165 ± 0.021	· RSD_r= 10.1% · RSD_R= 10.9% · Overall mean= 0.146 ± 0.032 · Rec= 88.7 ± 22.5	
	Mussels (ERM-CE278k)			iAs= 0.0863 ± 0.008	· RSD_r= 8.6% · RSD_R= 18.2% · Overall mean= 0.133 ± 0.048 ·Rec= 153.7 ± 57.6	

Cabbage (IAEA-359)	iAs= 0.091 ± 0.016	· RSD_r= 9.6% · RSD_R= 22.1% · Overall mean= 0.074 ± 0.033 · Rec= 81.6 ± 38.7	· Th in t agre expe by i orga spec
Mushroom (IMEP-116)	iAs= 0.321 ± 0.026	· RSD_r= 4.1% · RSD_R= 6.1% · Overall mean= 0.275 ± 0.034 · Rec= 85.8 ± 12.6	
Seaweed (NMIJ-7405a)	iAs= 10.10 ± 0.50	· RSD_r= 4.7% · RSD_R= 15.2% · Overall mean= 7.548 ± 2.301 · Rec= 74.7 ± 23.1	
Fish (DORM-4)	iAs= 0.271 ± 0.061	· RSD_r= 10.3% · RSD_R= 22.8% · Overall mean= 0.295 ± 0.134 · Rec= 108.8 ± 55.4	Poin cont sepa
Rice (ERM-BC211)	iAs= 0.124 ± 0.011	Pre-test item of participants laboratories	Labo the IME

[a] Assigned value for expert laboratories as $X_{ref} \pm U_{ref}(k = 2)$;

[b] In IMEP-107, IMEP-30/109, IMEP-112, IMEP-39/116 and IMEP-118: results of participants are referred to % of z-score to $z \leq 2$ (n=number of laboratories).

RSD_r= repeatability relative standard deviation; RSD_R= reproducibility relative standard deviation; Rec=Recovery= X participants· 100/X assigned value.

Inorganic arsenic determination in food: A review on analytical proposals and quality assessment over the last six years

Figure captions

Figure 1. Blue plot is the number of papers published each year dealing with the As species either iAs as a function of time (1985-2014). Red plot refers to number of papers dealing with speciation of As species and iAs in the field of food and alimentation. Green plot shows the number of publications dealing only with iAs and relationship with food and alimentation.

Figure 2. Distribution of publications (2010-2015) on the basis of research area of inorganic arsenic (a) and on the basis of types of analyzed foods of inorganic arsenic (b).

Figure 3. Scheme of the different steps required to perform total and inorganic arsenic determination in foodstuffs.

Figure 4. Anion exchange HPLC-ICPMS chromatograms of rice (a), infant multicereals (b), Hijiki seaweed (*Sargassum fusiforme*) (c), mushroom supplement (*Grifola frondosa,* commercially known as Maitake) (d), tuna fish (e), and mussel (f).

Figure 5. Inorganic arsenic concentration in NIST SRM 1568a reported in the literature (blue rhombus, 2010-2015). The continuous black line represents the average concentration and the red dashed lines delimit the target interval (X ± SD = 0.098 ± 0.009 mg As kg^{-1} of inorganic arsenic). X axis shows the measurement technique and reference.

Figure 6. Inorganic arsenic concentration in NRC-CNRC TORT-2 reported in the literature (green rhombus, 2010-2015). The continuous black line represents the average concentration and the red dashed lines delimit the target interval (X ± SD= 0.606 ± 0.215 mg As kg^{-1} of inorganic arsenic). X axis shows the measurement technique and reference.

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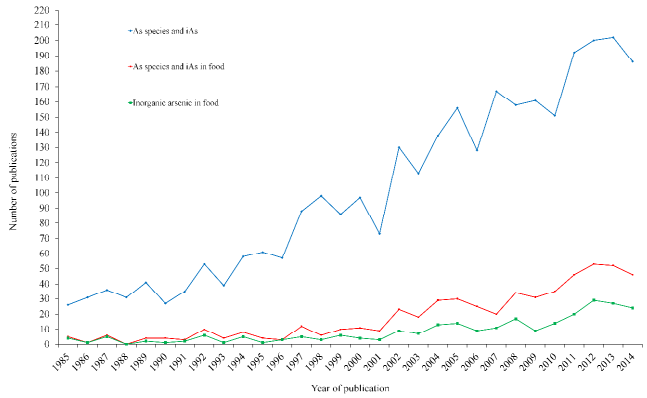

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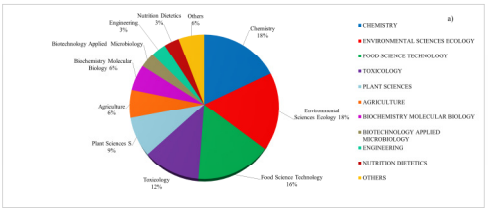

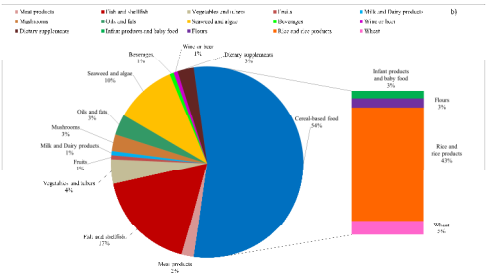

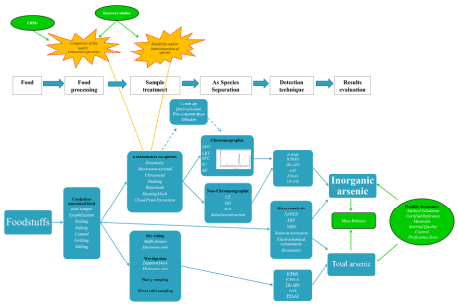

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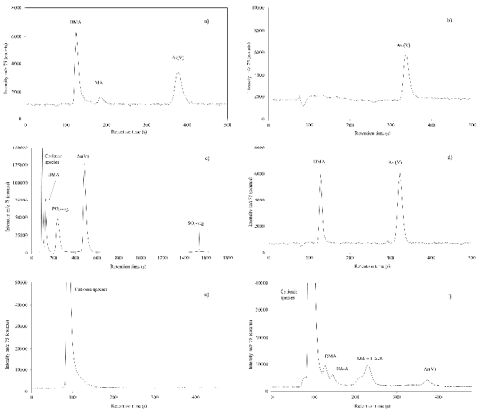

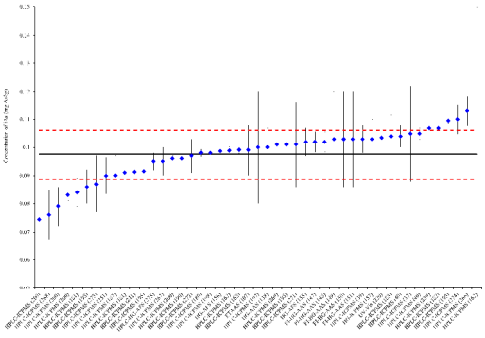

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