JAAS

Accepted Manuscript

This is an *Accepted Manuscript*, which has been through the Royal Society of Chemistry peer review process and has been accepted for publication.

Accepted Manuscripts are published online shortly after acceptance, before technical editing, formatting and proof reading. Using this free service, authors can make their results available to the community, in citable form, before we publish the edited article. We will replace this *Accepted Manuscript* with the edited and formatted *Advance Article* as soon as it is available.

You can find more information about *Accepted Manuscripts* in the Information for Authors.

Please note that technical editing may introduce minor changes to the text and/or graphics, which may alter content. The journal's standard Terms & Conditions and the Ethical guidelines still apply. In no event shall the Royal Society of Chemistry be held responsible for any errors or omissions in this *Accepted Manuscript* or any consequences arising from the use of any information it contains.

ROYAL SOCIETY OF CHEMISTRY

www.rsc.org/jaas

Measurement of arsenic species in environmental, biological fluids and food samples by HPLC-ICPMS and HPLC-HG-AFS

W Maher[1], F Krikowa[1], M. J. Ellwood[2], G Raber[3] and S Foster[1]

[1]Ecochemistry Laboratory, Institute for Applied Ecology, University of Canberra, Bruce, ACT 2601, Australia

[2]Research School of Earth Sciences, The Australian National University, Canberra, ACT 0200, Australia.

[3]Institute of Chemistry, Karl-Franzens, University Graz, Universitaetsplatz 1, 8010 Graz, Austria

Abstract

The importance of measuring arsenic (As) species has been appreciated for a long time mainly because of the wide spread knowledge of arsenic's toxicity and its use as a poison. Increasingly health, environmental and food regulations have been written around As species rather than total concentrations. Knowledge of As speciation is important as the chemical form of As controls its bioavailability, toxicity, mobility and therapeutic benefits. Arsenic is present as inorganic (arsenate, arsenite, thioarsenates), complexed (arsenic glutathionines and phytochelatins), low molecular weight (monomethylarsonate, dimethylarsenite, arsenobetaine, arsenocholine etc.) and high molecular weight (arsenic hydrocarbons and arsenic phospholipids) species. In this review we cover the intergrity of As species during collection, storage, sample preparation and measurement by HPLC- ICPMS and HPLC-HG-AFS. The major conclusion is that it is essential to ensure that As species, especially in waters and sediments, are not artefacts of the preservation or extraction procedure. Most biota and sediment samples can be stored frozen (-20^{o}C), but the stability of water and sediment samples is matrix dependent and depends on preservation technique applied. Arsenic cannot be extracted from samples using a single set of conditions but must be optimised for each sample type. Methanol-water mixtures with microwave heating are commonly used to extract polar As species from tissues while As-lipids required a non-polar solvent. Dilute acid can be used to increase the efficiencies of extraction of hard to extract tissue As species. Freeze drying is suitable for the drying of biotic material while sediments should not be dried before analysis. Extraction efficiencies are critically dependent on particle size. Polar As species have a wide variety of ionic characteristics thus complimentary chromatographic

approaches utilising ion-exchange or reverse phase columns with modifiers are needed to separate all the As species. Arsenic-lipids require the use of a reverse phase columns and gradient elution with high concentrations of organic solvents and require compensation for carbon enhancement effects in the ICPMS. Care must be taken that chromatographic peaks are not misidentified and matrix interferences accounted for that may influence quantification. Finally, to ensure accurate results, mass balances and extraction and column recoveries need to be determined at all steps. Methods need to be evaluated using As spikes and certified reference materials to provide a means of assessing the quality of results

No of pages: 113 (with Tables and Figures)

No of Tables: 7

No of Figures: 9

17/4/ 2015

Introduction

In nature, arsenic (As) is widely distributed and found at low concentrations in all living matter, and while As has no known biological function, a growing body of evidence suggests that As may be an essential element, playing a role in methionine metabolism as well as in DNA methylation [1]. The importance of measuring As species has been appreciated for a long time because the toxicity of As varies depending on its redox state and its chemical form [2, 3]. Until the early 1980s, however, it was common practice to only measure total As concentrations. Understanding the chemical species of As is also necessary from other standpoints as it controls bioavailability, mobility and therapeutic benefits. The importance of measuring and quantifying As species includes:

Food standards: Where knowledge of the potential toxicity of As species or its role as the active ingredient in food stuffs and supplements is known, food standards require the concentration of that particular As species to be determined [4, 5]. For example, As concentrations in rice require inorganic As (AsO_3^{3-}, AsO_4^{3-}) concentrations to be determined.

Acceptance of agricultural goods: Often agricultural goods will not be accepted without knowledge of the As species present. For example, lobsters exported from Western Australia to Japan was not allowed until it was shown that the As content in lobster tissues was present as benign arsenic species, primarily arsenobetaine ($(CH_3)_3As^+CH_2COO^-$) rather than the toxic inorganic arsenic species (AsO_3^{3-}, AsO_4^{3-}) [6]. Similarly, to import seaweed products it is necessary to prove the products contain the relatively benign arsenoribosides (see Fig 1, arsenoribosides) than the toxic inorganic As species.

Human occupational and environmental exposure: Often urine and blood measurements of arsenic are used to assess occupational exposure to arsenic. However, if the subject has eaten a seafood meal their urine may contain high As concentrations [7]. Measurement of the arsenic species present can resolve this problem as environmental exposure to inorganic arsenic invariably results in high dimethyl arsenate ($(CH_3)_2AsOOH$) concentrations while ingestion of seafood results in high arsenobetaine concentrations.

Ecosystem protection: Knowledge of As species is essential for the protection of aquatic life. For example, inorganic As in water may be toxic to some freshwater organisms

Understanding the action of a chemical species in a food stuff or nutritional supplement: As mentioned above, some food regulations require specification of the active ingredient of foodstuffs or supplements. However, another important reason for determining the chemical species is to understand the beneficial action of an element. For example, many food stuffs are promoted for their anti-carcinogenic activity [8]. Evaluation of the role of As in preventing cancers has required the active species to be identified [8, 9].

Increasingly health, environmental and food regulations have been written around a knowledge of As species rather than total concentrations. In the environment, As is present as inorganic (arsenate (As(V)), arsenite (As(III)), thioarsenates), complexed, (As glutathionines (AsGSH) and phytochelatins (AsPC)), low molecular weight [monomethylarsonate (MA), dimethylarsenite (DMA), arsenobetaine (AB), arsenocholine (AC) etc.] and higher molecular weight (As hydrocarbons and As phospholipids) species (Table 1). Volatile As species (TMAs, As-hydrides) are also produced by bacteria and fungi [10, 11].

Arsenic is present in all organisms, but is found at high concentrations in marine organisms as a variety of As species. Seaweeds mainly contain arsenoribosides, while AB is the major As species in marine animals [12], but there are at least 40 minor arsenic species [13]. Recently two new classes of As species, the thio-As species where the 'O' bonded to As is replaced by an 'S' and As-lipids (As hydrocarbons and As phospholipids), have been revealed thereby increasing the complexity of As species that exist in organisms [14-17].

The advent of inductively coupled plasma mass spectrometry (ICPMS) has made it relatively easy to measure As concentrations [18] and it provides some important benefits when coupled to high performance liquid chromatography (HPLC), which is used to separate As species prior to As measurement. ICPMS has low detection limits and a high sampling rate (~ 1 ms), thus transient signals can be determined and closely eluting As species from HPLC can be separated and quantified. The disadvantage of ICPMS is its inital captial cost, the on-going maintaince and running costs, and its high argon usage. Atomic fluorecence spectroscopy (AFS) provides a low cost alternative and is increasing being used in conjunction with HPLC and hydride generation (HG) to measure As species in biological extracts, urine, blood, wine, beer etc [19-23]; typical applications using these approaches are presented in Supplementary Table1.

The last comprehensive critical review of methods and applications was published in 2004 and reviewed publications in the period 2000-2003 [24]. Since then reviews covering (1) the preservation of As species in water [25], (2) sample preparation and extraction procedures for plants [26, 27], algae [26, 28] and air particles [29], (3) HPLC-ICPMS speciation analysis [28, 30-32] have been published. As well, a review of complementary As speciation methods (HPLC-ICPMS, EIS-MS and XAS) has been undertaken [33]. Information on storage, preparation and extraction is scattered; information that is essential for maintaining the integrity of As species while information on instrumental analysis is of a general nature. An exception is Neigel and Mtysik's [28] comprehensive review on the determination of arsenosugars in marine macroalgae. In this review we examine sample storage, preparation and extraction procedures and the pratical use, based on our experience, of HPLC-ICPMS and HPLC-HG-AFS to quantify As species concentrations in environmental, biological fluids and food samples. To highlight analytical issues with As determination, examples to illustrate important considerations will, where possible, come from the authors laboratories. We have chosen to focus on HPLC-ICPMS and HPLC-HG-AFS techniques because of their widespread use for measuring As species in 'real samples'. Techniques such as capillary electrophoresis and gas chromatography, although reported in the literature, are not widely used because they do not offer any signficant advantage over HPLC-ICPMS or HPLC-AFS, or as in the case of electrophoresis, does not have the required detection limits for routine As quantification. Arsenic species used in agriculture, e.g. arsanilic acid, are not reviewed. The nomeclature (names and abbreviations) used in this review are as proposed by [13] (See Table 1).

Sample preservation and storage

A summary of the effects of physicochemical variables on arsenic species stablity is given in Table 2.

Waters and biological fluids

<u>As (III), As (V) and simple oxo-methylated As species</u>

The interconversion of As(III) and As(V) in water samples readily occurs and appears to be matrix dependent with problems of As(III) being oxidised to As(V) being widely reported. The

oxidation of As(III) to As(V) can be facilitated by the presence of Fe(III), MnO_2 and dissolved organic matter [34-36]. The addition of air to anoxic samples promotes the oxidation of As(III) by Fe(III) as well as removal of As from solution through the precipitation of iron-hydroxy compounds [37, 38]. Sample exposure to light also promotes the photooxidation of As(III) to As(V) [39]. The storage of samples in the dark and the use of preservatives such as EDTA [40] or phosphoric acid [41] can help preserve As(III) and As(V) species, especially in solutions containing high concentrations of iron and manganese. Arsenates can also be reduced to As(III) by humic and fulvic acids [42, 43]. Given the problems with preserving As(III) and As(V), the use of solid phase anionic extraction cartridges [44-47], to selectively retain As(III), As(V), oxo-MA and oxo-DMA in the field provides a rapid means of immobilising and preserving these species. By choosing appropriate columns, loading pH and eluent concentrations, these species can be selectively retained and eluted. Generally, As species such as oxo-MA and oxo-DMA are stable if microbial activity is minimised or eliminated by acidification, the addition of a preservative or by freezing (Table 2).

Many different procedures have also been reported for the storage of biological fluids. For example, storage of urine at reduced temperatures and in the dark [22, 48, 49], saliva at – 20 ^{o}C [50] and blood separated into cells and plasma followed by storage at – 80 ^{o}C [51]. Goat blood spiked with As(III), As(V), oxo-MA and oxo-DMA stored at 4 ^{o}C and -20 ^{o}C without additives was stable for at least 2 months [52].

The stability of MA(III) and DMA(III) in aqueous solutions is questionable as MA(III) and DMA(III) are rapidly oxidised to MA (V) and DMA (V), respectively. For example, in urine MA(III) and DMA(III) are lost within 3 days and 17 hr, respectively, when stored at -20^{o}C [53].

Thio-methylated As species

Thio-MA and thio-DMA standards are stable for several days when stored at 4 °C, while the stability of thio-As species in samples is matrix dependent [54]. Wallschläger and London [55] showed that acidification of samples causes an immediate and complete loss of dithio-MA and dithio-DMA species, sometimes with an increase in mono thio-As species, and in some cases a decrease in oxo-As species occurs with thio-As species being formed. They recommended the use of cryofreezing to preserve As species.

Thioarsenates

The filtration of samples through 0.22 μm syringe filters to remove bacteria followed by storage in opaque bottles, to prevent photoxidation, helps with thioarsenate species presevation [56]. Suess and co-workers [57] reported that the preservation of mono- and di-thioarsenates can be achieved for a limited time (~21 days) by flash freezing, minimising oxygen exposure by reducing the head space within bottles, and by addition of EDTA to minimize the effect of Fe(III) oxidation. The addition of NaOH or ethanol also assists in minimising oxidation of thioarsenate species however, tri- and tetra thioarsenates cannot be stabilised. If samples contain tri- and tetra thioarsenates, after flash freezing, they need to be placed in an Anaerobe Container System to prevent exposure to any oxygen and stored on dry ice if transported to the laboratory,.

Changes in As speciation can occur within hours if air is introduced into samples with thioarsenate species degrading to As (III) or As (V). Thioarsenates are transformed to As(V) and sulfide via ligand exchange of OH for HS, ($HAsO_3S^{2-}+OH^- \rightarrow HAsO_4^{2-}+HS^-$), decomposition to As(III) and sulfur ($HAsO_3S^{2-}+H+ \rightarrow H_2AsO_3^{2-}+S$) or oxidation of S to SO_4^{2-} by oxygen, which is then replaced by OH^- ($2\ H_2AsO_3S^- + 5\ O_2 \rightarrow 2HAsO_4^{2-} + 2\ SO_4^{2-} + 2\ H^+$). Some of these pathways result in As(V) formation, however, the reduction of As(V) to As(III) can occur due to sulphide oxidation. A reduction in thioarsenates can also occur if solutions are purged with nitrogen or argon through the removal of HS^- from solution [58]. Excessive purging of thioarsenate solutions with N_2 or Ar therefore should be avoided.

Acid preservation should also be avoided as oxygen-sulfur exchange has been reported to occur in acid preserved sulfidic waters [59, 60]. If thioarsenates are to be stored for any period it is recommended that samples be flash frozen, stored at -80 °C, in the dark, and under a nitrogen atmosphere [60-62].

Biota

As (III), As (V) and simple oxo-methylated As species

Marine algae and animals: Arsenic species and totals in frozen and freeze dried tissues have been shown to be stable for an indefinite period [63-66], however, a decrease in As concentration can

occur in some samples that are frozen for periods greater than 1-3 months e.g. blue mussels [65]. Inorganic As concentrations remained the same indicating that degradation of organic As species did not occur. No explaination for loss of As was given. Failure to freeze samples will result in some degradation of As species due to microbial action. The production of $(CH_3)_3As$ as a degradation product has been reported in fish [67]. Freeze dried samples are not likely to result in changes in As speciation as microbial or chemical conversion cannot occur in dried samples as long as they are dessicated.

Although most As species are stable in frozen samples, freezing and thawing of samples before drying and extraction may result in the loss of As. For example, the thawing of frozen seaweeds results in water lost from samples which leads to a significant reduction in As concentration. Thus, seaweed samples should not be frozen and thawed before freeze drying.

Plants: Huang and Ilgen [68] evaluated the storage of fresh and freeze dried spruce needles and *Spagmum* moss at 2 ^{o}C, 25 ^{o}C and – 20 ^{o}C for a month. They found that the concentration of methanol-water extractable (1:5 v/v) As species decreased with storage except for wet needles. For wet needles, the concentration of organic As species varied with DMA concentrations decreasing with an increase in storage temperature in the order 25 ^{o}C < 2 ^{o}C < -20 ^{o}C . AB and TMAO concentrations also decreased after storage. They found that none of the storage procedures preserved As(III)/As(V) speciation. The concentration of As species varied less in freeze dried samples when stored for one month but As(III)/As(V) ratios decreased with increasing storage temperatures, indicating that the rate of As(III) oxidation increases with temperature . It was recommended that samples be freeze dried if plants are to be stored for long periods. Amaral and co-workers [69] evaluated the storage of *Brachiaria brizantha* samples. No significant differences were found between fresh samples and those freeze dried, chopped and stored at 4 ^{o}C, -18 ^{o}C or – 80 ^{o}C for 12 months, however, DMA was not extracted. Samples that were freeze dried, milled with liquid nitrogen and stored at room temperature gave higher As recoveries and similar results for As(III), As(V) and DMA over a 12 month period.

Thio-methylated As species

No information is available on the long term stability of thio-methylated As species in biota. It is presumed that similar precautions, e.g. freeze drying of samples, are needed to prevent microbial action and degradation/conversion of As species.

Arsenic glutathionines and phytochelatins

Raab and co-workers [70] found that when plant samples were stored at -20 ^{O}C for four weeks, As phytochelatin complexes were degraded. A subsequent study in which plant samples were stored at -80 ^{O}C showed that the major species AsPC3 are relatively stable, but some minor As species degraded [71]. Bluemlein and co-workers [71] recommended that freeze drying of plants not be performed for As-PC analyses as more than 90% of the As-PC complexes are destroyed. Munoz and co-workers [72], however, reported that freeze drying of *Chlorella vulgaris* before extraction did not result in the loss of As-PC complexes.

Sediment and soils

Little information is available on the stability of As species in stored sediment and soils, however, similiar to biota, failure to freeze samples will likely result in degradation of As species due to microbial action.

Huang and Illgen [68] found that for wetland soils, methanol-water (1:5 v/v) extractable and inorganic and organic As species concentrations decreased for fresh and freeze-dried sediments that were stored for one month at 25 ^{o}C, 2 ^{o}C and – 20 ^{o}C. It was noted that the freezing of fresh wetland soils released water, thus care needs to be taken that no As species are lost with water released, as can occur for seaweeds. For freeze-dried mineral soils that contained only inorganic As, methanol-water (1:5 v/v) extractable As concentrations varied little compared to freshly prepared samples. Extractable As concentrations increased in the order 25 ^{o}C > 2 ^{o}C > -20 ^{o}C.

Air particles

Oliveira and co-workers reported that As species in air particles collected on quartz air filters were stable for 33 months. Total As concentrations and speciation after extraction and analysis did not change significantly, however, no details on storage conditons were given other than that the filters were dried and wrapped in aluminium foil. Sánchez-Rodas and co-workers [73]

conducted a similar study in which samples were stored and determined monthly for a year and obtained similar results. Again no details of storage conditons were given.

Overview and recommendations

As waters and biological fluids undergo can undergo many physical, chemical and biological reactions a summary of the effects of physiochemical variables on As species stability is given in Table 2 with appropriate preservation techniques. As well, references are indicated that give more information on specific effects. It is evident that the reactions that can occur will be dependent on the sample matrix. Some reactions such as photoxidation can be easily prevented by excluding light while bacteria can be removed by filtration. Freezing or acidification is widely used to prevent a range of chemical (precipitation, complextion, hydrolysis)and biological (microbial and algal growth) reactions. These procedures, however, may cause other physical (photooxidation), chemical (oxidation-reduction, destabilisation of As-S species) and biological (algal cell disruption) effects. Acidification should be avoided as the As(III)/As(V) equilibrium and As-S species are disrupted. Unless preciptation of Fe, Mn or Ca is expected, removal of bacteria by filtering, removing oxygen in container head spaces by N_2 purging, flash freezing with liquid N_2 and storage under anaerobic conditons will probably prevent oxidation and dissociation of most As species. An exception is samples in which MA(III) and DMA(III) are to be determined; these species cannot be preserved or stored.

Most As species in biota are stable if samples are frozen (-20 ^{o}C) or freeze dried. An exception may be samples for AsPC analysis that need to be stored at least at -20 ^{o}C. Care should be taken with biotic samples such as seaweeds that contain a significant quantity of water. Freezing and thawing of samples will result in the loss of water and As. These type of samples should not be frozen and either analysed fresh or immediately freeze dried.

Drying and/or oxygenation of sediment and soils will cause the interconversion of As(III) and As(V)(see sample preparation section). Thus samples should be fozen to prevent microbial degradation of As species. If sediments are anoxic, precautions should be taken to exclude air to prevent oxygenation of samples.

Sample preparation

Removal of extraneous material

Macroalgae and plants, often need to be cleaned to remove surface material and epiphytes before analysis, as they can contain As species that can bias speciation results. Slejkovec and co-workers [74] advocated washing seaweeds with a 0.38% m/v NaCl solution so that cells are not disrupted due to osmotic pressure differences. In addition, a range of procedures including brushes and razor blades have been used to remove epiphytes [26], however, rarely are samples checked under a microscope to determine if surface material has been removed. For some samples, it is impossible to remove contaminating organisms. For example, seaweeds contain symbiotic fungi that are part of the plant matrix [75] and cannot be removed by washing or scrapping. Several studies have reported the presence of AB in seaweeds and seagrass leaves [74, 76] an As species not thought to be produced by these organisms and likely to be produced by associated epiphytes.

Animals need to be depurated before analysis as their digestive systems may contain sediment particles or undigested plant and animal tissues, which can contain As species that can bias speciation results. For example, many fish that fed on seagrass epiphytes contain undigested seagrass blades which contain mostly inorganic As [77]. Thus, if seagrass material is not depurated, elevated inorganic As concentrations will be determined in animals.

Efficacy of drying- changes in As speciation

Plants Huang and Illgen [68] compared the drying of two plants (*Picesabies* needles *Sphagnum* moss) by air (25 ^{o}C and 65 ^{o}C), nitrogen (25 ^{o}C) and freeze drying. The highest methanol-water (1:5 v/v) extractable As concentrations obtained for needles were in the following order: air (60 ^{o}C) > air (25 ^{o}C) > nitrogen > freeze dry > wet (extracted 27.1-63 %); for mosses the order was: wet > air (60 ^{o}C) > nitrogen > air (25 ^{o}C)~freeze drying (extracted 36.9-70.4 %). A shift in extractable As species occurs upon drying with a decrease in extractable TMAO and oxo-DMA after freeze drying, which is believed to result from demethylation: however, this is more likely

to be the result of shifts in the binding of As species to plant components on drying. All drying procedures caused changes in As (III)/As (V) ratios and organic As species concentations. Amaral and co-workers [69], however, found no significant changes in As(III), As(V) and DMA in *Brachiaria brizantha* samples when freeze dried, ground in liquid nitrogen and stored at room temperature. They noted that freeze drying was required to extract DMA. Smith and co-workers [78] investigated the speciation of As in radish plants using X-ray Absorption Near Edge Structure (XANES) and showed that drying converted As-S species to As(III), but with little oxidation of As(III) to As(V). Mir and co-workers [79] compared the XANES spectra of dried frozen plants (plants frozen after sampling then dried), dry ground plants and dried residues after the sequential extraction of plants. No significant changes in the oxidation state of As(III) and As(V) occurred for dried frozen plants and dried ground plants. However, shifts occurred from $As(Glu)_3$ to As(III). Bluemlein and co-workers [71] recommended that freeze drying of plants not be performed for As-PC analyses as more than 90% of the As-PC complexes are destroyed. Munoz and co-workers [72], however, reported that freeze drying of *Chlorella vulgaris* before extraction did not result in the loss of As-PC complexes. Jedynak and co-workers [80] examined the effect of drying on As speciation of White mustard (*Sinapis alba*). Although they state that drying did not significantly change As speciation, As(III)/As(V) ratios were influenced by drying and the use of liquid nitrogen during grinding.

Marine biota: It has been shown that oxo-methylated As species in extracts of fresh and freeze-dried material are identical [81]. Arsenic species in freeze dried samples are stable for years [66]. Kahn and co-workers [17] reported that oxidation of thio-methylated As species during freeze drying also does not occur. Lewis and co-workers [63] reported a small reduction of inorganic As (0.4 ± 0.21 %) in freeze-dried homogenised samples of two fish, Mergrim and Place, compared to wet homogenisation and analysis. No reasons could be given for the differences observed.

Marine sediments: To determine the effect of freeze drying and exposure to air on As species in sediment, Ellwood and Maher [82] compared the As species in three anoxic marine sediment samples before and after freeze drying. The percentages of As extracted from two of the samples that were freeze dried were higher than the non-freeze dried samples. The non-freeze dried samples contained significant amounts of arsenosugars. Upon freeze drying, there, however, was

a significant reduction in the concentration of arsenosugars and a corresponding increase in the concentration of As(V), but no evidence of oxo-MA or oxo-DMA formation. The increase in As(V) concentration probably resulted from the oxidation of Arseno-pyrite present within the samples. These results indicate that the speciation of As determined within sediments is strongly influenced by drying. Traditionally, sediment samples are freeze dried and exposed to air prior to being extracted. Clearly, this influences the speciation of As thereby giving a false impression of the "true" speciation of As within sediment samples.

Terrestrial sediments: Huerga and co-workers [83] compared the effects of freeze drying, oven drying, microwave heating and air drying on water and phosphate buffer exchangeable fractions of As (no details of the temperatures used were given). Drying procedures did not influence the amount of water extractable As, but freeze drying and air drying yielded higher amounts of phosphate extractable As. Arsenic speciation measurements were not performed on the initial wet sediment, thus the extent of As(III)-As(V) transformation is unknown. Huang and Ilgen [68] investigated the effect of drying on methanol-water (5:1v/v) extractable As species. For wetland soils, extractable As decreased in the following order: air (60 ^{o}C) > wet > freeze drying > air (25 ^{o}C) > nitrogen (25 ^{o}C) (Extracted 0.05-0.11 %). For mineral soils, variations in extractable As were small with air (60 ^{o}C) = air (25 ^{o}C) = nitrogen (25 ^{o}C) > wet > freeze drying (extracted 0.09-0.10 %). As (III)/As (V) ratios varied significantly between drying regimes as did oxo-MA, oxo-DMA, AB, TMAO and unknown As species concentrations for dried wetland soils.

Effects of sample grinding and particle size

Smith and co-workers [78] using XANES reported that As(III) in leafs and stems of radish plants is oxidised during grinding while Zheng and co-workers [84] could not find any As-PC complexes in plant extracts after samples had been freeze dried and ground.

Pizarro and co-workers [85] showed that due to microbiological activity, once rice grains were ground, As (III), As (V), oxo-MA and oxo-DMA were not stable under any storage conditons (4 ^{o}C and -20 ^{o}C in the dark). When ground rice was sterilised by gamma-irridation, As species remain stable. Rice can contain 10-20% moisture by weight providing a good medium for microbiological activity and conversion of As species.

Eventhough samples are often homogenised by grinding, particle size is rarely specified or characterised. The importance of particle size on As extraction has been demonstrated by Narukawa and Chiba [86] who showed that the extraction efficiency of As from rice with deionised water decreased by 10 to 30% when particle size increased from < 150 to 500 μm. Alava and co-workers [87] showed that extractable As from rice samples increased from 70% for whole grain, to ~80% for particle size below 1 mm, and to 90% for particle size below 0.5 mm to 100% when particle size was reduced to a powder. Grinding did not seem to affect As speciation. In contrast, Schmidt and co-workers [88] reported that the extracted amount of As(V) and oxo-DMA from rice did not depend on whether the rice was fresh or ground, but As(III) concentrations increase with milling.

Often analysis of certified reference materials (CRM) are used to validate methods. Most CRMs are ground to 50-400 μm e.g. NIST 1568a rice flour [89] and some are de-fatted. Most samples, however, are not de-fatted or adequately ground, bringing into question the performance of the methods validated using CRMs for 'real' samples.

Overview and rcommendations

Macroalgae and plant surfaces need to be cleaned and animals depurated or As analyses will be biased either in terms of As concentrations or As species determined. Careful consideration needs be given as to whether samples should be dried and the appropriate drying procedure. Drying is likely to cause the interconversion of As(III) and As(V) and oxidation of As-S species, especially in anoxic sediments: however, oxo- and thio- methylated As and AsPC species are generally stable. If drying is performed, the drying procedure may affect the extraction of as species, with freeze drying usually giving the best extraction efficiencies. Sample particle size critically affects extraction efficiencies and a particle size < 100 μm is recommended to obtain good extraction efficiencies. As noted, the use of CRMs to validate methods should be used with caution unless real samples are to be ground to a similar particle size and defatted.

Arsenic species analysis- general considerations

The extraction and separation procedures that can be used to isolate, separate and measure lipid, water-soluble and residue -associated As species in various samples are outlined below. There are three distinct steps in undertaking speciation analysis: (1) Total As measurement; (2) As species extraction and measurement of extract As concentration and (3) separation of As species by HPLC and ICPMS or HG-AFS quantification. Each step needs to be optimized and the selection of extractants and mobile phases for HPLC separation carefully considered. For example, when analyzing As species, if ICPMS is used, extractants and mobile phases containing chloride need to be avoided as chloride can form $^{40}Ar^{35}Cl^{+}$ molecules in the ICPMS plasma. $^{40}Ar^{35}Cl^{+}$ has the same mass to charge ratio as $^{75}As^{+}$ thus leading to overestimation of the "true" amount of As present. The use of a dynamic reaction or collision cell, however, can be used to reduce or remove this $^{40}Ar^{35}Cl^{+}$ interference [90]. The use of mobile phases with high organic contents can also extinguish plasmas, or cause As signal enhancement [91], thus effluent streams need to be split and oxygen added to the plasma to aid in the removal of carbon [92]. The choice of extraction solvent and mobile phase may also affect the integrity of As species, especially As complexes such as AsGSH [93].

Sample extraction

Arsenic species in plants, animals, sediments, soils and air particles

Water, methanol, methanol-water and buffer soluble

As (III), As (V) and oxy-methylated arsenic species

Francesconi and Kuehnelt [13] suggested that methanol was intially favored for extraction of As species from marine tissues because it extracted fewer non-arsenical compounds and was easy to remove by evaporation. Methanol is a poor extractant of inorganic As species [94], however, it appears that the efficient extraction of some As species such as TETRA requires methanol [95]. Most naturally occurring As species in marine tissues are polar and soluble in water, thus the use of methanol-water mixtures provides a good compromise between As solubility and ease of solvent removal.

Seaweeds: Most studies of As in macroalgae have used water or methanol-water mixtures [94, 96] to extract As species, with a 1:1 (v/v) the methanol-water mixture most commonly used. Mechanical agitation, sonication and pressurised liquid extraction systems have been used to aid As extraction (Table 4), however, even with the use of repeated extractions (3 or 4 extractions) recoveries of As are often low and variable (3 – 98%). Poor recoveries are often reported for red and green macroalgae [21, 74, 97]. Microwave heating is now widely used to extract As species from seaweeds and shown to give better recoveries [96].

For seaweeds, no single extraction method will remove all As species [94, 96]. The glycerol-arsenoriboside, arsenosugar 1, lacks an acidic group in the aglycone and is less polar than other arsenosugars and better extracted into methanol while the addition of water assists in the extraction of other arsenoribosides. Inorganic As is also not readily extracted into methanol. Tukai and co-workers [96] showed that the optimal methanol-water composition for As extraction varies for different genera and species of seaweeds. The extraction of As from three different macroalgae classes was optimised using a chemometric approach, with solvent composition and sample mass being the two significant factors influencing the extraction of As. Extraction temperature and extraction time did not significantly influence the extraction of As. The optimised conditions for As extraction using sample masses of 0.05-0.08 g per 10 mL of solvent at 70 ^{o}C for 5 min were: (% methanol) 56% for phaeophyta, 66% for rhodophyta and 78% for chlorophyta,. When repeat extractions were used, the percentage of As extracted from macroalgae were greater than 88%. No degradation of arsenoribosides was observed. In a subsequent study by Van Elteren and co-workers [94] they showed that the extraction of arsenosugar 1 was enhanced relative to other arsenosugars at higher methanol concentrations (>25%) because arsenosugar 1 is more polar in nature. The dimethyl arsinoyl group $(CH_3)_2As$-) is protonated below pH 3 thereby making arsenosugar 1 polar. At lower methanol concentrations, As(V) and arsenosugar 2 extraction is favored due to their ionic character. Arsenate is not soluble in pure methanol [98] while arsenosugar 2 is likely to be present in an ionized form and not readily extracted into methanol.

Narukawa and co-workers [99] demonstrated that when using microwave assisted extraction that high temperatures (90-100 ^{o}C) should not be used during the extraction process. For example, when NMIJ CRM 7405a (*Hizikia fusiforme*) was heated at 60 ^{o}C for 30 minutes, arsenosugars 2-

4 remained unchanged and extraction efficiencies were 42-50 %. At 100 ^{o}C, arsenosugars 2-4 were lost but the peak corresponding to arsenosugar 3 increased.

Plants: The use of methanol-water mixtures and water using mechanical agitation, sonification, microwave heating and pressurised liquid extraction systems have been shown to yield low extraction efficiencies (4-31%) for plant material, including rice (Table 4). Exceptions are the work of Heitkemper and co-workers [100] and Narukawa and Chiba [86]. Heitkemper and co-workers [100] extracted rice using methanol, water and mixtures of methanol-water of varying concentrations with the assistance of a pressurised liquid extraction system operated at room temperature. For CRM 1568a (rice flour) all solvent mixtures used gave good recoveries (76-105%), while "real world" samples only yielded between 24 - 36%. Narukawa and Chiba [86] extracted rice with water at 90^{o}C for 3 hrs and obtained good extraction efficiencies (97-102%). Narukawa and co-workers [101] subsequently showed that extraction of rice with water at 100 ^{o}C for 2 hours gave similar recoveries (94.7-101.6%). It has been claimed (no data given) that higher extraction efficiencies can be obtained for Chinese Brake fern (*Pteris vittata*) when it is freeze dried rather than air dried [102]. Quaghebeur and co-workers [103] obtained good extraction of As species from grasses using a solution containing 0.3 M sucrose, 50 mM 2-(N-morpholino)ethanesulfonic acid, 5 mM Ethylenediaminetetraacetic acid and 50 mM ascorbate (pH 5.5). Mir and co-workers [79] extracted plant tissues with methanol-water (1:1 v/v) followed by 0.1 M hydrochloric acid and increased extraction efficiencies from 32 ±23 to 57 ± 34 %. Others have used aqueous buffers (Tris(hydroxymethyl)aminomethane/HCl, Tris(2-carboxyethyl)phosphine, Phenylmethanesulfonylfluoride and Polyvinylpolypyrrolidone). Schmidt and co-workers [104] and reported increased extraction efficiencies (76.2 ± 1.7%). Some authors have used sequential extraction to increase extraction efficiencies. For example, Mrak and co-workers [105] extracted lichens with hot water followed by extraction with a tris buffer to increase extraction efficiencies from 19.2-22.4% to 45-83%.

Jedynak and co-workers [80] examined the effect of drying on As speciation of White mustard (*Sinapis alba*). Drying and the use of liquid nitrogen during grinding clearly increased the extraction efficiencies of As from roots, stem and leaves with water, but changed As(III)/As(V) ratios.

The use of sub-critical water (temperatures between 100 and 350 ^{o}C under pressure) has not been extensively considered as an extractant medium for As species from plants but may offer some advantages over conventional extraction techniques (see below sediment and soils). Schmidt and co-workers [106] used subcritical water and water-methanol mixtures (9: 1 and 8:2 v/v) at 150 ^{o}C to extract plants. Recoveries cannot be evaluated as only the sum of As species was given and not total As in extracts. The additon of methanol decreased the extraction efficiencies of As(III) and As(V). As(III) was not stable. MA and DMA were reported to be stable, however, data given in the paper indicates 6-18% loss of these species at 150 ^{o}C. We have used water with 2% hydrogen peroxide heated to 150 ^{o}C under presuure to quantitatively extract As species from rice samples (Recoveries 99-100%). As(III) is converted to As(V) but DMA is stable.

Animal tissues: Again water and methanol-water mixtures have been used extensively in combination with mechanical agitation, sonication, microwave heating and pressurised liquid extraction systems for the extaction of As species from animal tissues (Table 4). Thus, most methods only determine As species that are soluble in water or methanol-water solutions. This is usually not a problem when analysing marine animal muscle tissues, as As is normally present as AB and is readily extractable [12, 107], however, in other non-muscle tissues, such as in lobster heptapancreas tissues, As can be present in lipids and only isolated by extraction with solvents such as chloroform-methanol or hexane [92, 108, 109]. The extraction efficiency of As from the water-soluble fraction of marine animals using a methanol-water (1:1 v/v) mixture has been shown to be dependent on the animal species and the tissue being determined. High As extraction efficiencies has been obtained for muscle tissues (e.g. Dorm – 2; 103 ± 2%), however, lower recoveries (19-77%) are reported for other tissues (e.g. liver, hepatopancreas and digestive tissues) and whole animals (e.g. oysters and mussels) [107, 110-114]. The extraction efficiencies for fatty fish e.g. herring and mackerals, tend to be lower (37-54 %) than other fish, molluscs and crustaceans [115]. Similiarly, low As recoveries have been reported for terrestrial organisms such as benthic invertebrates (18-49 %)[116]], insects (32 ± 26 %) [117]], earth worms (28-82 %) [118]] and zooplankton (36-95 %, mean ± sd 61 ± 22 %) [119]].

Microwave assisted heating has shown to give better recoveries than shaking and sonication [94, 120]. Kirby and Maher [107] found that As can be extracted from most marine animal tissues, after freeze-drying, grinding and defatting with acetone, using a 50% v/v methanol – water mixture with microwave-assisted heating at 70ºC for 5 min. The extraction efficiencies from these tissues showed little improvement with increased extraction time (10 to 20 min).Three separate extractions were required to extract the majority of water-soluble As species. While some mechanical mixing does occur in the microwave oven from turntable rotation, high As extraction efficiencies from animal tissues will only occur at temperatures close to the boiling point of the methanol - water mixture. At temperatures around 70 °C mixing increases between the sample and solvent due to formation of thermal convection currents. The use of sub-critcal water gives similar recoveries, for example, Piñeiroand co-workers [121] used a Dionex ASE system to extract human scalp hair with water at 100 ^{o}C and 1500 psi for 5 min and obtained extraction efficiencies for GBW-07601 human hair of 80 ±1%.

Sediments and soils: Generally recoveries of As species extracted from sediments and soils with water, methanol-water mixtures or buffers are poor . An exception is the sub-critical extraction of As from soils with water [122, 123], where water is heated under pressure to 300 ^{o}C. Extraction efficiencies are increased from ~10% at 25 ^{o}C to 94-100% at 300 ^{o}C. At this temperature the viscosity, surface tension and dielectric constant of water is decreased and self ionisation increased. In comparison, sub-critical extraction with water containing citric acid, EDTA and sodium hydroxide gave similar recoveries indicating that temperature is the most important factor aiding As extraction and not the presence of a chelating agent [122]. The mechanism leading to efficient As extraction at elevated temperatures is not clear but may result from increased H^+/OH^- production or enhanced oxidative dissolution of As containing minerals e.g. $As_2O_3 + 5H_2O \rightarrow 2HAsO_4^{2-} + 8H^+$

Thio- methylated arsenic species

Thio-methylated As species can be efficiently extracted from marine algae and animal tissues with a methanol-water (1:1v/v) mixture [56]. Kahn and co-workers [17] reported that methanol is needed for extraction of thio-As species, but no data given to support this conclusion. The efficiency of As extraction is also unclear as published studies only report the total amount of As extracted with recoveries varying from 35% in gonodal material to 86-92% in Kelp powder [17,

124, 125]. Maher and co-workers [56] spiked *Ecklonia radiata* samples with three thio-arsenoribosides (arsenosugar 1, 2 and 3) at the 10 μg/g As level and extracted samples with methanol-water (1:1v/v) at 70 ^{o}C for 5 min; recoveries of 98 ± 5 (n = 5) were obtained. When extraction efficiencies of seaweed and marine animal samples containing thio- methylated As species are examined, most of the methanol-water extractant recoveries lie between 75-107 % (90 ± 15 %, n =12) of the total As present. This indicates that complete extraction of thio-methylated As species probably occurs if these species are present. For some samples, e.g. red seaweeds and the gastropod *Turbo torquatus,* extraction recoveries were low (62-75 %) and probably result from these samples containing large amounts of calcium carbonate or lipids that may inhibit extraction. A methanol-water mixture is usually chosen as the extractant because acid and alkali reagents can potentially degrade thio-As species or promote inter-conversion between oxidized and sulfide forms [54, 126]. Even with these reagents, As species degradation is only severe at high temperatures, at high acid or base concentrations and over long extraction periods. When seaweed tissues were spiked with thio-arsenoribosides at the 20 μg/g As level, Maher and co-workers [56] found that methanol-water (1:1 v/v) extraction, with microwave heating at 70 ^{o}C, gave good recoveries (107 ± 14 %, n = 12) with little oxidation of thio-methylated As species occurring over the 30 min extraction period. In contrast, extraction using rotational mixing at 25 °C resulted in the substantial oxidation of spiked thio-methylated As species (recoveries 5 – 40 %, n= 12,). Oxidation of the spiked thio-methylated As species probably resulted from interaction with air in the head space of the extraction vessel as the mixture rotated. When the two extraction methods were compared with tissues obtained from the marine gastropod *Cellana transemosica* containing only natural thio-methylated arsenoribosides, no significant differences are observed between extraction procedures. This finding indicates that when thio-arsenoribosides are incorporated under natural conditions, oxidation during extraction does not appear to occur.

Acid or base soluble As species

Low As extraction efficiencies for plant and other materials are usually obtained with methanol-water, thus acids and bases have been used with varying success to improve extraction efficiencies [117, 127]. Methods that employ microwave assisted heating generally give higher recoveries of As than non-microwave extraction techniques [128].

Seaweeds: Foster and co-workers [127] extracted BCR 279 *Ulva latuca* with 2% v/v nitric acid at 90 °C for 6 min and obtained 58 % recovery. The extraction efficiency of As from hard to extract seaweeds such as red algae *Porpyra yezonsis* can also be enhanced (113 ± 8%) using nitric acid [128].

When arsenoriboses (Arsenosugars 1-4) standards were extracted with dilute nitric acid they all degraded to a product eluting at the same retention time as the glycerol arsenoribose [127]. In practice dilute nitric acid, however, can be used for extraction because sea-weed bound arsenoribosides remain relatively stable if the samples are determined on the day of extraction.

Narukawa and co-workers [99, 129] extracted NMIJ CRM 7405a *Hizikia fusiforme* with 1 % v/v HNO_3 at 90-100 °C (time not specified) and obtained As recoveries of 96-100%. Similar to Foster and co-workers [127], they reported the conversion of arsenoribosides to other products. They also extracted *Hizikia fusiforme* with 2 % v/v Tetramethyl ammonium hydroxide at 90-100 °C (time not specified), but found As recoveries were lower (64-72%).

Plants: Some As species are "not easy" to extract and measure because they are unstable or dissociate during extraction [71]. Arsenic in rice and other plants, for example, is present mainly as inorganic As bound to glutathionines or phytochelatins [130]. If extactants are not chosen to minimise the dissociation of complexes, only inorganic As will be determined. As-phytochelatins extracts can be prepared by grinding wet samples with liquid nitrogen and extraction with chilled 1% v/v formic acid for 1 hr at 0 °C [131]. A range of dilute acids and bases such as 0.3-1.5 M orthophosphoric acid, 2 M trichloroacetic acid, 2 M tricflurooacetic acid, 1 M hydrochloric acid, 0.28-1 M nitric acid, 0.2-1 M acetic acid, 1M sulfuric acid, 1.25 M EDTA at pH 4.7, 0.66 M sodium hydroxide and 10 mM tetrabutylammonium hydroxide at various temperatures (70 - 100 ºC) and times (10 min to 6 hr) have also been used to remove As from plants utilising mechanical mixing and microwave heating [117, 132-136]. Acids tend to extract reasonable amounts of As (67-112%), whereas recoveries for base extractions are typically lower (21 – 36 %). Lui and co-workers [137] in a comprehensive study extracted rice and Chinese herbal medicines with a range of acids and heating steps (1% v/v nitric acid, 1% v/v

nitric acid-1% v/v hydrogen peroxide and microwave heating, at 55-95 °C for 60 minutes, and 2 M trifluoroacetic acid in a digestion block at 100 °C for 5 hours followed by evaporation to dryness at 160°C). They found that microwave extraction with nitric acid or nitric acid-hydrogen peroxide gave the best extractions (79-128%) compared to water (51-64%) and trifluoroacetic acid (74-84%). Recoveries of As from a range of Chinese herbal medicines (roots and shoots) with nitric acid-hydrogen peroxide were 48-160%. Narukawa and co-workers [101] compared the use of acids (nitric, hydrochloric, sulphuric, perchloric, bromide, phosphoric, formic and methane sulfonate), hydrogen peroxide, tetramethyl ammonium hydroxide and ammonium nitrate using a hot plate to extract As from rice. They found the use acids quantatively extracted As (97-104.7%0 when acid concentration was > 0.05 mol L^{-1} though some As(V) was reduced to As(III). It was suggested that I^- in rice extracts is oxidised and As(V) reduced to As(III). Extracted As under neutral to basic conditons was lower (81.7-98.5%) as some As(III) could not be extracted.

Under the conditons used, both acids and bases are likely to have destroyed any As-GSH and As-PC species present and also have facilitated As redox transformations. For example, the use of 2 mol/L trifluoroacetic acid as an extractant has been found to reduce As(V) to As(III) while the use of 30% v/v phosphoric acid as an extractant leads to the oxidation of As(III) to As(V) [136, 138, 139]. Munoz and co-workers [72] recently showed that the use of focussed sonification with 1% v/v formic acid for 30 seconds gave improved extraction efficiencies (~71%) from *Chlorella vulgaris*, an increase from 11-27% [70] and preserved the As-PC complexes. The effects of bases on the speciation of As extracted from plant samples has not been assessed.

Animal tissues: Foster and co-workers [127] extracted marine animal tissues with four extractants (water, methanol-water (1:1 v/v), 1.5 mol/L orthophosphoric acid and 1-3% v/v nitric acid). The most efficient extractant was 2% v/v nitric acid (90 °C for 6 min) which gave excellent As recoveries across a range of reference materials and "hard to extract tissues" e.g. digestive tissues (76-107%). As species (As(III), As(V), oxo-MA, oxo-DMA, AB, TMAO, DMAE, DMAA, TMAP, AC, TETRA and glycerol trimethyl arsonioribose) but not arsenosugars 1-4 were found to be stable under these optimised conditions. Batista and co-workers [140] used a modification of the 2% v/v nitric acid procedure in which 10% v/v methanol was added

and sonified for 2 minutes. Recoveries from a range of terrestrial and marine tissues including three reference materials ranged between 86-112%. A few studies have reported the use of bases to extract inorganic As species from animal tissues [141, 142]. For example, Pétursdóttir and co-workers [143] used sodium hydroxide in 50% ethanol with microwave heating at 85 ^{O}C for 5 minutes, to extract inorganic As from fish tissues. Extraction efficiencies for total As ranged between 66-102%.

Sediments: A range of acids including phosphoric, sulphuric and hydrochloric acid with and without reducing agents (ascorbic acid, hydroxylamine hydrochloride) and sonification or microwave heating have been used to extract As from sediments (Table 4). Sediments usually contain a range of As-binding sites, thus a number of sediment classification schemes have been devised to investigate the distribution of As within sediments [144, 145]. The major adsorptive phases within the sediment that have been identified, include an exchangeable fraction, an iron/manganese oxide fraction, a carbonate fraction, an organic fraction or adsorbed or incorporated into a residual or lattice bound fraction. Sodium hydroxide, hydroxylamine hydrochloride and ascorbic acid have been used to remove As associated with amorphous and well-crystallised Fe-Mn oxides, phosphoric acid or phosphoric acid/methanol (1:1, v/v) mixtures are used to remove As associated with organics while hydrochloric acid has been used to remove As from carbonates [82, 146, 147]. Procedures to extract As species from sediments have had limited success in preserving the original As redox species during extraction. As(III) appears to be stable in solutions used for extraction, however, when sediments are added As(III) is quickly oxidised to As(V). Ellwood and Maher [82] tested a number of extractants known for their ability to remove As associated with different sediment phases accompanying marine sediments. Overall the best extractant for removing As from oxic sediments was phosphoric acid, which was able to extract up to ~75% of As from some sediments. For anoxic sediments, hydrochloric acid and sodium hydroxide proved to be the best reagents for extracting As, followed by phosphoric acid. Repeated extraction of NRCC BCSS-1 with each reagent showed that the amount of As released to solution during the second extraction was 4-8%, indicating that only a single extraction step is required to obtain ~90% of extractable As. The best extractant for both oxic and the anoxic sediments was phosphoric acid. For oxic sediments spiked with 100 μg L^{-1} As(III), the recovery of As(III) after extraction was low with values ranging between 15 to 30 %.

A corresponding increase in As(V) concentration indicated that a significant amount of the As(III) added to oxic sediment solutions was being oxidised to As(V) during the extraction procedure. During the extraction process, it is likely that the oxidation of As(III) to As(V) is facilitated by redox active metals, such as iron and manganese, which are co-extracted with As. A number of "sacrificial oxidants" were added to the phosphoric acid solution in an effort to reduce the oxidation of As(III) to As(V) during the extraction procedure, but without reducing As(V) to As(III). The sacrificial oxidants tested in combination with phosphoric acid (0.5 mol/L) were hydroxylamine hydrochloride (0.1 M), cysteine (2.5 % w/v), ascorbic acid (0.5 mol/L) and mercaptoethanol (2.5 % w/v). The best results for preserving As(III) from oxidation were achieved when hydroxylamine hydrochloride was used in combination with phosphoric acid. Only a slight increase in As(V) concentration occurred for all but one reference sediment spiked with As(III), thereby indicating that little As(III) was converted to As(V) during the extraction process. No increase in the As (III) concentration was observed for samples spiked with As(V), indicating that As(V) was not reduced during the extraction process. Of the other sacrificial oxidants tested, cysteine reduced As(V) to As(III), ascorbic acid did not prevent the oxidation of As(III) to As(V), and with mercaptoethanol neither As(V) and As(III) were recovered. Similar approaches using added ascorbic acid have been used to extract As species from soils [148] and iron minerals [149]. The recoveries of As from oxic and an anoxic sediment extracted with 0.5 mol/L phosphoric acid and 0.1 mol/L hydroxylamine hydrochloride ranged between ranged between 32 % As extracted for NIST 1646 Estuarine sediment to 72 % for NIST 1941 Marine sediment indicating that there is a significant amount of As present in the sediment that is not extractable. Extraction efficiencies were greater for freeze dried ground sediments than anoxic sediments (15-79% vs 18-26%). Maher [150] also found that a significant amount of As could not be extracted (13-30 %) from sediments collected from the African coast and estuarine sediments from southern England. Only after digestion with HNO_3/HF/$HClO_3$ acids was this As recovered. It appears that if the sediment contains minerals such as arsenopyrite, little of this As is extractable. As noted previously, the freeze drying of anoxic sediments results in a significant reduction in the concentration of arsenosugars and an increase in the concentration of As(V). Although freeze drying leads to a greater extraction efficiences, the true speciation is not obtained. Other authors have also reported the oxidation of As(III) to As(V) on drying sediments [151].

It should be noted that the use of hydrochloric acid is not particulary useful for the extraction of As from sulfidic sediments such as those containing pyrite compounds; hydrochloric acid promotes the formation of H_2S and precipitation of As-sulfide complexes e.g. As + H_2S = AsS [152]. The use of alkai provides better extraction of As from sulphur rich sediments.

Air particles: Similiar to sediments, a range of acids with and without reducing agents and sonification or microwave heating have been used to extract As from air particles (Table 4). As recoveries are variable (60-100%) with sonification giving lower recoveries than microwave assisted extraction. Most studies have only reported As(III) and As(V) concentrations in samples [73, 153-155]. One study has reported measurable concentrations of DMA and TMA in airborne particulate matter [118].

Sequential extraction of As species with methanol-water and dilute nitric or hydrochloric acid

Foster and co-workers [127] described a sequential As extraction procedure for algae, plants and animal tissues using methanol-water (1:1 v/v) followed by 2% v/v nitric acid with microwave assisted heating (90 ^{o}C, 5 min). This approach was used to preserve the intergrity of As species (As(III), As(V), oxo-MA, oxo-DMA, AB, TMAO, DMAE, DMAA, TMAP, AC, TETRA, arsenosugars 1-4, glycerol trimethyl arsonioribose). The increased extraction efficencies of hard to extract organisms such as *Ulva*, seagrass and salt marsh plant leaves varied between 30-40% to 50-90% respectively. The methanol-water extraction removed most of the organic As species while the 2% v/v nitric acid removed the remaining inorganic As and some oxo-DMA. Whaley-Martin and co-workers [95] have also reported the use of this approach to increase the extraction efficiencies of hard to extract As species from terrestrial organisms.

Mir and co-workers [79] used methanol-water (1:1 v/v) followed by 0.1 M hydrochloric acid to extract As from plants grown in As contaminated soils. Methanol-water extraction efficiencies ranged between 13-105%. The use of hydrochloric acid increased the median extraction efficiency from 29 to 46%.

Enzyme soluble As species

A number of studies have reported that the use of trypsin [123], trypsin in 0.1 mol/L ammonium hydrogen carbonate [156], amylase [157], pepsin and pancreatin [134], protease Type XIV and

amylase [158] and protease and lipase [159] with and without the use of sonification. All give good recoveries of As (80-110%) extracted from hair, rice, baby foods, fish and crustaceans (Table 4). Long extraction times are normally required (12-24 hours) but can be shortened to 3-10 minutes if samples are ultrasonificated [159-161]. The use of ultrasonification disrupts cell walls and facilitates the interaction of enzymes with cells. For example, Sanz and co-workers [159] extracted human hair with lipase and protease and released 60% of the As within 10 minutes.

Organic solvent soluble As species

To extract arseno-lipids from fish tissues or oils, hexane [92, 160], methanol [162-165], ether [166], chloroform/methanol (2:1 v/v) [108, 109, 167-173], hexane-methanol [14] and hexane-methanol-dichloromethane [174], and methanol-dichloromethane [175] have been used. When methanol is used in conjuntion with dichloromethane as a component of the solvent mixture, greater recoveries of the arsenic phospholipids are obtained [175].

Validation of the use of extractants

There is on-going concern that extraction procedures alter the As species extracted. XANES has been used to analysis As species in solid samples to determine whether As species change during extraction. As-S species in particular have been shown to convert to As(III)/As(V) when extracted and determined by HPLC-ICPMS, for example, in rice [129]. Three reasons are given for conversion of As species during extraction and HPLC-ICPMS:

1) *Oxidation and dissociation during grinding and drying*. The release of cellular compounds causes As-S to dissociate and As(III) to oxidise to As(V). Maher and co-workers [176] extracted freeze dried and ground rice samples with 2% v/v nitric acid at 90 ^{o}C for 10 minutes and used XANES and HPLC-ICPMS to compare As species, pre- and post extraction. Good agreement using both techniques for total inorganic As and oxo-DMA in a range of rice samples was found with clear evidence of As(III)-S species dissociating to As(III). Some minor differences in As(III) and As(V) were found as a result of photooxidation in the XANES beam. Lombi and co-

workers [129] also found that As(III)-S species in rice survive drying and grinding. Langdon and co-workers [137] determined methanol-water (1:1 v/v) extracts of the earthworm *Lumbricus rubellus*. Worms from the same site with comparable As concentrations had good agreement of the percentage of As(III)/As(III)-S and As(V) by HPLC-ICPMS (68 and 31% respectively, 81% extracted) and XANES (65 and 35% respectively). Bluemlein and co-workers [71] compared the measurement of As-peptides in plants by HPLC-ICPMS after extraction with 1% formic acid and XANES and showed that As bound to S of peptides was similar (HPLC: 55-64%, XANES: 53%). As-S bonds were not formed during extraction or chromatography thus the extraction procedure preserved the integrity of the As-S species. Caumette and co-workers [119] extracted fresh water phytoplankton and zooplankton with water and compared the results of anion HPLC-ICPMS with XANES of solid samples. For one zooplankton sample (95% extracted, 89 ± 12 % column recovery) a good agreement between total inorganic As (XANES, 32%, HPLC-ICPMS, 38%) and total arsenosugar (XANES, 67%, HPLC-ICPMS, 67%) contents were obtained.

Mir and co-workers [79] used XANES to examine the As species of dried ground plants and dry residues of plants extracted with methanol-water (1:1 v/v) and 0.1 M hydrochloric acid. As(III)/As(V) ratios were preserved during sample preparation and extraction but As-S species wer not major species in these plants. The As species in dried residues are not consistent with the original As species in plants showing that when these solvents are used transformations occur during extraction.

2) *HPLC buffers cause oxidation and dissociation.* Raab and co-workers [130] showed that As-PCs in *Holcus lanatus* and *Pteris cretica* dissociated during chromatography. Bluemlein and co-workers [177] showed that As in peptides could be extracted from plants by formic acid and separated by HPLC-ICPMS using with good agreement between XANES (As(III)-S, 53%) and HPLC-ICPMS (As(III)-PCs, 55-64%).

3) *Retention of As species by column.* It has been shown that As-S species can have long retention times when chromatographic conditons normally used to separate oxo-As species are used [22, 178, 179]. Thus differences observed between XANES and HPLC-ICPMS may not be due to sample preparation but poor chromatography.

Other studies have used HPLC-ICPMS and XANES to examine As species but it is not possible to compare results because of low extraction efficiencies. For example, two terrestrial invertebrates [144, 180], 28-82% and 32 ± 26% respectively), rice (Merharg et al 2008, 63-86%) and *Mytilus edulis* (42-62%) [181]. Most of the unextracted As is inorganic As, but not always [181].

XANES cannot be used to confirm the presence of AB and TETRA as these As species have similar line energies and cannot be discriminated. Also organic As species are often below the instrumental detection limits [119, 144, 180, 181]. Often XANES and HPLC-ICPMS are used together to measure As species. For example, Smith and co-workers [182] reported Inorganic As, AB and DMA in white button mushrooms *Agaricus bisporus* using a combination of these techniques.

Storage of extracts

As (III) and As (V)

The stability of As(III) and As(V) in extracts is unclear, but standards have been reported to be unstable even when frozen at -21 °C [183], and it is likely that As(III) is oxidised to As(V) in extracts. Pizaro and co-workers [85] showed that As (III) and As (V) in methanol-water (1:1 v/v) extracts of rice were stable when stored at 4 ^{o}C in the dark. These rice samples have been γ-irradiated and the applicability of these findings to non-sterile samples containing bacteria needs to be investigated. García Salgado and co-workers [66] reported that As (V) in water extracts of NIES No 9 Sargasso are stable in polystyrene containers at -18 ^{o}C for 15 days, while Hijiki extracts needed to be stored at +4 ^{o}C in order to ensure stability for 10 days. There was, however, some uncertianty as to the type of container (polystyrene, glass etc.) that is the most suitable for the storage of extracts.

Oxo-methylated As species

Generally aqueous and methanol-water extracts of oxo- methylated As species stored at 4-20 ^{o}C are stable for short periods of 15-20 days [26, 85]. Phosphate and sulphonated arsenoribosides

can hydrolyse to glycerol sugars when in solution, thus arsenosugar extracts are best stored as freeze dried extracts. MA(III) and DMA (III) stocks have been reported to be unstable if stored for more than a week at 4 ^{o}C, but stable if stored at -20 ^{o}C [184]. Thus it is likely that sample extracts will need to be stored below -20 ^{o}C, if the integrity of these As species are to be maintained. Acidification of extracts should also be avoided as this will also led to the degradation of arsenosugars [185].

Thio-methylated As species

During storage at 25 ^{o}C, thio-methylated As species in deionised water slowly convert into their oxy-analogs. Elevated temperatures (60 ^{o}C) accelerate S to O conversion rates of thio-DMA and thio-TMAO in solution whereas refrigeration (4 ^{o}C) retards conversion (10 % vs 0.4 % per week) [186]. The authors point out that even at 60 ^{o}C it would take 2 days for conversion to occur that exceeds the 95% confidence interval, effectively extracts are stable for this period. In contrast at 80 ^{o}C and a pH < 3.5, complete conversion of thio- to oxo-arsenosugar-2 occurs within 24 hours [125]. Maher and co-workers [54] reported a loss of 1-2% of thio-methylated As species in deoxygenated deionised water over a week at 25 ^{o}C. Sample extracts, however, were not stable at 25 ^{o}C and within 48 hours a complete loss of thio-arsenoribosides in extracts occurred. Hansen and co-workers [185] also have shown that thio-As sugar extracts stored at 25 ^{o}C degrade within 24 hours. Kahn and co-workers [17] have shown that for aqueous extracts of great scallops, thio-arsenosugars are stable for 6 months if extracts are stored at -16 ^{o}C. If sample extracts are rotary evaporated to dryness and the residues stored in a desiccator and redissolved prior to analysis in deoxygenated deionised water (pH 6-7), As species are stable for at least two weeks with conversion rates of less than 1%. This indicates that the oxidation of thio- methylated As species is minimized. Multiple freeze-thawing of extracts results in 30-50% loss of thio methylated As species [54].

Acidification has been shown in a number of studies [55] to be unsuitable as a preservation method for samples because it leads to an immediate decrease, or complete loss of dithio-MA and dithio-DMA, often accompanied by an increase in the corresponding monothio- methylated As species. Thio-MA and dithio-DMA may also be formed from MA and DMA respectively, under acidic conditions, in the presence of free sulfide or other reduced sulfur species. Similarly

the conversion of oxidized arsenosugars to thio-arsenosugars has been shown to occur on acidification of seafood extracts [185, 187].

As glutathionines and phytochelatins

As-PC complexes extracted from plants with 1% formic acid are stable for 3 days at 1^{o}C, but not present after four weeks [130]. As-GSH species are stable when extracted witho.1% formic acid (pH 2.5) for 12 hours when stored at 4 ^{o}C; the stability of complexes was much less when extracts stored at 25 ^{o}C [70].

As lipids

No information is available on the stability of As-lipids in extracts, however, as As-lipid species are stable even when undergoing procedures utilizing acidic and alkaline solvents [108] it would be expected that As-lipids are relatively stable in extracts.

Overview and recommendations

A compilation of extraction methods for various application is given in Table 3 to illustrate the extraction media and procedures that are commonly used to isolate As species from sample matrices. References are given to allow the full exploration of each approach. It is apparent that As cannot be extracted from all sample matrices using a single set of conditons. For example, As species in marine animals, present as mostly AB, are easily extracted with methanol, water and methanol-water mixtures, however, extraction of inorganic As species from angiosperms such as mangroves and seagrasses and rice requires the use of a dilute acid or base [127, 188]. Sequential extraction with methaol-water followed by dilute acid has been shown to increase extraction efficienies while maintaining the integrity of As species for hard to extract samples. Extracting media should be based on the As species on interest. Most As species are polar and soluble in water, thus the use of methanol-water is a good compromise between As solubility and ease of solvent removal. The use of acids or alkalis will degrade thio-As species, however, the use of formic acid helps preserve AsPC species by minimising the dissociation of As complexes.

Extraction of As-lipids requires an organic solvent such as hexane-methanol or chloroform-methanol. The use of enzymes, doent appear to offer any additonal advantages.

Determination of As species in sediments and soils remains a challenge as full extraction without altering As (III)/As(V) and As-S species appears not to be possible. This in practice, however, may not be important if only total inorganic arsenic concentrations are required. Sediments contain several adsorptive phases (exchangeable, Fe-Mn oxides, carbonates , organics, lattice incorporated) and require several solvents to removed As adsorbed to the different phases.The use of subcritical extraction where water is heated under pressure to ~ 300 ^{o}C provides promise for the full extraction of As from sediments and soils while maintaing the integrity of As species.

Most oxo-methylated As species are stable to short-term heating at temperatures below 100 ^{o}C and exposure to dilute acids and bases [127]. An exception to this are dimethylarsenoribosides that have been shown to undergo side-chain hydrolysis upon heating with acid [127]. In addition, published methods have employed shaking, micowave assisted extraction, sonification or pressurised liquid extraction systems using a variety of temperatures, and times to assist in As extraction (Table 2), but often without any justification for their use. The use of microwave assisted heading is now in widespread use as its use reduces extraction times, requires less reagents, is subject to less contamination and gives good recoveries of As from most sample matrices.

There are two important considerations when extracting As from biota: 1) the necessity to lyse cells, and; 2) whether samples need to be defatted. Cells and membranes need to be ruptured to ensure quantitative extraction of As species. The use of freeze drying and grinding will normally break-up most biological cells and membranes. The presence of fat can lower As extraction efficiencies and influence HPLC column performance [107]. Fats can be easily removed with an acetone or ether wash with little co-extraction of As species in non-fatty tissues such as mucsle tissue [107].

Sample extraction procedures need to be optimised for the tissues of interest. For example, Rahman and co-workers [189] found that the extraction of As from the roots, stem, leaves and grain of rice gave poor extraction efficiencies from roots (3-10%) but better extraction efficiencies for other tissues (50- 60%). Schmidt and co-workers [190] also showed variable

recoveries of As (46-96%) when the leaf, stalk and stems of Indian cress (*Tropaeolum majus*) were extracted with a phosphate buffer. Similiarly methanol-water (2:1 v/v) gives good As recoveries from marine muscle tissues (> 95%) but poorer recoveries (19-71%) from other tissues [107].

The importance of sample particle size is often overlooked. As mentioned previously, often methods are validated using CRMs that have well characterised particle distributions (50-400 μm) while the particle size distribution of "real world" samples is unknown, but unlikely to be as fine as CRM particles [87]. The higher surface area to solvent contact for CRMs may result in better extraction recoveries than "real world" samples. Furthermore, As may be trapped on or within tissues pellets post extraction, thus a wash with the extractant solvent is needed to remove any trapped As.

It is evident from the literature that little information is given on the purity of reagents or steps taken to purify reagents. A notable exception is for enzymes where it has been reported that enzymes may contain up to 2 μg/g of As(V) [191].

The stability of As(III) and As(V) in extracts is unclear as even in frozen extracts (-21 ^{O}C) , As(III) was oxidised to As(V). Similiarly AsPC complexes are only stable for short periods at 4 ^{O}C (~12 hr). Generally aqueous and methanol-water extracts of oxo- and thio- methylated As species at 4^{O}C are stable for short periods (15-20 days) although some degradation of arsenosugars has been reported. Acidification should be avoided as arsenosugars are degraded and thio-As species are destroyed. As-lipids are expected to be relatively stable in extracts. Based on this information, if As(III), As(V) or AsPCs are of interest, extracts should be analysed immediately. Eventhough oxo- and thio- methylated As species can be stored for long periods we generally freeze dry extracts for prolonged storage and have found little loss or conversion of these As species.

HPLC-ICPMS or HPLC-HG-AFS

Instrumental setups

Mode 1: HPLC-ICPMS

The most common set up for the analysis of As species is the direct coupling of a HPLC to an ICPMS via small diameter PEEK tubing without loss of peak resolution. Chromatographic flow rates are usually compatible with conventional ICP spray chambers. The high sampling and data acquisition rates of the ICPMS allow adjacent chromatography peaks to be separated and quantified. However, typically only 1% of the As in the eluent is vaporized into the ICPMS plasma. A typical analysis of As species standards and a gastropod sample, *Bembicium namun* are shown in Figure 1 A - C.

Mode 2: HPLC-HG-ICPMS or HPLC-HG-AFS

The sensitivity of the HPLC-ICPMS technique can be substantially increased by the incorporation of a hydride generation system after chromatographic As species separartion; note that the AFS requires the use of a hydride generation system to operate. Many As species form volatile hydrides e.g. AsH_3, CH_3AsH_2, $(CH_3)_2AsH$ etc. approximately 70-80% of the As as a hydride gas reaches the ICPMS plasma or AFS hydrogen flame. Typically sodium tetrahydroborate (III) is used as the reductant to generate hydride species [192]. The efficiency in generating As-hydride species is critically depends on the As species species and the sample matrix. For example, AB and AC do not form volatile hydride species, while arsenoribosides form volatile analytes, but the efficiency of generating hydride species is poor (~5%) unless the hydride generation system is specifically optimized for arsenoribosides (21-28%) [193]. Regmi and co-workers [194] identified the volatile species generated by arsenoribosides to be $(CH_3)_2AsH$. A typical analysis of inorganic As standards and species in the sea weed, *Macrocystis pyrifera*, is shown in Figure 2A and B. If only inorganic As species concentrations are required, for example to satisfy food regulation standards, the use of hydride generation eliminates the overestimation of these species as the signals of other As species not generating hydrides are eliminated [143]. Alternatively if the organo-As concentrations are needed, a post-column reactor is required to transform compounds to species that can form a hydride. Usually this process involves the addition of an oxidant e.g. Potassium peroxyodisulfate along with UV irradiation to convert As species such as AC and AB to As(V) before hydride generation [195, 196]. Arsenic species dependent responses are often obtained reflecting the variable efficiency of the reactor in degrading organic As species to As(V) [197].

Mode 3: Cryogenic trapping ICPMS or AFS

This set up incorporates the trapping of hydride forming As species using a packed column and cooling with liquid nitrogen (Figure 3A). After trapping, the column is heated and volatile As species flushed into the ICPMS or AFS for analysis [198]. This cyrogenic trap set up is useful when extreme sensitivity is required and is particularly suitable for aqueous samples and biological extracts. We have used this approach to measure As profiles in open ocean waters (Figure 3B). This approach can also be used with selective hydride generation based on pH to separate and measure MA(III) and DMA (III) concentrations in biological fluids [199].

Mode 4: In-situ cryogenic trapping ICPMS or AFS

Bacteria are known to form volatile As species [10, 11]. Solutions, extracts and head space samples can be purged with helium and the evolved volatile As species trapped using a packed column cooled with liquid nitrogen. The columns can then be attached to an ICPMS or AFS, warmed, and purged As species determined [200, 201].

ICPMS and AFS considerations

Optimisation

It is common for optimised instrument parameters for ICPMS (plasma conditions and mass spectrometer settings) to be reported. Some authors report that different As species (e.g. As(III), As(V) and AB) have different ICPMS responses [202, 203]. Responses are dependent on the micronebuliser/spray chamber configeration as well as flow rates, spray chamber temperatures and the sample matrix. Differences in responses of As species reported when HPLC-ICPMS is used are attributed to

(1) The ICPMS plasma: differences in ion extraction processes i.e. defocussing, buffer salts modifying plasma chemistry and ionic interactions in the plasma-mass spectormeter interface.
(2) HPLC: Variations in adsorption of As species to column packing materialand different transport efficiencies in nebulizers.

Cooling of the spray chamber to 4 °C improves the relative responses and the presence of ammonium phosphate i.e. in HPLC eluents can mitigate differences.

Generally papers reporting the use of AFS do not give many details relating to the optimisation of AFS instrument and probably use the defaults settings setby the instrument manufacturers. Zhang and co-workers [128] showed that lamp current, PMT voltage, carrier gas and shield gas can be adjusted to optimise the As signal. Light scattering and background interferences due to the sample matrix can cause problems when using AFS, however, the use of HG-AFS reduces these problems but the hydride system needs to be carefully optimised to reduce noise. There are three sources of noise that reduce signal to noise ratios [204].

(1) Radiation scattering generated by carry over of moisture form the gas-liquid separator to the AFS flame. The relatively low temperature of the flame cannot vaporise spray particles.
(2) Introduction of molecular species generated by the use of tetrahydroborate e.g. boranes and OH radicals that quench fluorescence.
(3) Excessive changes in hydrogen gas evolution that change flame stoichimetry, flame volume and temperature causing residence time changes, dilution of atoms and self absorption all affecting fluorescence intensity [205].

These can be controlled by minimising the use of tetrahydroborate, acids etc. and the lowest purge gas rates possible. The use of optical filters may also eliminate some noise. The use of lower tetrahydroborate and acid concentration can exacerbate the effects of transistion elements on hydride generation of As species but can be masked with cysteine or thiourea.

If As species are not converted to As(III) before hydride generation, different As species give different AFS responses as the dissociation of As species in the coll flame is different. Atomisation of AsH_3 is 41-56% greater than MAH_2 and DMAH [205]. As well, responses are concentration dependent as recombination of free atoms and self adsorption depend on atom density.

There are few reports that compare HPLC-ICPMS and HPLC-HG-AFS detection limits. Gómez-Ariza [206] reported that detection limits for HPLC-ICPMS (As(III) 0.7 µg/L; As(V) 0.8 µg/L; MA 0.5 µg/L) are much lower than HPLC-HG-AFS (As(III) 16 µg/L; As(V) 17 µg/L; MA

3 µg/L). Decreased sensitivity was attributed to the use of compromise conditons to generate hydrides. In a later publication by the same authors [195] similar detection limits were reported for both techniques with HG-AFS having better precison and reproducibility. Pétursdóttir and co-workers [143] also reported that the limits of quntification for HPLC-ICPMS (0.026 µg/g) is much lower than HPLC-HG-AFS (0.1 µg/g).

Use of hydride generation

Generally organic As species in HPLC eluents are converted to As(V) by use of UV-photolysis and potassium peroxodisulphate [195] with cysteine used to reduce As(V) to As(III) [207] before the formation of AsH_3. It has been proposed that the As-cysteine complexes in which an O is replaced by an SR group, reacts with BH_4^- more readily as it is less sterically hindered than $As(OH)_3$ [208]. The use of cysteine allows the use of lower acid concentrations [209] and the same response for As(III), As(V), oxo-MA and oxo-DMA are obtained. The use of charged surfactants also enhances the generation of As-hydrides [210], while some organic solvents e.g. ethanol can supress hydride generation [211].The UV decompositon-HG steps should be carefully evaluated as the degradation of AB and arsenoribosides may be influenced by the sample matrix causing incomplete conversion to As (V) or suppression of hydride formation [196].

Thioarsenate species can be quantitatively converted to As(III) at low pH (< 3) by the use of potassium iodide and ascorbic acid [212], as cysteine has been found to be less effective in the formation of AsH_3 for these As species. Mamindy-Pajany and co-workers [213] also reported that UV irradation at 30 ^oC with 2% w/v $K_2S_2O_8$ - 2% w/v NaOH converted thioarsenates to As(V).

Hydride generation can results in excessive amounts of water being entrained in the gas stream used to purge hydrides from solution. The gas stream needs to be dried before entering the AFS flame as quenching of fluorescence will occur. Water entraiment can be minimised by attention to the design of the hydride generation system, especially the introduction of the carrier gas stream [214].

ICPMS interferences and signals

The optimum mobile phase for the separation of anion and cation As species may not be compatible with the analytical detection system. For example, chlorinated solvents may result in ICP-MS polyatomic interferences especially for ^{75}As [90] e.g. $^{40}Ar^{35}Cl^{+}$. Substitution of problem buffers, for example buffers containing chloride with carbonate, is often possible. Mass interferences by polyatomic species with the same mass to charge ratio can be removed by the use of a dynamic reaction or collision cell during the measurement phase ([90]. Typically helium, ammonia, hydrogen and oxygen gas are used to eliminate interferences [30, 90, 215] and more recently SF_6 [216]. Helium, for example, can be used to suppress $^{40}Ar^{35}Cl^{+}$ formation but also suppresses $^{75}As^{+}$ intensity (~ 50%) at high helium flow rates [217]. Addition of methanol (1-5%) is commonly used to improve As sensitivity (2.5-3 times) and also supresses $^{40}Ar^{35}Cl^{+}$ formation.

Interference by Cl forming polyatomic species are in practice rarely a problem as they can be separated from As species during chromatography. For example, Cl^{-} elutes after As(V) on a PRPX-100 anion exchange column. Care, however, must be taken that large amounts of Cl^{-} do not overlap with As(V) peaks. Doubly charged interferences in extracts can be significant , if for example, extracts contain high concentrations of rare earths e.g. NIST 1547 Peach leaves and NIST 1515 Apple leaves [218]. Rare earth elements have low ionisation potentials (11-12 eV) and readily form doubly charged ions. In practice, interferences from these ions appear not to be a problem when HPLC-ICPMS is used.

High concentrations of organic solvents used for C_{18} reverse phase separations can extinguish the ICP-MS plasma, thus the amount of organic solvent introduced into the plasma needs to be reduced and oxygen gas added to the plasma to ensure removal of the additional carbon entering the mass spectrometer. Alternatively, for some organic solvents a chilled spray chamber (-5 to –10 ^{o}C) or a desolvation device can be used to reduce or eliminate the organic carbon load.

The ionisation of As in the ICPMS plasma is sensitive to the carbon loading of the HPLC mobile phase being aspirated. Thus, the use of gradient elution with mobile phases containing variable organic content will result in a variable response in the As signal. For example, the As response changes by a factor of 4 as the methanol content of the HPLC mobile phase increases from 20 to 80%. To overcome this problem, the HPLC effluent can be split and methanol or acetone added

to the spray chamber to equalise As signals i.e gradient compensation [219]. The loss of sensitivity is compensated by the carbon enhancement effect.

If a mobile phase containing high concentrations of sodium hydroxide is required for chromatography, the sodium will need to be removed as sodium entering the ICPMS suppresses the As signal [56, 215] and causes severe baseline drift. A self-regenerating suppressor can be used to remove sodium and OH converted electrochemically to water prior to sample introduction into the ICPMS [220]. As the suppressor is also a cation exchanger any cation species present such as oxo-DMA will be lost. The use of a suppressor improves detection limits and enhances the long-term signal stability and robustness of ICPMS operation.

The limits of detection for As determination by ICPMS are limited by the signal to noise ratios. To improve the detection power, signal treatment (Gaussian distribution curves, Fourier transform, wavelet transform) can be applied [221]. Detection limits may be improved by factors of about 6 using these techniques i.e. As(III) 0.25 µg/L to 0.04-0.1 µg/L; As(V) 0.72 µg/L to 0.12-0.2 µg/L; DMA 0.54 µg/L to 0.09-0.16 µg/L and AB 0.35 µg/L to 0.06-0.11 µg/L.

Standards

As(III), As (V) and oxo-methylated As species

Many As species such as As(III), As(V), oxo-MA (V), oxo-DMA (V), AB, AC, oxo-DMAA, oxo-DMAE and TETRA can be obtained commercially or synthesised with good yields. The common arsenoribosides and TMAP can be isolated from seaweeds or from reference materials e.g NRCC DORM 2 [222]. The preparation of MA(III) and DMA(III) is more problematic. For example, the use of thiosulfate to reduce oxo-MA produces two products; thio-MA and dithio-MA [54]. Cullen and co-workers [223] showed that MA(III) could be produced by first synthesisng tetramethyl-cyclo-tetraarsaoxane (cycl-$(CH_3AsO)_4$), which then hydrolyses in deionised water to give MA(III). MA(III)I_2 and DMA(III)I can be synthesised from oxo-MA and oxo-DMA by the additon of KI and acid following saturation with sufur dioxide. The newly formed precipitates then can be washed, dried and purified by extraction with diethylether [MA(III)] or distillation [DMA(III)] [224]. Hansen and co-workers [225] also showed that the reaction of oxo-DMA with $KI/H_2SO_4/SO_2$ produces DMAI giving DMA(III).

Thio-methylated As species

Thio analogues of oxo-MA, arsenosugars, DMAE, DMAA can be synthesized by adding a saturated sulfide solution (prepared by bubbling H_2S gas through deionized water for one hour) to oxo-As standards and reacting for 30 min at pH 4 [226]. The excess H_2S generated is removed by purging with argon and the solutions evaporated and recrystallised using acetone or dichloromethane. Thio-DMA can be prepared according to Raml and co-workers [227] where a solution of oxo-DMA is adjusted to pH 3, a saturated H_2S solution added and ethylacetate extraction used to ensure that only thio-DMA is formed. Dithio-DMA can be prepared by adjusting a solution of oxo-DMA to pH 6 and adding a saturated H_2S solution. added by Fricke and co-workers [228] also published a procedure to produce dimethylthioarsinic anhydride ($(CH_3)_2AsSOAs(S)(CH_3)_2$), which is stable and when dissolved in water produces the monomer. Fricke and co-workers [228] have shown that the conditons of Reay and Asher [229] purported to produce DMA(III) actually produced thio-DMA. Wallschlager and London [55] amd Hansen and co-workers [225] also showed that reactions of oxo-DMA with H_2S gave Dithio-DMA as the major product and Thio-DMA as a minor product. Oxo-MA reacted with H_2S gave Thio-MA, Dithio-MA and Trithio-MA.

As-glutathione complexes

$As(GS)_3$, $MA(GS)_2$ and DMAGS can be synthesised by adding As(V), oxo-MA or oxo-DMA to glutathionine in water under a stream of argon to prevent oxidation [230, 231]. Solutions are then stored at 4 ^oC under oxygen-free conditions. Further purification of $As(GS)_3$ and $MA(GS)_2$ can be achieved by adding methanol or ethanol, with filtering and air drying of precipitates. The remaining DMAGS in solution can be concentrated by rotoevaporation and solids purified by extraction with methanol.

As phytochelatins

A mixed solution containing glutathione (36%), PC2 (50%) and PC3 (14%) in 1% formic acid can be reacted with a surplus of As(III) to form $As(PC2)_2$, GSAsPC2, AsPC3 and AsPC2 [70].

Thioarsenate species

Sodium monothioarsenate ($Na_3AsO_3S.7H_2O$) can be synthesized as described by Schwedt and Rieckhoff [232] by adding solid sulfur (0.045 mol S) to a mixture of As_2O_3 (0.05 mol As) and NaOH (0.15 mol Na) in 20 ml H_2O and heating at 90°C for 2 hours. The excess sulfur is filtered off and the solution cooled down slowly to 4°C. The colorless crystals obtained are dried under vacuum for 1 hour. Sodium dithioarsenate ($Na_3AsO_2S_2.7H_2O$), sodium trithioarsenate ($Na_3AsOS_3.10H_2O$) and sodium tetrathioarsenate ($Na_3AsS_4.8H_2O$) are obtained using the general approach used by Wilkin and co-workers [233] by mixing an excess of sodium bisulfide (NaHS, formed by dissolving NaS_2 in deionized water) to sodium arsenite to obtain a mixed standard. A 1:1 ratio of As:S is used to obtain monothioarsenate, whereas a 1:100 molar ratio of As:S is used to obtain di-, tri- and tetrathioarsenate. All thioarsenate species should be stored under nitrogen at 4 ^oC to prevent oxidation.

As-lipids

The synthesis of As-lipids is complex and a number of studies have been published for the preparation of a limited number of As-hydrocarbons and As-fatty acids [166, 234, 235].

Separation of methanol, water, methanol-water and buffer soluble As (III), As (V) and oxo-methylated As species

Anion and cation exchange chromatography

Ion exchange chromatography is used to separate free ions and ionisable species. The stationary phase consists of a polystyrene-divinylbenzene polymer or silica backbone, which has an ionic functional group such as quaternary ammonium or sulfonate. Analytes will interact with the stationary phase if they are oppositely charged to that of functional group bonded to the stationary phase. A comprehensive summary of ion-exchange columns and mobile phases has been presented by Ammann [236]. An overview of the use of ion-exchange chromatography for various sample matrices is given in Table 4.

Biological fluids: As species in urine, saliva and blood are readily separated by anion and cation chromatography with isochratic or gradient elution [237-241].

Biota: Over fifty water soluble As species have been identified in extracts of marine organisms using anion, cation and reverse phase chromatography. Factors that can affect the separation of anion and cation species by HPLC include pH, temperature, mobile phase concentration and/or methanol concentration. Mobile phase pH determines the charge of As species. At pH < 5, As (V), sulphonate, sulfate and phosphate arsenoribosides will have a negative charge. Glycero-arsenoriboside has no charge in the range pH 3.8-9. Arsenoribosides have different functional groups on their side chains, thus will have different retention characteristics. The addition of methanol, lowers the retention times of arsenoribosides on anion-exchange columns as interaction of these species with the stationary phase is not entirely via anion exchange [242]. Examples for the separation of As species found in seaweed and marine animal tissue extracts are given in Figure 4 & 5. This figure serves to illustrate the limitation of undertaking As speciation measurements using HPLC-ICP-MS or HPLC-HG-AFS. If the As species has not been identified, or a standard is not available for the As species, it is not possible to be identified. A HPLC coupled to an electrospray mass spectrometer is required for this purpose. It is difficult to synthesize many of the natural occurring As species e.g. arsenoribosides and arsenolipids. We have used HPLC-MS-MS to characterise these species for use as standards. For example, an unknown As species in *Haliotis rubra* intestine tissues was identified using tandem mass spectrometry as 2', 3' - dihydroxypropyl 5 - deoxy - 5 - trimethylarsonioriboside (trimethyl glycerol arsenoribose) [243]. The concentration of trimethyl glycerol arsenoribose in intestine tissue was estimated to account for 28 % (5.0 μg g^{-1} dry mass) of the methanol-water soluble As fraction. Seventeen As species have been separated in one run using an anion exchange column in conjunction with an ion-pairing reagent and gradient elution with nitric acid [244]. Sloth and co-workers [245] reported the separation of 23 As species by cation exchange with gradient elution using an aqueous pyridine-formate mobile phase, but large matrix effects were experienced. In addition, many samples can contain large amounts of a particular As species, e.g. AB, that can obscure other minor As species during sample elution. Longer elution times are often better as there is less chance of co-eluting unknown As species, and the use of complementary separations techniques reduces problems from matrix components. For example,

when using anion and cation chromatography, cations are voided from the anion column and anions voided from the cation column, as well as reducing matrix interferences.

Sample matrix components such as sodium can affect chromatography and spiking is essential to account for matrices influencing retention times. For example, Sloth and co-workers [245] have shown that a four-fold increase in the loading of a TORT-2 sample extract on to a HPLC column decreased the retention time of AB from 10 min to 7 min. Peak suppression and the splitting of the AB peak by sodium and potassium occurs during cation chromatography, but can be eliminated by dilution or adjustment of eluent pH to separate AB from these cations. Slejovec and co-workers [74] and Masden and co-workers [246] also reported severe matrix effects during the separation of sulphonate-arsenoriboside on a PRP X- 100 anion exchange column. Matrix effects seems to be more pronounced when gradient elution is used [97, 247]. Sodium, potassium and other unretained material migrate with the solvent front during anion exchange chromatography and may interfere with As(III) and glycerol arseno riboside measurements. We have found that As (III) and low concentrations of oxo-MA, oxo-DMA and As (V) in rice can be reliably determined using anion chromatography without hydride generation with ICP-MS detection [188]. We have also found that when acetone is used to clean up tissue samples i.e. remove fats prior to extraction [107], retention times are very stable and column life is prolonged.

Column recoveries reported in the literature are highly variable (30-100%) and can vary significantly for extracts obtained from the same organism [21, 97, 247]. Some As species, for example thio-arsenoribosides, have non-ionic interactions of As=S with stationary phases such as PRPX-100 and require high pH (>10) to elute As species within 10 -15 min [179]. Schmeisser and co-workers [178] and Nischwitz and co-workers [248] showed that oxidation of extracts with H_2O_2 converted As=S to As=O and can be used to confirm the presence of thio-arsenoribosides in extracts being determined by anion chromatography when low column recoveries are obtained.

Reversed phase chromatography

A comprehensive summary of reversed phase columns, ion pairing reagents and mobile phases has been presented by Ammann [236]. An overview of the use of reverse phase chromatography

for various matrices is given in Table 4. A typical separation of As species by C18 reversed phase chromatography is shown in Figure 6. An ion pairing reagent is added to the mobile phase to simultaneously separate anions, cations, and non-charged species. An ion pairing reagent is a salt with a cationic or anionic polar head group and a nonpolar tail such as sodium alkyl sulfonate and tetraalkyl ammonium salts. The separation mechanism is not completely understood. One theory states that an ionic analyte is electrostatically attracted to the charged portion of the ion pair reagent, charge neutralization causes the charged analyte to be retained by the non-polar stationary phase [249, 250]. A second theory is that the hydrophobic portion of the ion pair reagent adsorbs to the stationary phase and a pseudo ion exchange stationary phase is formed. Thus, charged species interacts with the pseudo ion exchange stationary phase [251].

The choice of the ion pairing reagent is critical. For example, changing from tetra methyl ammonium hydroxide (TMAH) to tetra butyl ammonium hydroxide (TBAH) increases the retention times of As species as it is less polar [252]. The separation mechanism when using tetra butyl ammonium hydroxide changes from ion pair formation to dynamic ion exchange (Figure 9) i.e. solute ions binding to ion pairing reagents that are already bound to the stationary phase. This results from the increased hydrophobicity of the ion pairing reagent. Some published papers have use mixtures of ion pair reagents [253], however, mixtures of different ion pairing reagents are probably not needed as they have the same capacity factor as an ion pair reagent with the same mean chain length [250].

Reverse phase chromatography seems to be prone to matrix and pH effects [254, 255] in comparison to ion chromatography. One of the problems of using ion pairing reagents is that ion pairing with matrix components occurs as well, thus causing shifts in retention times [183, 256].

The use of C18 reverse phase and a mobile phase consisting of 4.7 mM TBAH, 2 mM malonic acid and 4 %v/v methanol (pH 5.85) has been successfully used to separate MA(III), MA(V), DMA(III) and DMA(V) [257].

Separation of acid/base soluble As (III), As (V) and oxo-methylated As species

Plants: Rice is commonly extracted with dilute acids such as 2% v/v nitric or 2M trifluoroacetic acid and determined by anion exchange chromatography using malonic acid or phosphate buffers (Figure 7) [126, 188]. Arsenite is eluted near the void and careful control of the acid content (< 0.5%) is required to prevent the co-elution of As(III) and oxo-DMA. Raber and co-workers [126] replaced the phosphate buffer ($pKa_2 = 7.2$) with malonic acid ($pKa_2 = 5.7$) as it has a higher apparent charge (-1.44 compared to -1.02) at pH 5.6 to obtain more reproducible separations. Because only knowledge relating to total inorganic As concentrations in rice and seafood is required for regulatory purposes, oxidation of As(III) to As(V) by H_2O_2 can be used and the single As(V) peak quantified [143, 258, 259] as this peak does not elute near oxo-MA or oxo-DMA. Often there is a small peak in the void volume that is attributed to carbon, however, Hansen and co-workers [260] have shown that in some rice samples this peak is TETRA. Cation chromatography should be used to check the composition of any peaks in the void volume.

Biota: Acid extracts of animals can be chromatographed on anion exchange columns [127] after dilution, but suffer from the same problems as described above for plants.

Sediments: Phosphoric acid concentrations, commonly used for extraction of sediments, greater than about 0.32M, result in significant peak distortion and hinders the quantification of As(V) [261]. The retention times for As species can also change depending on column usage and on the sample matrix. Older "well-used" columns tend to have shorter retention times compared to new columns. For samples that contain hydroxylamine hydrochloride to prevent oxidation of As(III) to As(V), retention times are shorter than for samples that do not contain hydroxylamine hydrochloride [82].

Separation of lipid soluble species

Until recently, As lipids in fish oils were saponified with potassium hydroxide [173, 262] while tissues were extracted with a mixture of chloroform/methanol (2:1 v/v), the solvent removed and residues hydrolysed with an acid, an alkali or phospholipase D enzyme. These procedures cleaved the As moieties in lipid extracts, thereby liberating the water-soluble As species that can be determined by HPLC-ICP-MS (Table 5). Lipid soluble As species such as phosphatidyl

arsenocholine and phosphatidyl arsenoriboside on treatment released As (III), As (V), oxo-MA, oxo-DMA, AC, DMAE and glycerol and phosphate arsenoriboside.

Now analysis of intact As-lipids is undertaken (Table 5). Rigorous cleanup of extracts is required for two purposes: first to prolong the lifetime of HPLC columns and second to enable molecular identification of complex As-lipids by reverse phaseHPLC-MS, which can only be achieved with "clean" and highly concentrated extracts. A more rigorous clean up is required to isolate the As species in lipid fractions to achieve good separation of species by reverse phase (C8 or C18) HPLC [108, 160, 161]. Typically after centrifugation of, for example, a chloroform-methanol extract, the supernatant is washed with bicarbonate solution (1% w/v) to remove water-soluble As species. The chloroform layer is separated and evaporated to dryness to yield a crude As-lipid fraction, which is re-dissolved in a mixture of chloroform/acetone (1:1 v/v). A portion of this solution is applied to a silica column and eluted with chloroform/acetone, (1:1 v/v) containing formic acid (1% v/v), methanol and finally methanol containing aqueous ammonia (1% v/v). The methanol–ammonia fractions containing 85% of the total As content are evaporated to dryness and re-dissolved in methanol. Extraction of As-lipids from algae, for example, is easy to accomplish since most of the species are relatively stable. In general, the recoveries of As-lipids after cleanup are higher than 80% with matrix removal efficiencies of > 90%. The As-lipid species are stable even when undergoing procedures utilizing acidic and alkaline solvents.

Lipid extracts, without hydrolysis, can be determined by HPLC-ICPMS using a Zorbax Eclipse XDB-C8 column (4.6 mm x 150 mm; 5 µm particle size; Agilent Technologies, Waldbronn, Germany) and a mobile phase comprising 10 mM acetic acid at pH 6 and methanol under the following gradient elution conditions: 0-25 min, 50%-95% methanol; 25-40 min, 95% methanol; flow rate 1 ml·min^{-1}, 40°C.

To prevent deposition of carbon on the interface cones of the ICPMS, 1% v/v oxygen is introduced into the argon gas stream. PO^+ [*m/z* 47] is also monitored to confirm the presence of As phospholipids. Methanol or acetone is also introduced directly into the ICPMS spray chamber to compensate for the variable amounts of carbon in the mobile phase entering the ICPMS [219]. A typical chromatograph of As lipid species in a Wakame and Hijiki seaweed extracts are presented in Figure 8A and B. A difficulty when determining As-lipids is the high number of As species with similar masses and chromatographic behavior. Whereas methanol-water soluble As

species can be separated under isocratic HPLC conditions, As-lipids can only be separated under gradient elution conditions with acceptable chromatographic efficiency and within a reasonable time frame. As the ICPMS responses of As-lipids are dependent on the amount of carbon in the plasma, ICPMS cannot be used for species independent quantificiation without the introduction of methanol, ethanol or acetone directly into the ICPMS spray chamber [219]. This is to compensate for the variable amounts of carbon in the mobile phase entering the ICPMS. Without compensation, As species eluting with higher organic content in the mobile phase are overestimated by a factor of 8-10 whereas with gradient compensation the results for all As species are comparable to results obtained for isocratic separations. The simultaneous monitoring of phosphorus also confirms that the As-lipids in the phospholipid fraction are indeed As phospholipids.

Separation of thio-As species

Thio-methylated As species

Thio methylated As species cannot be separated using typical conditions used for oxo-methylated As species, e.g. anion exchange on PRPX-100 and phosphate buffers (pH 6), as they have very long retention times e.g. thio- As sugars, or do not elute, e.g. thio DMAA, and peak broadening occurs. Increasing the pH to 8-10 with the addition of methanol will elute some thio-methylated As species, e.g thio-arsenosugars within 20-30 min [17, 263]. Some researchers have added hydrogen peroxide to extracts to confirm the presence of thio-methylated As species or to measure the concentration of thio-methylated As species by difference [178].

The common thio-methylated As species can be separated using an Atlantis C18 column (150 mm x 4.4 mm, 5μm) eluted with 20mM ammonium phosphate, pH 3, 1 ml/min, 25 °C (Figure 9) [54]. Buffer concentrations in the range of 10-50 mM have little influence on retention times with the higher mobile phase concentration reducing retention times by less than 1 min (t= 7-24 min at 10 mM; t= 6.5-23 min at 50 mM). The addition of methanol significantly reduced the retention of thio-methylated As species especially the thio-arsenoribosides (t= 7-23 min at 0% methanol; t= 3-8 min at 5% methanol) and causes peak broadening. pH in the range 3-6 only has a minor effect on the retention times of thio-methylated As species (t= 7-23 min at pH 3; t= 6-21 min at pH 6) except for thio-DMAA (t= 8.5 min at pH 3; t= 3 min at pH 6), because most of the

As species are either uncharged or anions at pH 3. At pH 3,oxidation of thio-methylated As species on the column during a chromatographic run does not occur. Recoveries of As standards (50 µg/l) are greater than 98%. Thio- MA coelutes with oxo- sulfate arsenoriboside (Figure 8), thus for samples containing large amounts of oxo-arsenoribosides measurement of thio-MA is difficult. Our experience is that excellent separation of thio-methylated As species can be achieved with new columns, but retention times shorten when several 'real' samples have been run.

Thioarsenate species in waters

Thioarsenates are commonly determined using an Ion Pac AS16 (250 mm x 4-mm) anion column (Dionex, Sunnyvale, CA, USA), but eluted with a gradient of 20–100 mM NaOH, 1 ml/min, 25 ºC (Figure 10). An self-regenerating suppressor (Dionex, Sunnyvale, CA, USA) is used to remove sodium from the solutions prior to introduction into the ICP-MS [220]. Later eluting mono, di- and tri- thioarsenate species are quantitatively eluted from the column (95-100%), however, the baseline early in the chromotograph is unstable and it is not possible to quantify early eluting thio-methylated As species. To determine thioarsenates in waters, the samples need to be thawed in a glove box filled under nitrogen and then transferred into Teflon screw cap glass vials so that air is excluded to prevent oxidation of thio- species. Water samples, if possible, should not be diluted before analysis as alteration of pH or HS^- concentration may alter the distribution of thioarsenate species present [264].

Separation of As glutathionine and phytochelatin species

Complexed As species in bile, urine and plants such as rice presents a challenge to speciate as they are easily denatured and difficult to chromatograph, because species are only stable for a short period, 1-2 hr, and easily dissociate on chromatographic columns unless a mobile phase with a low pH is used [71, 93].

As-GSH species can be separated and quantified using C18 reverse phase chromatography with 0.1% formic acid (pH 2.65) and an acetonitrile gradient (0-40%) [265]. As-PC species in plants can also be separated and quantified by C18 reverse phase chromatography with gradient elution

using formic acid and methanol to separate As species (Fig 13) [131, 266]. It is recommended by [131] that extracts be spiked with As(III) to check that As-PCs are not formed during extraction although this does not appear to occur. A mass spectrometer detector that can precisely measure the mass of the As species eluting needs to be used concurrently to allow definitive identification of the As-PC species.

Overview and recommendations

As species have a wide variety of ionic characteristics that are pH dependent, thus finding one separation scheme that will separate all the common As species is difficult. At pH 7, As(III) (pKa_1 = 9.3) is an uncharged species; As(V)(pKa_1 = 2.3), oxo-MA (pKa = 3.6) and oxo-DMA (pKa = 6.2) are anions; AC, TETRA and TMAO (pKa = 3.6) are cations while AB (pKa = 2.18) is a zwitterion. Different chromatographic approaches using anion exchange, cation exchange, reverse phase, ion-exclusion and size exclusion that been used to separate As species are illustrated in Table 4. Normally at least two complimentary techniques are required to fully separate and characterise As species although the coupling of an anion and a cation column can be used to simultaneously separate anion and cation As species [149]. The general approach is to use ion exchange chromatography to separate the anions and cations or use reverse phase chromatography in cojunction with an ion pairing reagent to separate charged and uncharged As species.

Care must be taken with choice of columns. Columns with the same chromatographic resin often produce different elution profiles depending on if glass or PEEK lined columns are used. For example, As anions separated using Hamilton PRPX-100 anion exchange columns, which are extensively used As speciation studies, have longer retention times in glass lined columns than PEEK lined columns. Whether the effects are due to the lining is not clear as glass columns have a 4.1 mm bore while PEEK columns have a 4.6 mm bore. There has been a shift to the use of microbore columns packed with smaller particles for HPLC chromatography [152, 267] to obtain greater resolving power and lower detection limits. The use of micorbore columns requires low dead volumes, low flows and the use of cooled spray chambers and micronebulisers with higher mass transfer efficiencies. Low flow systems may cause problems due to instability of the

ICPMS signal resulting in a decrease in chromatographic resolution and decreased sensitivity. In practice, these problems seem not to occur [268, 269].

Factors affecting separation and eluting times include, pH, mobile phase composition and temperature. HPLC columns are normally operated at elevated temperatures (30-70 ^{o}C) to improve solution diffusion and mass transfer because of lower vicosities, lower back pressures and higher flow rates [253, 270]. For example, increasing column temperatures from 25 to 55 ^{o}C reduces the retention times of sulfonate and sulfate arsenoribosides on PRPX-100 anion columns by 10-20 % [271]. The advantages of using very high temperatures has been demonstrated by Terol and co-workers [272] who used a porous graphitic carbon column (Hypercarb, Thermo Electron Corporation) with a 2% methanol , pH 8 mobile phase operated at 120 ^{o}C to separate arsenoribosides in seaweed and krill samples. When column temperatures were increased, retention times and peak dispersion substantially decreased along with an accompanying increase in sensitivity.

Evethough gradients have been used to separate As species in one run, we prefer isochratic mobile phases and the use of anion and cation chromatography to separate water soluble As species. Sample extracts often contain large amounts of a particular species e.g. AB, that obscur minor As species The use of anion and cation chromatography is attractive as anions and cations arelute in the void from cation and anion columns respectively reducing coelution of As species and matrix interferences. A major problem, however, seems to be the coelution of As(III) and DMA on anion columns especially if anlysing acid extracts or extracts contain a large amount of organic matter. Similiarly the analysis of phosphoric acid can distort the As(V) peak shape. We have also found that the use of reverse phase chromatography with ion-pairing reagents is prone to severe matrix and pH effects as ion-pairing reagents also pair with matrix components.

Some As species (Thio-As, AsGSH and As-lipids) cannot be readily separated by ion-exchange and require the use of reverse phase chromatography. Thio-As species bingd to ion-exchnge columns with AsGSH species requir acidic mobile phases to prevent degradation and the use of acetonitrile gradients to separated species.

Lipid-As species used to be analysed by subjecting extracts to acid or enzymatic hydrolysis to convert species to water soluble As species, now reverse phase chromtagrphy is used to

determine intact As-lipid species. Rigorous clean up of extracts is required as well as gradient elution with mobile phases containing high contents of organics (e.g. 95 % methanol) to separate closely eluting As species with similar masses. Besides needing to prevent carbon build up on interface cones, the different response of As-lipids in the ICPMS due to variable carbon content affecting the ionisation of As-lipid species in the plasma needs to be accounted for. Post column addition of carbon as acetone or methanol can be used to give a consistence response for As-lipid species.

What ever chromatographic system is chosen, spiking is essential to account for matrices influencing retention times, peak suppression and splitting.Column recoveries also need to be measured to account for As species e.g. Thio- As species adsorbing to columns.

Quality assurance and control

Mass balances

Mass balances and recoveries must be determined for all steps of the analytical procedure. It is essential that both total As and extractable As be determined to allow the percentage of unextracted As species to be determined. In many published studies low extraction and column efficiencies are reported resulting in little of the As species present being characterised.

Use of As additions

Methods need to be evaluated using standards addition technique for As. Two types of spikes are used; (1) during extraction to determine if As species conversion or degradation are occurring, and (2) during chromatographic separation to account for matrix effects on retention times, peak shapes and peak areas. For example, a large amount of starch material is present in rice [86], which can lead to a decrease in peak resolution and a shift in retention times. Meanwhile the carbon in the extract may enhance the As signal.

Use of certified reference materials

Digestion, extraction, separation and measurement processes are all subject to errors including contamination, degradation, matrix effects and calibration errors. Certified reference materials (CRMs) are available to assist in quantifying full procedural errors. Many laboratories have published values for As species in certified reference materials (Table 6 and 7). Although relatively few CRMs have been certified for As species, a large range of As species have been reported for CRMs. Relatively few As species concentrations have been reported for terrestrial water and soils, human tissues (urine, hair and blood) and crops (rice, tomatoes, peaches and wheat), while there is only one report for terrestrial animal tissues (Bovine liver). As expected the common species reported are As (III), As (V), MA and DMA as these occur naturally in most samples. AB is also reported in human tissue CRMs as it is present from the ingestion of seafood. Other As species (TMAO, AC, TMAP and Thio-As) are sporadically reported.
A large range of As species have been reported in marine CRMs reflecting the high As concentrations, relative ease of extraction and large range of naturally occurring As species. Common species reported are As (V), MA, DMA and arsenosugars in algae and plankton. While As(III), As(V), MA, DMA, AB a nd AC are reported for mollusc, crustacean and fish. Other As species that are sporadically reported are TMAO, TETRA, DMAA and TMAP. Notable gaps in As species reported include Thio-As and As-lipid species, probably reflecting the difficulty of their measurement.

We have not attempted to compile the concentration of As species in these publications to provide consensus values as this is outside the scope of the review. If this is to be undertaken, this will require each paper to be critically reviewed in terms of (1) the extraction procedure used (i.e. extraction efficiencies), (2) the chromatographic system used (i.e. coelution of As species such as As(III) and AS1, column recoveries) and (3) quantification (i.e. ICPMS conditions and standards used).

Interlaboratory studies

In the absence of CRMs, interlaboratory studies also provide a means of assessing the quality of results.

Morabito and co-workers [273] prepared a new reference material, BCR 710 Oyster tissue, from *Crassostreae gigas*. No agreement was found with respect to inorganic As, oxo-DMA,

arsenosugars and residual As concentrations. AB results were scattered but a concensus value of 33 ± 7 μg/g was given and an indicative value of 0.82 ± 0.18 μg/g for oxo-DMA.

Raab and co-workers [97] distributed seven algae samples (Five purchased from food stores and two BCR 279 Sea lettuce samples) to thirteen laboratories. Five laboratories characterised the water soluble fraction with respect to As species. Extraction efficiencies ranged from 3-96% depending on the algal sample. Although different chromatographic procedures were used, three of the five laboratories gave results in agreement for As (V), oxo-DMA and arsenosugars 1-4. For BCR 279, extraction efficiencies ranged from 38-58% and column recoveries from 68-82%. The trial showed that the identification of As species using only one chromatographic system is problematic as the elution order of As species for some algal samples were altered when other chromatographic conditions were used.

Baer and co-workers [274] published the results of an interlaboratory study measuring inorganic As in NRCC DOLT-4. Only 22 out of 95 laboratories reported inorganic As concentrations. 16 laboratories reported As concentrations below 0.25 μg/g while 3 laboratories reported results as < 1 μg/g. Results were not method dependent, but inexperience laboratories reported higher values.

Ito and co-workers [52] investigated the measurement of As species in blood. Four laboratories reported values for five As species in blood materials. For most As species, good agreement was obtained and the concensus values obtained were assigned as target values so these samples can be used as quality assurance materials. All As species were stable for up to 2 months when stored at 4 ^{o}C and -20 ^{o}C without additives. Quantification of AB concentrations in blood was poor, possibly because of signal supression due to the coelution of other components.

de la Calle and co-workers [259] conducted an interlaboratory comparison exercise for the determination of inorganic and total As concentrations in rice. Six extraction procedures were compared and general agreement found between methods. When discussing the results the authors highlighted the problem of not correcting for sample moisture content.

de la Calle and co-workers [258] conducted a similar interlaboratory comparison exercise for the determination of inorganic and total As concentrations in dried samples of spinach (NIST CRM1570a), wheat and seaweed (*Fucus vesiculosus*). 71 laboratories from 31 countries,

including 30 European reference laboratories, participated and again results did not appear to be method dependent. 85%, 65% and 20% of results for spinach, wheat and seaweed were acceptable. Spinach results were good despite the low As concentration (0.05 μg/g). The results from this exercise highlighted the need for hydrogen peroxide to extract As from wheat. Overestimation of inorganic As concentrations in seaweed was common.

Briscoe and co-workers [275] conducted a similar interlaboratory comparison exercise for the determination of As(III), As(V), MA, DMA and total As concentrations in rice, kelp powder and apple juice. The authors conclude that as the majority of laboratories participating in this study (66%) achieved an overall score of 3 or 4 (good or outstanding) there is generally good intercomparability amongst most laboratories that are producing total As and As speciation data for these matrices. 93% of the laboratories received an overall score of 2 or better, and only 2 laboratories (7%) received scores of 1 or 0 (poor or unacceptable, respectively). As only 6 laboratories (15%) receiving an overall score of 4, further analytical method development is required in order to achieve a high level of consistency across multiple laboratories using various methods worldwide. Examination of data shows there was a considerable variation in results even for total As concentrations. Problems were evident for the measurement of As(III), As(V), MA and DMA in the kelp sample and As(III) and As(V) in apple juice.

Concluding remarks

The aim of this review was to examine published information on storage and sample preparation procedures and the use of HPLC- ICPMS and HPLC-HG-AFS to extract and measure As species concentrations. The continuous challenge in speciation analyses is to quantitatively extract and maintain the integrity of species. As illustrated above, some As species such as the arsenosugars and AB are relatively stable but As(III), As(V), MA (III), DMA (III), As-GSH and As-PC species are not. Considerable care should be taken to ensure that the As species determined are not artifacts of the preservation or extraction procedures. Some general observations that arise out of this review are:

Sample preservation: For waters and biological fluids, flash freezing in liquid nitrogen with the exclusion of air and adding a preservative such as EDTA is suitable for the preservation of most As species. Stability of As species is critically dependent on the sample matrix and the preservation technique used should be evaluated for each sample type. If aqueous As(III) and As(V) measurements are required the use of "in field" solid phase extraction cartridges should be considered to isolate these species before oxidation changes can occur. Most biota and sediment samples can be stored at -20 ^{o}C to -80 ^{o}C, however, on thawing some samples can lose considerable amounts of water containing As species. If As species in plants such as As-GSH or As-PCs are to be determined , samples need to be determined fresh and not stored.

Removal of extraneous material: It is essential that all biota be cleaned to remove surface material and epiphytes and animals be depurated to remove gut contents before As species analysis

Drying of samples: Animal tissues can be freeze dried before analysis with a low likely hood that As species will change. Plants can be oven or freeze dried if only a measure of inorganic As and methylated As species is required. If As species such as As-GSH or As-PCs are to be determined, the effects of drying on samples needs to be evaluated as the loss of As-PC complexes have been reported. Similarly, sediments and soils should not be dried as redox changes will occur affecting the As(III) and As(V) species and other As species such as arsenosugars.

Sample grinding and particle size: Extraction efficiencies have been shown to be critically dependent on paricle size and substantial increases in extraction efficiencies occur when particle size is reduced from 500 µm to less than 50 µm. Grinding, however, can result in the loss of some As species e.g. As-PC complexes from plants. It should be noted that CRMs are supplied ground to 50-400 µm while real samples are not, bringing into question the performance of methods validated only with CRMs.

Sample extraction: As cannot be extracted from all sample matrices using a single set of conditions. Extraction procedures need to be optimised for each tissue type e.g. roots, stems and

leaves of plants, animal muscle and liver tissues. Cells and membranes need to be ruptured by grinding, freeze drying or the use of sonification. Samples may also need to be defatted e.g. using acetone as the presence of fats can lower extraction efficiencies and influence HPLC column performance. Methanol, water and methanol-water mixtures are commonly used to extract non-lipid As species from marine algae and animals, but are inefficient in extracting inorganic As species from angioperms, terrestrial animals, sediment, soils and air particulates. For these samples the use of a dilute acid is required. The use of a sequential extraction procedure, where for example, methanol-water extraction is followed by dilute acid extraction, will increase the extraction efficiencies of hard to extract As species. Micowave heating is now widely used and often has been shown to give better recoveries relative to mechanical mixing and sonification. The use of sub-critcal water (temperatures between 100-350 ^{o}C under pressure) shows promise to quantitatively extract As species from plant and sediment samples. A number of studies have verified the efficacy of extraction procedures using XANES. Good agreement has been reported between XANES and HPLC-ICPMS for the analysis of plants, rice, earthworms, phytoplankton and zooplankton extracts, but, speciation information such as the binding partners of As(III) e.g. GSH, PCs may be lost on extraction. As-lipids can be extracted using a variety of organic solvents with the traditional chloroform-methanol (2:1 v/v) mixture being popular.

Storage of extracts: Similar to waters and biological fluids, the behaviour of As species in sample extracts is critically dependent on the sample matrix and the preservation technique used should be evaluated for each sample type. Generally aqueous and methanol-water extracts of oxo- and thio-methylated As species stored at 4-20 ^{o}C are stable for short periods of 15-20 days Some As species such as phosphate and sulphonated arsenoribosides can hydrolyse to glycerol sugars when in solution. As well, thio-methylated As species slowly convert into their oxy-analogs. Arsenosugar and thio-methylated As species extracts are best stored as freeze dried pellets. Arsenosugars also degrade slowly at low pH while acification leads to an immediate decrease, or complete loss of dithio-MA and dithio-DMA, often accompanied by an increase in the corresponding mono thio-As species, thus acidification of extracts should be avoided. Sample extracts for MA(III) and DMA (III) analysis need to be stored below -20 ^{o}C, if the integrity of

these As species are to be maintained. As-PC complexes extracted form plants are only stable for short periods (< 3 days) at 1 ^{o}C and their stablity when frozen is unknown.

HPLC –ICPMS or HPLC-HG-AFS: Water soluble As species have a wide variety of ionic characteristics that are pH dependent, thus finding one separation scheme that will separate all the common As species is difficult. Consequently different chromatographic approaches using anion exchange, cation exchange, reverse phase, ion-exclusion and size exclusion have been used to separate As species. Normally at least two complimentary techniques are required to fully separate and characterise As species although the coupling of an anion and a cation column can be used to simultaneously separate anion and cation As species. The general approach is to use ion exchange chromatography to separate the anions and cations or use reverse phase chromatography in cojunction with an ion pairing reagent to separate charged and uncharged As species. HPLC columns are normally operated at elevated temperatures (30-70 ^{o}C) to improve solution diffusion and mass transfer because of lower vicosities, lower back pressures and higher flow rates There has been a shift to the use of microbore columns packed with smaller particles for chromatography to obtain greater resolving power and lower detection limits. Use of these columns requires the minimisation of dead volumes and low flows require the use of cooled spray chambers and micronebulisers with higher mass transfer efficiencies. The analysis of water soluble As species is relatively straight forward as long a sample peaks are not misidentified and matrix interferences accounted for that may influence quantitation. The use of reverse phase chromatography seems to be prone to more severe matrix and pH effects in comparison to ion chromatography. One of the problems of using ion pairing reagents is that ion pairing with matrix components occurs as well causing shifts in retention times. Thio methylated As species cannot be separated using typical conditions used for oxo-methylated As species, e.g. anion exchange on PRPX-100 and phosphate buffers (pH 6), as they have very long retention times or do not elute and peak broadening occurs . Increasing the pH to 8-10 with the addition of methanol will elute some thio-methylated As species, e.g. thio-arsenosugars within 20-30 min. Some researchers have added hydrogen peroxide to extracts to confirm the presence of thio-methylated As species or to measure the concentration of thio-methylated As species by

difference. The common thio-methylated As species can be separated using an Atlantis C18 column eluted with 20mM ammonium phosphate, pH 3, 1 ml/min, 25 °C.

Until recently, As lipids in fish oils were saponified with potassium hydroxide while tissues were extracted with a mixture of chloroform/methanol the solvent removed and residues hydrolysed with an acid, an alkali or phospholipase D enzyme. These procedures cleaved the As moiety in lipid extracts, and the water-soluble As species liberated were determined by HPLC-ICP-MS. Now analysis of intact As-lipids is undertaken . Rigorous cleanup of extracts is required and As-lipids can only be separated using reverse pahse chromatography using gradient elution conditions. Methanol or acetone is commonly introduced directly into the ICPMS spray chamber to compensate for the variable amounts of carbon in the mobile phase entering the ICPMS and standardising As signals

Thioarsenates in water are commonly determined using an Ion Pac anion column eluted with a gradient of 20–100 mM NaOH, 1 ml/min, 25 ºC with an anionic self-regenerating suppressor used to remove sodium from the eluent prior to introduction into the ICP-MS to prevent the suppression of As signals.

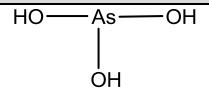
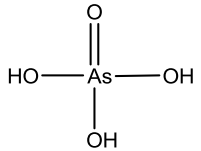
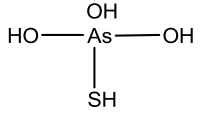
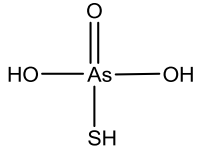
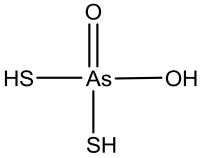
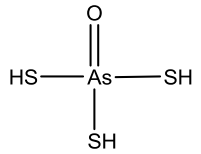
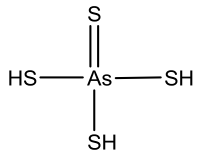
Complexed As species in bile, urine and plants such as rice presents a challenge to speciate as they are easily denatured and difficult to chromatograph because species are only stable for a short period, 1-2 hr, and easily dissociate on chromatographic columns unless a mobile phase with a low pH is used. As-GSH species can be separated and quantified using C18 reverse phase chromatography with 0.1% formic acid (pH 2.65) and an acetonitrile gradient (0-40%). As-PC species in plants can also be separated and quantified by C18 reverse phase chromatography with gradient elution using formic acid and methanol to separate As species. A mass detector techniques that precisely measure the mass of the As species needs to be used concurrently to allow definitive identification of the As-PC species.

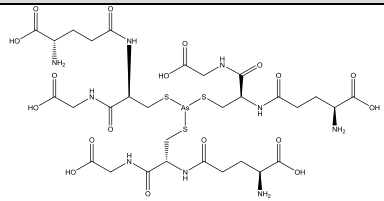
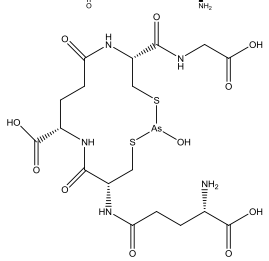
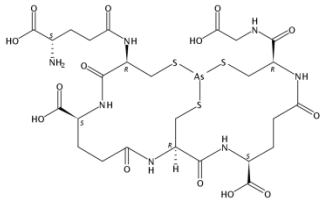
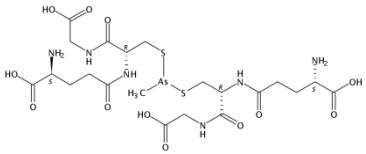
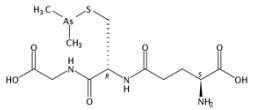
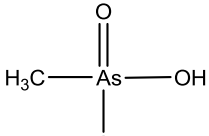
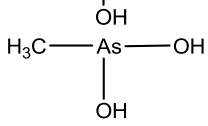
Quality assurance and control: Mass balances and recoveries must be determined for all steps of the analytical procedure. It is essential that both total As and extractable As be determined to allow the percentage of unextracted As species to be determined. In many published studies low

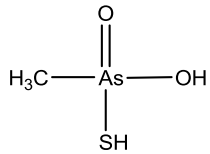
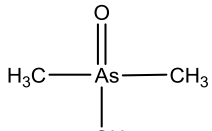
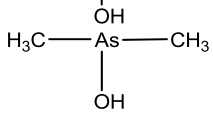
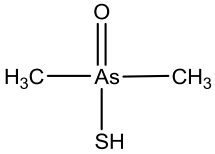
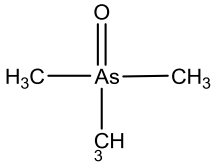
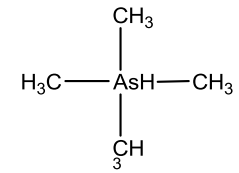
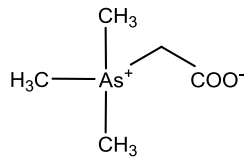
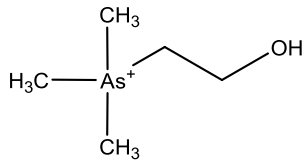
extraction and column efficiencies are reported resulting in little of the As species in samples being characterised. Methods need to be evaluated using As standards addition. Digestion, extraction, separation and measurement processes are all subject to errors including contamination, degradation, matrix effects and calibration errors. Certified reference materials with data on As species are available to assist in quantifying full procedural errors. In the absence of CRMs, interlaboratory studies also provide a means of assessing the quality of results.

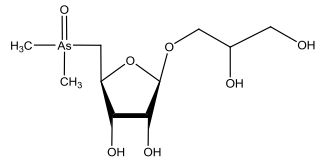
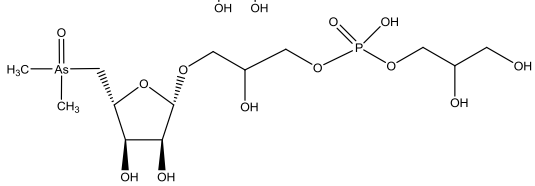
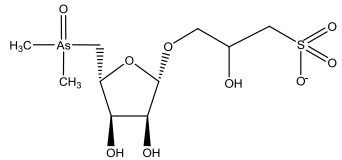
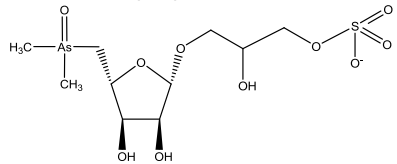
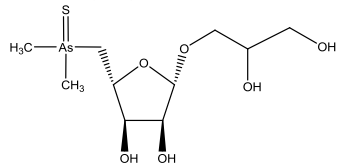
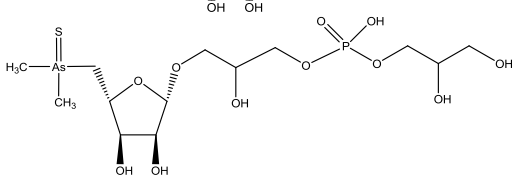
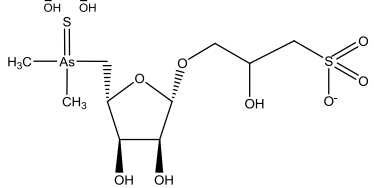
Environmental and food guidelines e.g for rice are being implemented world wide that require not only the accurate measurement of the total As concentration, but As species as well. Protocols developed need to be defensible and be able to show that the integrity of the As species has been maintained through the entire analysis program and that measurements are quantitative and not subject to matrix or other interferences. At a minimum, mass balances need to be undertaken together with As standards additions and a series of quality control samples with known concentrations of As species need to be determined. Participation in proficiency trials are also required to evaluate method performance under normal laboratory operations.

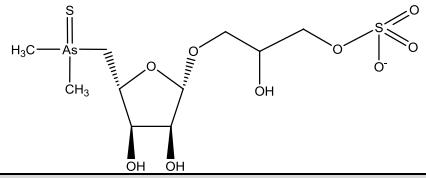
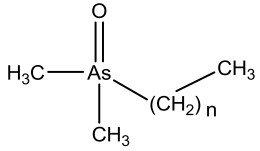
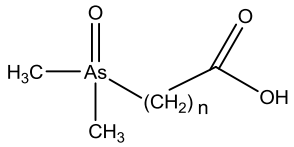
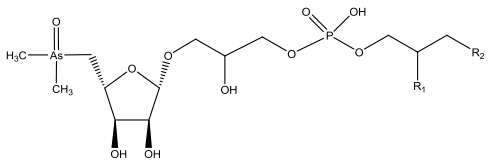
Table 1: Name, formula, molecula mass and CAS number for selected arsenic species.

Species name [a]	Abbreviation [a]	Formula	Molecular mass *m/z* [b]	pKa[c]	CAS	Structure
Inorganic						
Arsenite	As(III)	$As(OH)_3$	125.94	6.86±0.53	13464-58-9	
Arsenate	As(V)	$AsO(OH)_3$	141.94	3.09±0.10	7778-39-4	
Thioarsenite	TAs(III)	AsH_3O_2S	142.01	4.63±0.10	50288-24-9	
Thioarsenate	TAs(V)	H_3AsO_3S	158.01	2.49±0.10	58904-80-6	
Dithioarsenate	DTAs(V)	$H_3AsO_2S_2$	174.07	13.50±0.70	50288-27-2	
Trithioarsenate	TTAs(V)	AsH_3OS_3	190.14	-	50288-22-7	
Tetrathioarsenate	TetraTAs(V)	AsH_3S_4	206.21	-		

Complexed						
Arsenic triglutathione	As(III)[GSH]3	$C_{30}H_{48}AsN_9O_{18}S_3$	993.87	1.74±0.10 9.76±0.16	145903-88-4	
Arsenic phytochelatins	As(III)PC2; GSH-As(III)PC2; As(III)PC3; As(III)[PC2]2	$As(C_8H_{11}N_2O_4S)_n$ $C_{18}H_{28}AsN_5O_{11}S_2$ $C_{26}H_{38}AsN_7O_{14}S_3$	629.49 [276]; 843.73; 918; 1150 [277]	2.21±0.10 9.29±0.16	1113020-54-4 887122-60-3 [276]	 
Methyarsenate glutathionine	MA(III)[GSH]2	$C_{21}H_{35}AsN_6O_{12}S_2$	702.59	1.91±0.10 9.59±0.16	91919-81-2	
Dimethyarsenate glutathionine	DMA(III)GSH	$C_{12}H_{22}AsN_3O_6S$	411.31	2.21±0.10	69819-86-9	
Low molecular weight						
Oxo-monomethyarsenate (V)	MA	CH_5AsO_3	139.97	3.87±0.10	124-58-3	
Oxo-monomethylarsenate (III)	MA(III)	CH_5AsO_2	123.97	9.73±0.53	25400-23-1	

Thio-monomethyarsenate	Thio-MA	CH_5AsSO_2	156.04	4.41±0.70	937022-98-5	
Oxo-diimethylarsenate (V)	DMA	$C_2H_7AsO_2$	138.00	6.30±0.30	75-60-5	
Oxo-diimethylarsenate (III)	DMA(III)	C_2H_7AsO	122.00	12.72±0.53	55094-22-9	
Thio-diimethylarsenate	Thio-DMA	C2H7AsOS	154.06	-	754217-65-7	
Trimethy arsine oxide	TMAO	C_3H_9AsO	136.02	-	4964-14-1	
Tetra methy arsenic oxide	TETRA	$C_4H_{12}As$	135.06	-	27742-38-7	
Arsenobetaine	AB	$C_5H_{11}AsO_2$	178.06	-	64436-13-1	
Arsenocholine	AC	$C_5H_{14}AsO$	165.09	-	39895-81-3	

Arsenosugar 1 (glycerol arsenosugar)	Arsenosugar - OH	$C_{10}H_{21}AsO_7$	328.19	15.02±0.10	1227057-97-7	
Arsenosugar 2 (phosphate arsenosugar)	Arsenosugar- PO_4	$C_{13}H_{28}AsO_{12}P$	482.25	14.95±0.10	88216-76-6	
Arsenosugar 3 (sulfonate arsenosugar)	Arsenosugar- SO_3	$C_{10}H_{20}AsO_9S$	391.25	-	123288-10-8	
Arsenosugar 4 (sulfate arsenosugar)	Arsenosugar- SO_4	$C_{10}H_{20}AsO_{10}S$	407.25	-	123257-94-3	
Thio-arsenosgar glycerol	Thio-OH	$C_{10}H_{21}AsO_6S$	344.26	15.02±0.10	761458-55-3	
Thio-arsenosugar phosphate	Thio -PO_4	$C_{13}H_{28}AsO_{11}PS$	498.32	14.95±0.10	761458-56-4	
Thio-arsenosugar sulfonate	Thio -SO_3	$C_{10}H_{20}AsO_8S_2$	407.31	-	1227407-67-1	

Thio-arsenosugar sulfate	Thio -SO_4	$C_{10}H_{20}AsO_9S_2$	423.31	-	1227407-68-2	
High molecular weight						
		$C_{15}H_{33}AsO$	304.34		1456610-35-7	
		C17H35AsO	330.38		1456610-38-0	
		$C_{16}H_{35}AsO$	318.37		6145-24-0	
		C17H37AsO	332.40		1083077-42-2	
		C18H39AsO	346.42		1423745-41-8	
Arsenic hydrocarbons	AsHC	C19H39AsO	358.43		1456610-45-9	
		C19 H41 As O	360.45		1083077-43-3	
		C20H43AsO	374.48		1423745-42-9	
		C21H45AsO	388.50		1393357-63-5	
		C22H47AsO	402.53		1423745-43-0	
		C24H39AsO	418.49		1456610-47-1	
		C17H35AsO3	362.38		1032052-02-0	
		C23H37AsO3	436.46		1032052-10-0	
Arsenic fatty acids	AsFA	C24H37AsO3	448.47		1296225-43-8	
		C22H35AsO3	422.43		1423745-44-1	
		C22H37AsO3	424.45	4.75±0.10	1423745-45-2	
		C45H88AsO14P	959.07		115921-38-5	
		C43H84AsO14P	931.01		1423745-30-5	
		C44H86AsO14P	945.04		1423745-31-6	
		C46 H90 As O14 P	973.09		1423745-32-7	
		C47 H92 As O14 P	987.12		1423745-34-9	
		C48 H94 As O14 P	1001.15		1423745-35-0	
		C49H96AsO14P	1015.17		1393357-61-3	
		C51H100AsO14P	1043.23		1631038-74-8	
Arsenic phospholipids	AsPL	C53H104AsO14P	1071.28	13.15±0.20	1393357-62-4	
		C47H90AsO14P	985.10		1423745-37-2	
		C47H88AsO14P	983.09		1423745-38-3	
		C47H86AsO14P	981.07		1423745-39-4	
		C45H86AsO14P	957.05		1423745-40-7	
		C43 H84 As O14 P	931.01		1423745-46-3	
		C47 H86 As O14 P	981.07		1423745-47-4	
		C45 H86 As O14 P	957.05		1423745-48-5	

C45H84AsO14P	955.04	1393357-60-2
C45 H84 As O14 P	955.04	1425509-86-9

[a] some common names and abbreviations taken from Francesconi and Kuehnelt 2004[13]
[b] formula, molecular mass and chemical properties taken from SciFinder™, predicted pKa and molecular weight calculated using Advanced Chemistry Development (ACD/Labs) Software V11.02 (© 1994-2015 ACD/Labs).

Table 2: Preservation techniques: Reactions that may occur in containers and effect on total arsenic concentrations and arsenic species

Reaction	Effect	Comment	Preservation	References
Physical				
Change in temperature	Total As ↑↓ As(III)/As(V) ↑↓ $(CH3)_xAs-$ ↑↓	Increasing temperature can dissolve precipitates e.g. FeS. Destabilization of As associated with colloids. Freezing may cause precipitates, Fe(III) oxides, calcite, MnO_2, CaP Temperature increase: Microbial activity increases Temperature decrease : Microbial activity decreases	Water: Store in cool room. Use in-field preconcentration procedures	[25, 34, 36, 38, 57, 60, 183, 186, 237, 278-280]
Freeze/thawing	Total As ↑↓ As(III)/As(V) ↑↓ $(CH3)_xAs-$ ↑↓	Defrosted samples may lose water on thawing	Analyse fresh	[279, 281]
Exposure to light	As(III)/As(V) ↑↓	Photoxidation. Reaction of As(III) with Fe(II/III), MnO_2 or organic matter. Additon of acid can increase oxidation rate.	Store in dark. Avoid acid or store acidified samples in dark with EDTA	[25, 34, 38, 39, 282, 283]
Chemical				
Sorption	Total As ↑↓	Loss of As to container walls	Use PTFE containers	[23, 183, 237, 284]
pH change and Chemical hydrolysis	As(III)/As(V) ↑↓ $(CH3)_xAs-$ ↑↓	AsS species unstable. Preservatives can hydrolyze compounds in solution and associated with particles	Flash freeze, avoid preservatives	[25, 38, 39, 57, 59, 60, 186, 187, 231, 264, 280, 282]
Enzymatic hydrolysis	As(III)/As(V) ↑↓ $(CH3)_xAs-$	Organic associated with particles may be hydrolyzed by enzymes	Flash freeze	
Oxidation/reduction	Total As ↑↓ As(III)/As(V) ↑↓ $(CH3)_xAs-$ ↑↓ $(CH3)_xAs-$ ↑↓	Oxidation by Fe(III), O_2, MnO_2 Fe/Mn oxides precipitate or dissolve	Remove oxygen in head space by N2 purging. Store in Anaerobic bag	[25, 34, 38, 39, 57, 60, 231, 264, 280, 282]
Precipitation	Total As ↑↓ As(III)/As(V) ↑↓ $(CH3)_xAs-$ ↑↓	Calcite formation. Ca, Mg or trace metal arsenates. Addition of H_3PO_4, if high [Fe] can form $Fe_3(PO_4)_2$ Fe/Al salts of phytic acid are not soluble Coprecipitation with Fe(III) or MnO_2 High S, As_2S_3 ppt	Acidify, avoid H_3PO_4	[25, 34, 37, 38, 60, 237, 279, 280, 282]
Complexation	Total As ↑↓ As(III)/As(V) ↑↓	Dissociation of complexes. Particles that are removed on filtration	Acidify	[25, 39, 187, 231, 264, 280, 285]
Biological				
Microbial growth	Total As ↑↓ As(III)/As(V) ↑↓ $(CH3)_xAs-$ ↑↓	Bacteria adhere to container walls, demethylation occurs	Freeze/acidify	[25, 34, 85, 279]

Microbial death	Total As ↑↓ As(III)/As(V) ↑↓ $(CH3)_xAs-$ ↑↓	Particle associated As may be released	Freeze/acidify	[25, 38, 65, 85, 279]
Algal growth	Total As ↑↓ As(III)/As(V) ↑↓	May occur in samples stored at room temperature without exclusion of light	Exclude light	
Algal cell disruption	Total As ↑↓ As(III)/As(V) ↑↓	May occur during filtration and freezing	Centrifuge	[25, 183]

Table 3: Extraction procedures to isolate arsenic species form sample matrices. M – mechanical extraction; H – hot plate extraction; US – ultra sonic extraction; PE - pressure extraction; MAE – microwave assisted extraction.

Application	**Methanol-water, water and buffers**					**Aid or base**					**Sequential Extraction**			**Enzymatic**		
	M	H	US	MAE	PE	M	H	US	MAE	PE	M	US	MAE	M	US	MAE
Human																
Urine																
Blood	[286]					[286]										
Hair	[286, 287]															
Finger nails	[286]															
Terrestria**l**																
Atmospheric particles			[154, 288]					[153, 154]	[20, 153, 154, 288, 289]							
Soil/sediment	[290-292]		[68, 83, 154, 290, 293]	[290]		[151]		[294]	[147]							
Iron minerals						[295]										
Coal																
Plants		[70, 71, 277]	[68, 79, 296]		[106]	[177, 297]		[79]			[144, 296, 298]	[79]				
Grasses				[103]												
LIchens												[289]				
Mushrooms			[182]			[299]										
Fungus			[300]													
Castor beans			[301]													
Mung beans	[302]															
Indian cress			[190]													
Pepper	[303]															
Rice		[86]	[100, 304]	[305]	[100, 306]	[100, 134, 259, 306]	[100, 138, 307-310]	[259]	[188, 259, 260, 305, 311]					[134]	[100, 157, 294, 305, 306, 312]	
Dietary supplements				[313]					[313]							
Cereals									[314]							
Tomatoes																
White			[80]													

mustard																
Radishes			[78]													
Spinach															[306]	
Apples						[306]										
Carrots	[315]		[315]		[316]											
Algae			[317]					[72]								
Wheat			[289, 318]						[318]						[289]	[289]
Chicken			[319]	[319]*											[294, 306]	
Baby foods														[156]		
Herbal medicines				[320]			[320]		[320]							
Bird eggs			[321]													
Plankton																
Earthworms	[137, 180, 322]															
Invertebrates	[144]															
Rodents	[298]										[298]					
Fish			[317]													
Sponges			[317]													
Molluscs			[317]													
Frogs			[317]													
Marine																
Sediment						[77, 323]										
Phytoplankton	[119]								[324, 325]		[167, 168, 326-328]					
Angiosperms				[76, 112, 127, 329]		[77, 323]			[127]				[127]			
Seaweeds	[193, 242, 330-332]	[128]	[157, 300]	[56, 77, 96, 127, 128, 192, 222, 243, 323, 333-339]	[340]		[128]		[128, 341]				[127]			
Animals																
Mollusca	[17, 178, 342,		[196, 321, 344]	[56, 77, 107, 112, 115, 222,	[345]	[187]					[95, 125]	[95]				

	343]			243, 323, 329, 333]												
Crustaceans	[332, 342, 343, 346]		[346, 347]	[77, 107, 112, 115, 323, 329, 346, 347]		[346]								[123]		
Fish	[65, 255, 342, 343, 348, 349]		[294, 344, 347]	[56, 77, 107, 113, 115, 127, 243, 323, 333, 347]	[345]			[347]	[127, 347]				[127]	[123, 348]		
Polychaetes			[350]	[77, 323]					[127]				[127]			
Echinoderms				[243, 333, 341]					[127]				[127]			
Amphipod				[329]												
Pinnipeds	[351]															
Sea birds	[351]															
Sea turtles	[351]															

Table 4: Overview of extraction and chromatographic separation conditions used for various sample matrixes

Application	Anion exchange					Cation exchange				Reverse phase			Other
	None	Methanol-water or water or buffer	Acid	Sequential	Enzymes	None	Methanol-water or water or buffer	Acid	Sequential	None	Methanol-water or water or buffer	Acid	
Biological fluids													
Gut microflora	[184]												
Urine	[22, 50, 214, 240, 270, 280, 286, 352-369]					[49, 245, 280, 356, 357, 359-361, 370, 371]				[227, 253, 270, 356, 357, 360, 370, 372-374]			[22, 375]
Rat urine	[376]												
Sheep's urine	[263, 377]					[263]							
Blood-serum	[22, 52, 360, 361, 377]	[287]	[287]			130 [360]				[52, 360, 378, 379]			[22, 52, 378]
Saliva										[241]			
Hair		[287]											
Finger nails		[287]											
Liver cytosol	[185]					[185]							
Terrestrial													
Atmospheric particles		[154, 288]	[20, 153, 154, 288]	[380]					[380]				
Water	[34, 47, 55, 57, 60, 267, 278, 355, 381-386]					[387-390]				[46, 56, 205, 344, 372, 389, 391-396]	[83]		
Soil/sediment		[47, 68, 267, 290, 292, 293]	[80, 147, 397]				[292]						
Coal													
Leachate	[398, 399]												
Algae		[317]					[317]					[72]	
Plankton		[119]					[119]						
Mushrooms		[182]					[182]						
Lichens				[380]					[380]				
Fungus		[300]									[300]		
Plants		[68, 79, 106, 296, 302]	[79, 297]	[79, 144, 298]				[144]				[71, 130, 177, 277]	
Invertebrates		[144]					[144]						
Rodents		[298]		[298]			[298]		[298]				

Mushrooms													[299]
Rice		[85, 100, 188, 305, 306, 400]	[100, 134, 138, 188, 305, 307-312]	[100, 134]	[157, 305, 306, 312]			[260]					[157]
Sun flowers													
Grasses		[103]											
Indian cress		[190]											
Apples		[306]			[306]								
Spinach		[80, 306]	[306]		[306]								
White mustard													
Pepper		[303]											
Wheat		[289, 318]	[289, 318]		[289]								
Carrots		[315, 316]										[401]	
Radishes		[78]					[78]						
Castor beans		[301]											
Herbal medicines		[320]	[320]										
Chicken		[319]											
Beverages	[211, 354, 402-404]					[405]							
Dietary supplements								[313]					
Baby food					[156]								
Fish sauce	[16, 406]												
Earthworms		[137, 180, 322]					[137, 180, 322]						
Fish		[317, 347]	[347]				[317]						
Sponge		[317]					[317]						
Mollusca		[179, 317]					[179, 317]						
Frog		[317]					[317]						
Marine													
Water	[213, 325]												[407]
Sediment		[213]	[77, 123, 323, 325]					[325]					
Phytoplankton		[167]		[326-328, 408]					[326-328, 408]				
Sea anemone		[409]											
Angiosperms		[76, 112, 329, 341]	[77, 323, 341]	[341]			[76, 329, 341]	[77, 341]	[341]				
Seaweeds		[96, 128, 192, 193, 242, 243, 323, 330-334, 336-338, 340,	[128, 341]	[341]			[77, 323, 330, 333, 334, 338, 341, 409, 412]		[341]		[56, 331, 410]		[332]

		341, 408, 410-412]											
Polychaetes		[77, 323, 350]	[341]	[341]			[77, 323, 335, 341, 413]	[341]	[341]				
Mollusca		[17, 65, 77, 107, 115, 178, 196, 222, 243, 323, 329, 333, 341-343, 345]	[187]	[95, 125, 181, 341]			[77, 107, 112, 178, 222, 243, 323, 329, 333, 341]	[187, 341]	[95, 181, 341]		[56, 222, 333, 344]		
Crustaceans		[77, 107, 115, 329, 332, 342, 343, 347, 414]		[347]	[123]		[77, 107, 112, 323, 329]						[332]
Fish		[65, 77, 107, 112, 113, 115, 243, 323, 333, 342, 343, 345, 348, 349, 415]			[123, 348]		[77, 107, 112, 113, 243, 323, 333, 415]				[333, 344, 415]		
Echinoderms		[243, 333, 341]	[341]				[243, 333, 341]	[341]	[341]				
Amphipods		[329]					[329]						
Pinipeds		[351]					[351]						
Sea birds		[351]					[351]						
Sea turtles		[351]					[351]						

Table 5: Separation of lipid soluble species by HPLC-ICPMS

Applications	Extraction	Treatment	Separation	Reference
Terrestrial				
Sheep tissues	CH/M	Silicic acid/ enzyme hydrolysis	Anion exchange	[170]
Marine				
Seaweed	CH/M	Silicic acid/ enzyme hydrolysis	Anion exchange	[170]
Seaweed	CH/M	Silica	C8	[109]
Seaweed	DCM/M	Silica	C18 and Anion exchange	[416]
Seaweed	CH/M	Silica	C8	[109]
Mollusca	CH/M	Phospholipase hydrolysis		[417]
Crustaceans	M	TMAH hydrolysis	GPC/RP C18	[418]
Seals	CH/M	Alkaline hydrolysis	Anion/cation exchange	[171]
Fish oils	CH/M	Acid hydrolysis	Anion exchange	[262]
Fish oils	H/W	Silica gel	RP C18	[160]
Fish oils	Heptane/M/W	M/A partitioning	RP C18	[419]
Fish	H/ M/DCM	Silica gel	RP C18	[92]
Fish	CH/M	DEAE- anion/Silica	RP C18	[420]
Fish	H /M	Size exclusion	RP C18	[14]
Fish	CH/M	Silica, alkaline hydrolysis	Anion exchange	[173, 421]

A = Acetone, CH = Chloroform, M = Methanol, H = Hexane, DCM = Dichloromethane, W = Water, GPC = gel permeation, RP= reverse phase

Table 6: Arsenic species reported in non- marine certified reference materials

CRM	As species												References
	As(III)	As(V)	MA	DMA	AB	TMAP	AC	TMAO	Thio-DMA	DMAA	Thio-DMAA	Thio-DMAE	
Geological													
Coal GBW11117	x	x											[422]
Soil GBW07450	x	x											[148]
Soil CRM025-050	x	x											[148]
Soil IAEA 7	x	x	x	x	x								[147, 158]
Soil BCR 320	x	x	x	x									[147, 151]
Soil BCR 141	x	x	x	x									[147]
River Sediment APS 1066		x											[403]
Human													
Urine Urichem N	x	x	x	x									[353, 354]
Urine NIST SRM 2670	x	x	x	x	x								[23, 50, 237, 253, 287, 353, 354, 374, 423-433]
Urine NIST SRM 2670a	x	x	x	x	x								[49, 362, 365]
Urine NIST SRM 2669	x	x	x	x	x		x	x					[238, 434]
Urine NIES CRM 18	x	x	x	x	x	x			x	x	x	x	[362, 370, 375, 379, 435, 436]
Urine Utack normal	x	x	x	x	x								[437]
Urine Utack high	x	x	x	x	x								[437]
BioRad 1	x	x	x	x	x								[437]
BioRad 2	x	x	x	x	x								[437]
Sigma 1	x	x	x	x	x								[437]
Sigma 2	x	x	x	x	x								[437]
Hair GBW-07601	x	x	x	x									[121, 159]
Hair NIES 13	x	x	x	x									[287, 433]
Blood Utak 1	x	x	x	x	x								[437]
Blood Utak 2	x	x	x	x	x								[437]
Blood Utak 3	x	x	x	x	x								[437]
Plants													
Rice NIST CRM -1568a	x	x	x	x									[86, 87, 100, 126, 133, 134, 138, 157, 159, 176, 305-308, 312, 400, 438-443]
Rice NMIJ CRM -7503a	x	x	x	x									[176, 307]
Rice NMIJ CRM -7405a	x	x		x									[86]
Rice IMEP- 107	x	x	x	x									[188, 307]
Rice ERM BC211	x	x	x	x									[188]
Rice NIES 10a	x	x	x	x									[188]
Rice NIES 10b	x	x	x	x									[188]
Rice NIES 10c	x	x	x	x									[188]
Rice FAPAS T07151QC	x	x	x	x									[188]

Rice GBW 10010	x	x	x	x									[305, 320]
Tomato leaves NIST CRM 1573a	x	x											[132]
Peach GBW82301	x	x	x	x									[297]
Wheat NIST RM 8436	x	x	x	x									[289]
Water													
NIST 1643d	x	x											[444]
NIST 1643c	x	xx	x	x									[205]
EC SLRS-2	x	x	x	x									[47, 391]
APS 1075	x	x											[403]
APS 1071	x												[403]
Animals													
Bovine liver NIST SRM1577	x	x	x	x	x								[140, 286]

GBW= NRCCRM China; CRM = Resource Technology Corporation USA; ERM = European Reference Materials (Europe); IAEA = International Atomic Energy Agency, Belgium; BCR = ; Community Bureau of Reference, Belgium; Urichem = Urine Control Fisher Scientific; IMEP = International Measurement Evaluation Program (Europe), NMIJ =National Measurement Institute (Japan), NIES = National Institute of Environmental Science (Japan), Utack = Utack, Valencia, USA; Biorad = Biorad, Munchen Germany; Sigma = Sigma, St Louis USA; FAPAS = Food Analysis Performance Assessment Scheme (USA), NIST = National Institute of Science and Technology (USA), EC = Environment Canada; APS = ; NFA = National Food Agency Denmark; GBW = Standard materials of soils component, China; NRCC = National Research Council Canada; MURST = Institute for Reference Materials and Measurement, Belgium..

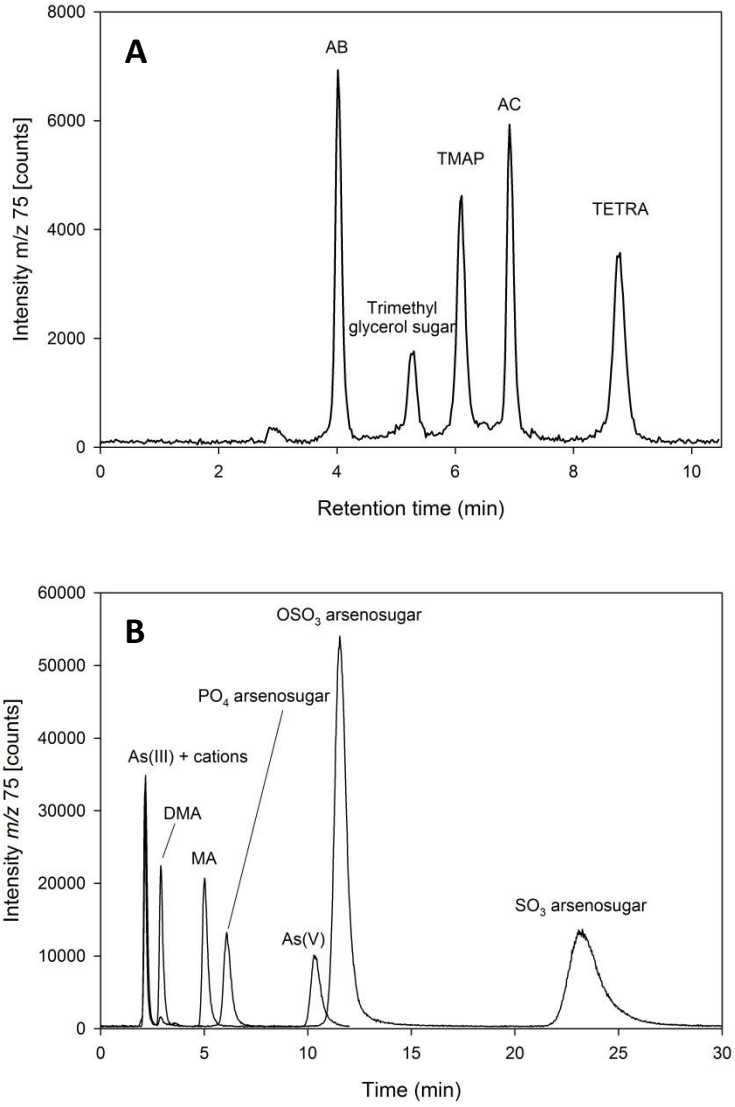
Table 7 As species concentrations reported in marine certified reference materials.

CRM	As species															Reference
	As(III)	As(V)	Total In As	MA	DMA	AB	AC	TMAO	TETRA	DMAA	TMAP	AS1	AS2	AS3	AS4	
Marine sediment																
MURST-ISS-A1	x	x		x	x	x										[294]
IAEA 405	x	x		x												[151]
Marine biota																
Algae/diatoms/plankton																
Seaweed IAEA/TM 140	x	x		x	x					x		x	x	x	x	[74, 94, 96, 294, 336, 445, 446]
Seaweed NIES No 14												x	x	x	x	[432, 447, 448]
Seaweed BCR 279	x	x	x	x	x	x	x		x		x	x	x	x	x	[97, 119, 127, 168, 328, 339, 449]
Seaweed NIES 9		x			x							x	x	x	x	[21, 66, 96, 168, 328, 336, 339, 450]
Seaweed NIES 14	x	x		x	x	x	x	x	x			x	x	x	x	[432, 447, 448]
Seaweed NMIJ CRM 7405a		x														[99]
Seaweed *Fucus* extract		x			x							x	x	x	x	[157, 193, 246, 432, 446, 451]
Seaweed extract					x								x	x		[157]
Plankton BCR 414	x	x														[452]
Oyster/shrimp/scallop tissue																
Oyster NIST 1566													x			[453]
Oyster NIST 1566a	x	x	x	x	x	x	x	x	x		x	x	x			[432, 454-461]
Oyster NIST 1566b	x	x			x	x	x	x	x			x	x			[432, 459, 462, 463]
Oyster BCR710	x	x		x	x	x							x			[227, 273, 462, 464]
Shrimp NFA				x	x	x	x	x	x							[465, 466]
Scallop NIES 15	x	x		x	x	x	x	x	x			x	x			[432]
Mussel tissue																
BCR 278R		x	x		x	x	x	x	x		x	x	x			[63, 345, 460, 462, 463, 467]
BCR 525					x	x						x	x			[345, 455]
NIST CE 278	x	x		x	x	x										[140, 463]
NIES 6					x	x	x	x	x	x		x	x			[448, 458, 468, 469]
Mussel GBW-08751		x			x	x	x									[345]

Fish tissue																
NMIJ CRM 7402a (Cod fish)	x	x		x	x	x										[395, 459]
BCR 627 (Tuna fish)	x	x		x	x	x	x	x	x		x	x	x			[63, 120, 247, 294, 375, 462, 465, 470-473]
NFA				x	x	x	x	x	x							[455, 458, 465, 466, 469]
BCR422 (Cod fish)						x										[63, 463]
BCR 627 (Tuna fish)						x										[306]
NIES 11 (Sea bass)						x										[448]
*NRCC DORM 1 (Dog fish)	x	x	x	x	x	x	x	x	x			x	x	x		[123, 255, 432, 460, 463, 469, 473-476]
*NRCC DORM 2 (Dog fish)	x	x	x	x	x	x	x	x	x		x	x	x	x	x	[63, 76, 77, 107, 112, 119, 120, 127, 156, 157, 168, 192, 222, 243, 247, 323, 327, 333, 335, 343, 345, 349, 365, 393, 409, 430, 459, 460, 462, 465, 466, 470, 472, 474, 477-486]
*NRCC DORM 3 (Dog fish)	x	x	x	x	x	x	x									[140, 143, 472, 487, 488]
**NRCC DOLT 1 (Dog fish)	x	x		x	x	x	x	x	x			x	x			[432]
**NRCC DOLT 2 (Dog fish)		x	x	x	x	x	x		x		x	x	x	x		[459, 479, 480]
**NRCC DOLT 3 (Dog fish)	x	x		x	x	x	x									[140, 472]
**NRCC DOLT 4 (Dog fish)			x													[487]
Lobster tissue																
**NRCC TORT 1 (Lobster hepatopancreas)	x	x		x	x	x	x	x	x			x	x			[123, 195, 432, 455]
**NRCC TORT 2 (Lobster hepatopancreas)	x	x	x	x	x	x	x	x	x		x	x	x	x	x	[107, 127, 156, 346, 393, 414, 459, 460, 465, 472, 479, 480, 485, 487-492]

*Muscle tissue (defatted), ** Liver tissue (defatted)

Figure 1: A) Cation exchange chromatogram of arsenic standards, using a Supelco Supelcosil SCX column (250 mm x 4.6 mm x 5 µm), mobile phase of 20 mM pyridine pH 2.6 adjusted with HCO_2H, flow rate 1.5 ml/min, column temperature 40 °C; B) Anion exchange chromatogram arsenic standards using a Phenomenex PRP-X100 column (250 mm x 4.6 mm x 10 µm), mobile phase of 20 mM $(NH_4)_3PO_4$ pH 5.6 adjusted with NH_4OH, flow rate 1.5 ml/min, column temperature 40 °C; C) Cationic arsenic species in the gastropod *B. nanum* [222] using the conditions outlined for cation exchange chromatography.



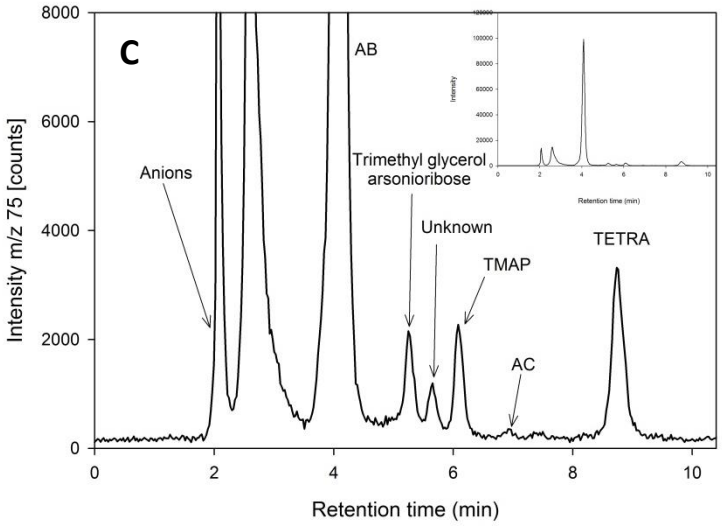


Figure 2: HPLC–HG–ICP–MS chromatograms for: (A) Anion exchange chromatogram arsenic standards using a Phenomenex PRP-X100 column (250 mm x 4.6 mm x 10 µm), mobile phase of 20 mM $(NH_4)_3PO_4$ pH 5.6 adjusted with NH_4OH, flow rate 1.5 ml/min, column temperature 40 °C, hydride formation by post column mixing with 1% v/v HCl, 2% m/v L-Cysteine, 3% $NaBH_4$ heating to mixed reagents to 70°C to speed up the reaction before separtion of the gas and liquid phases prior to ICPMS analysis; and (B) *Macrocystis pyrifera*, conditions as above. Redrawn with permission from Kirby and co-workers [192].

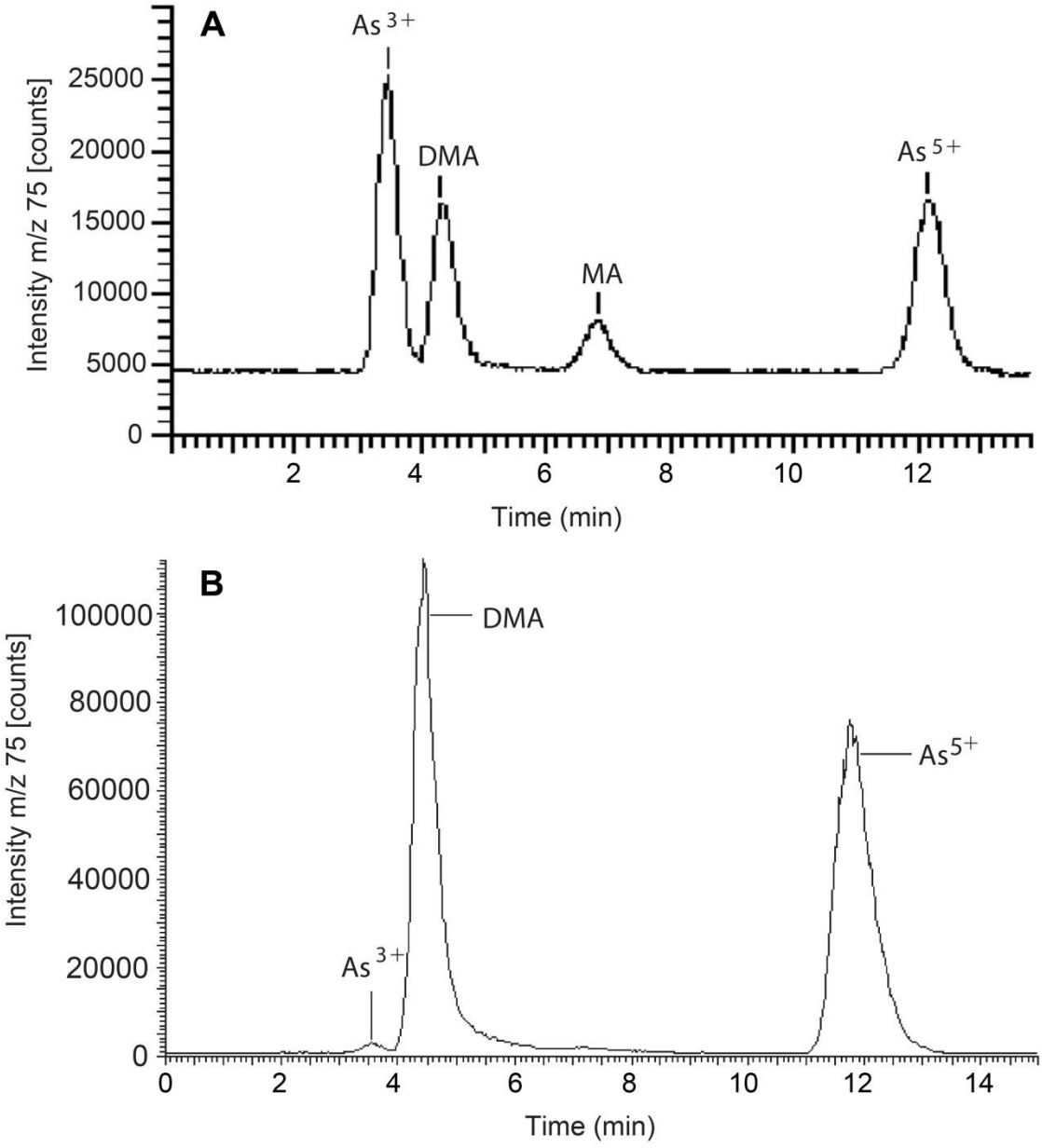
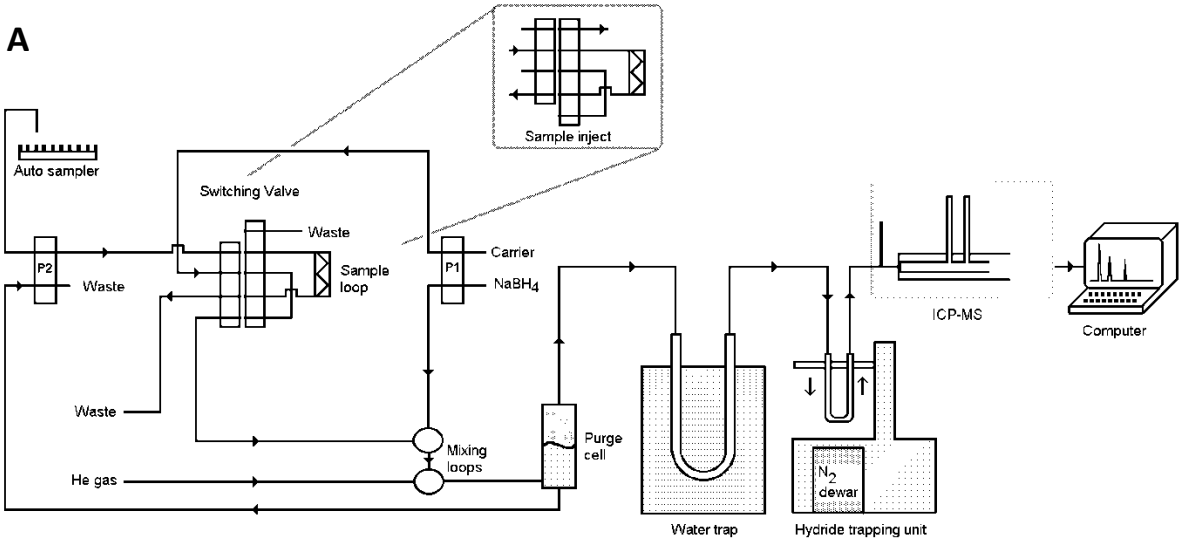


Figure 3: Cryogenic trapping ICPMS (A) Schematic of system (B) Separation of arsenic species in open ocean seawater. Reproduced with permission from Ellwood and Maher [198] and Maher *et al*. [81].



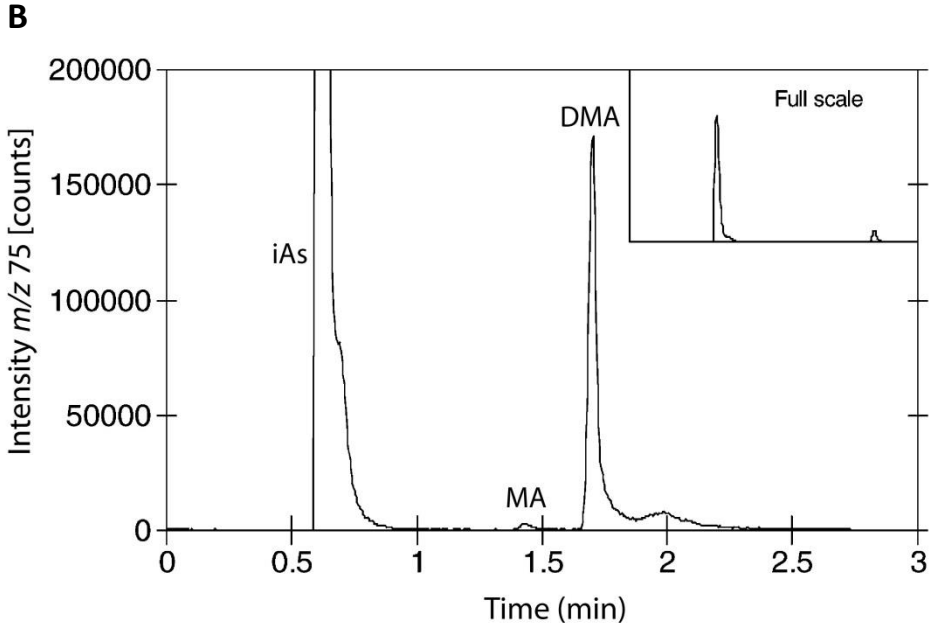


Figure 4: Arsenic species in *Fucus serartus*, separated using a Phenomenex PRP-X100 column (250 mm x 4.6 mm x 10 µm), mobile phase of 20 mM $(NH_4)_3PO_4$ pH 5.6 adjusted with NH_4OH, flow rate 1.5 ml/min, column temperature 40 °C (A) and *Homerseria Banksii* (B) separated using the same conditions as above.

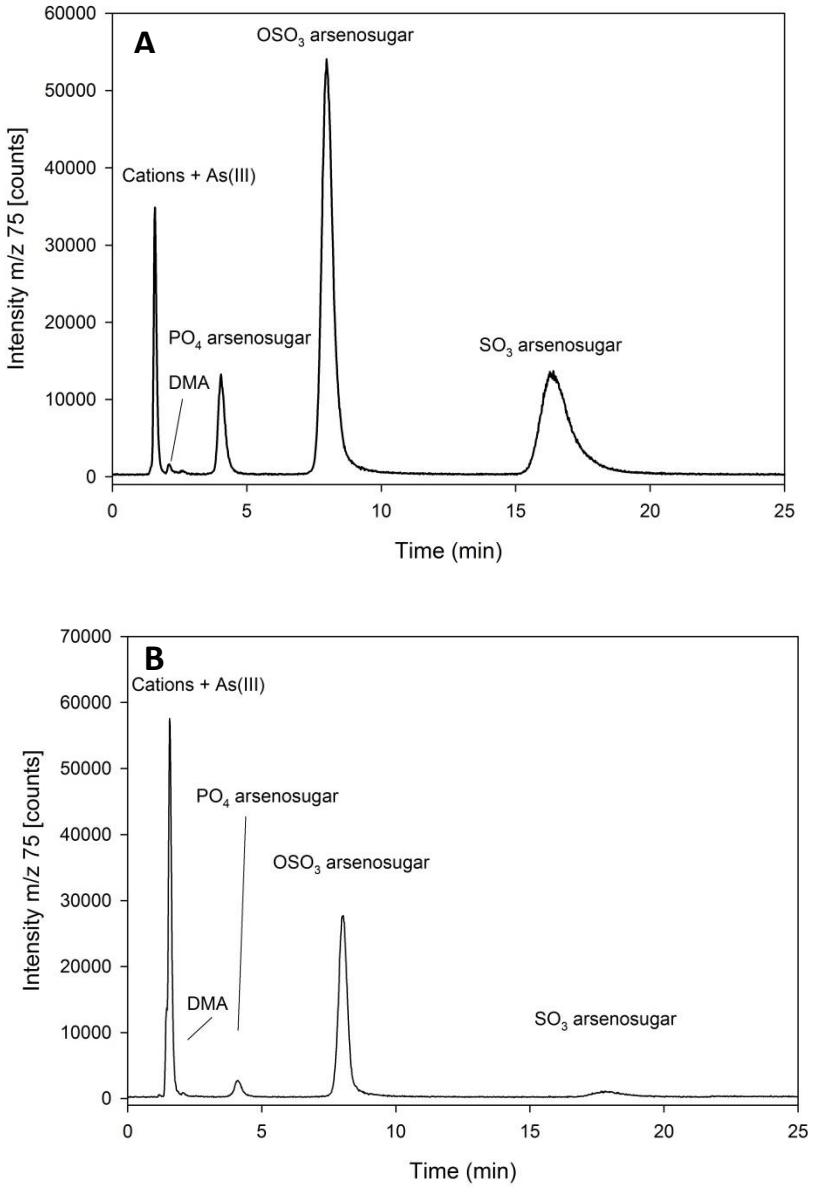


Figure 5: Arsenic species in bivalve tissues, separated using a Supelco Supelcosil SCX column (250 mm x 4.6 mm x 5 µm), mobile phase of 20 mM pyridine pH 2.6 adjusted with HCO_2H, flow rate 1.5 ml/min, column temperature 40 °C [222].

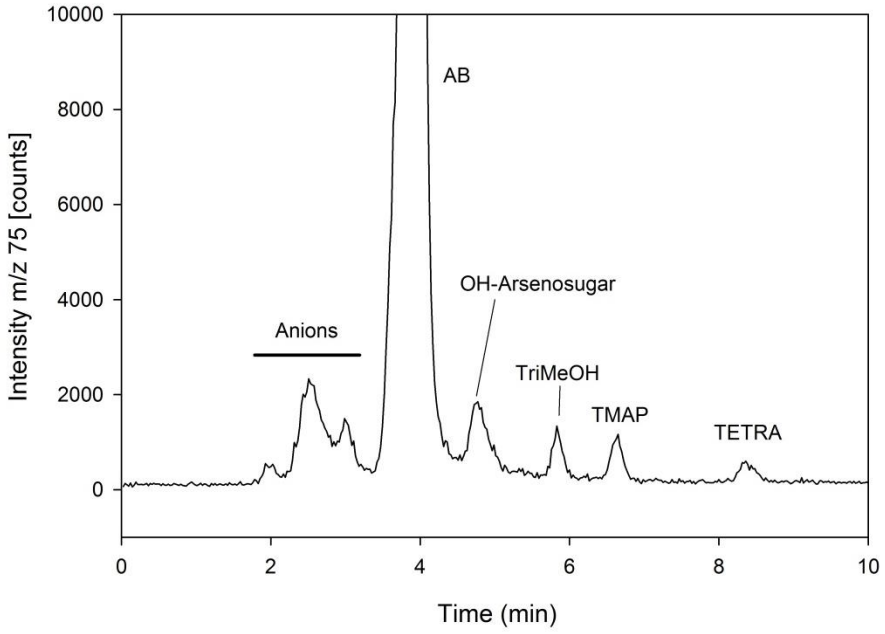


Figure 6: Arsenic species in long grain white rice. Arsenic extracted with 2% (v/v) HNO_3 at 95°C and separated on a anion exchange column (PRP-X100 150 mm x 4.1 mm x 5 µm) using a 5 mM $CH_2(COOH)_2$ buffer pH 5.6 adjusted with NH_4OH at 1 ml min^{-1}, column temperature 25 °C.

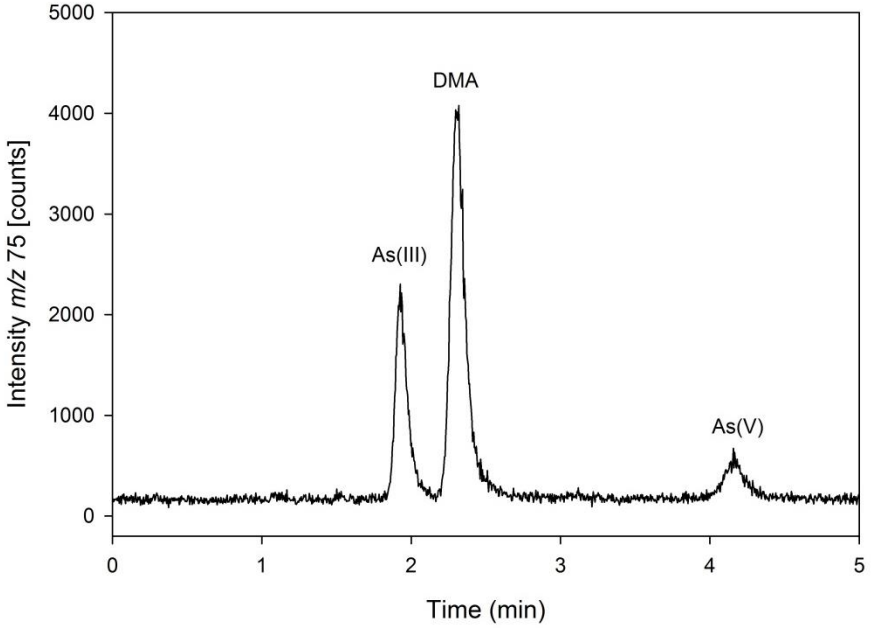


Figure 7: Arsenic lipids in seaweed extracts. HPLC separation conditions were carried out by reverse phase chromatography using a Zorbax Eclipse XDB-C8 column (150 mm x 4.6 mm x 5-µm particle size) and a mobile phase comprising A) 10 mM CH_3COOH pH 6.0 adjusted with NH_4OH and B) methanol with the following gradient elution conditions: 0–25 min, 50–95% mobile phase B; 25–40 min, 95% mobile phase B, Figure redrawn with permission from Raber et al.[109]

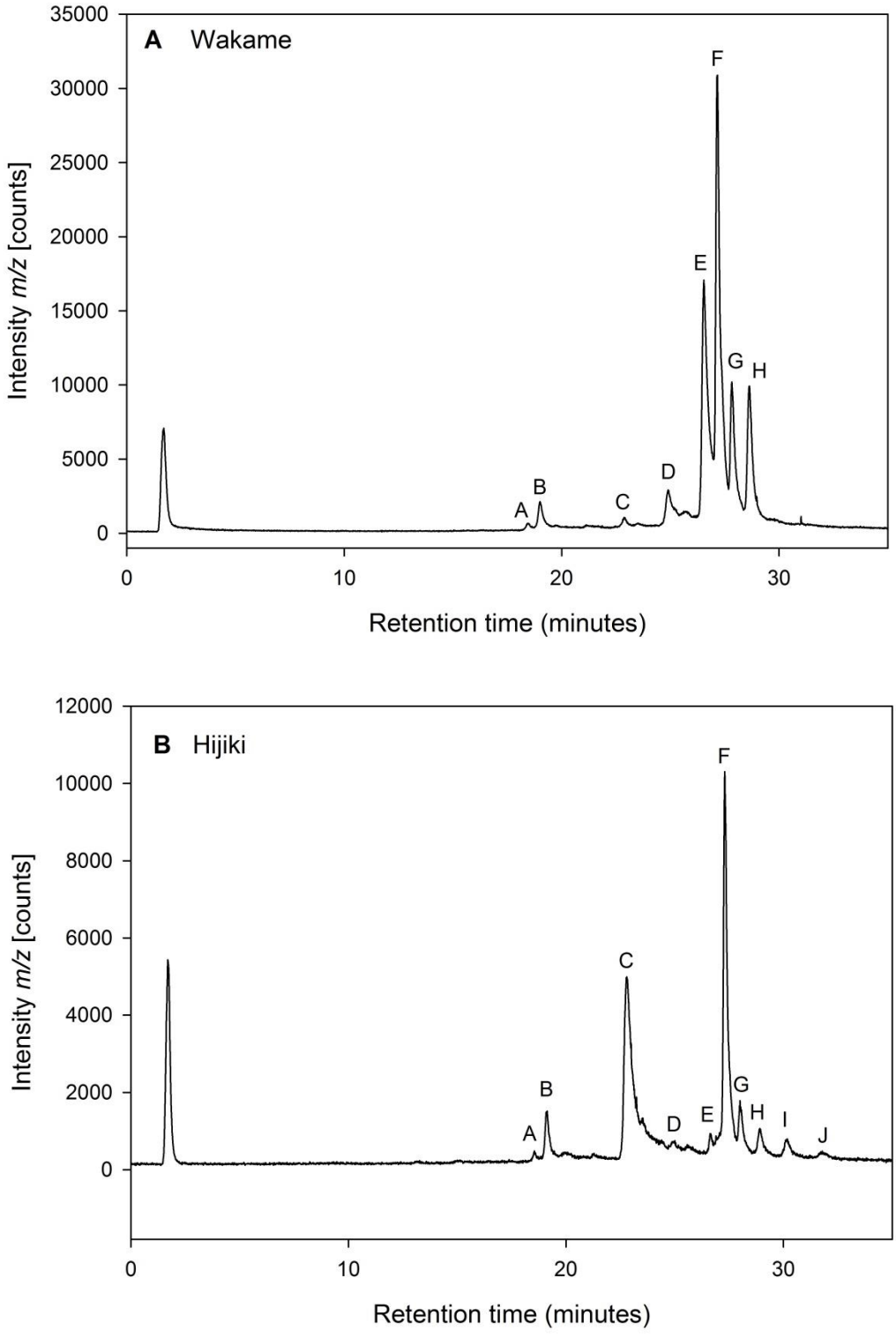


Figure 8: Thio-arsenic species separated by C18 reverse phase chromatography using a Atlantis dC18 column (150 mm x 4.6 mm x 5-µm particle size), mobile phase of 10 mM NH_4HCO_2 pH 3.0 adjusted with NH_4OH, flow rate 1 ml/min, column temperature 25 °C. Figure redrwn from Maher and co-workers [62].

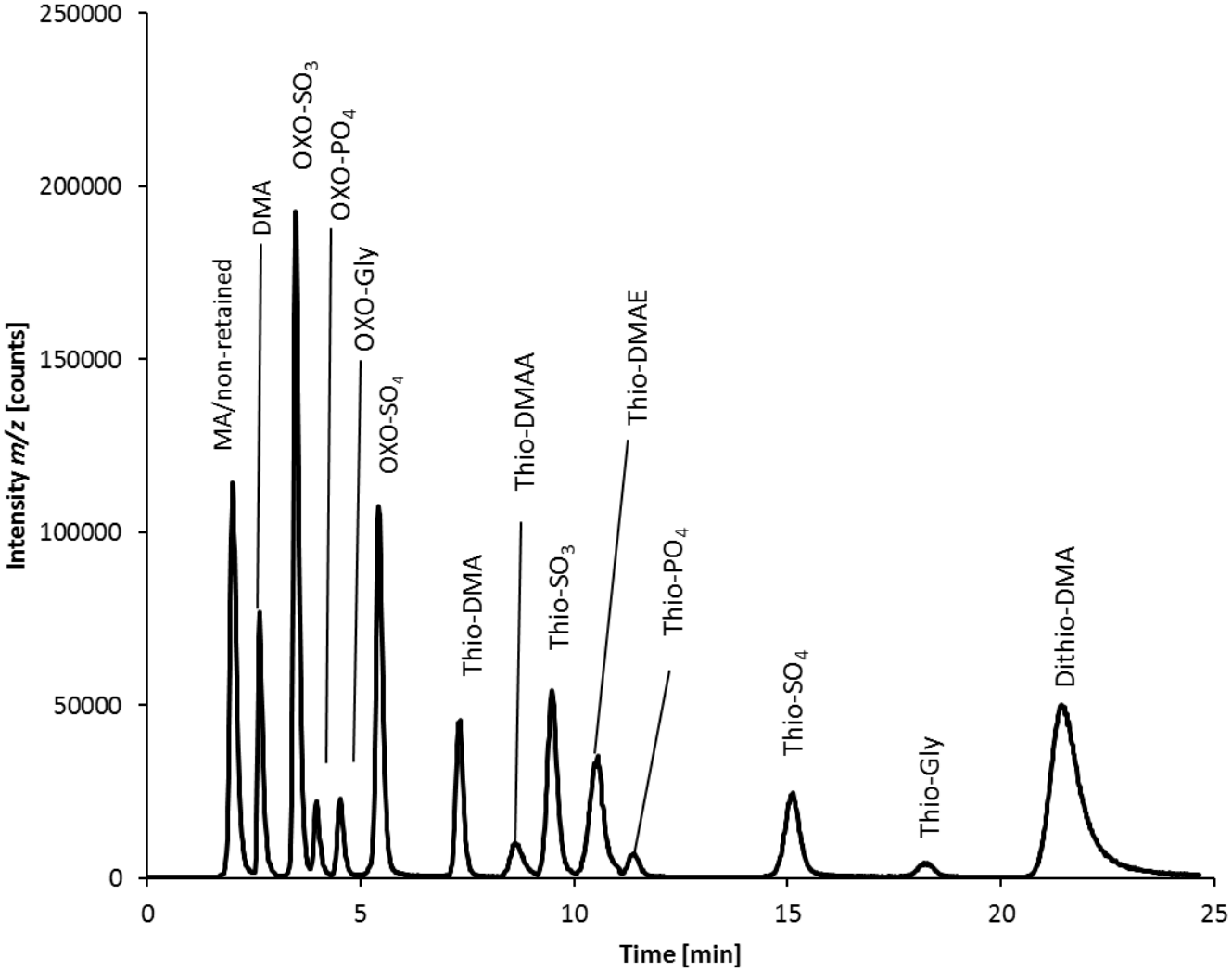


Figure 9: Separation of common anions by reverse phase ion paring with tetra butyl ammonium hydroxide (TBAH) as the ion pairing reagent. Conditions were modified from those of Wangkarn and Pergantis [405]. Column: Waters Atlantis dC18 (250 mm x 4.6 mm x 5 µm), flow rate 1.200 ml/min, column temperature 25 °C, injection volumn 5µl, mobile phase A: H_2O, mobile phase B:10 mM TBAH pH 6.2 with a gradient of 50% B held for 1 min, 50 % B to 100 % B from 2 min to 5 min, 50% B from 5 min to 7 min, standards of As(III), DMA, MA and As(V) are ~ 5 ppb.

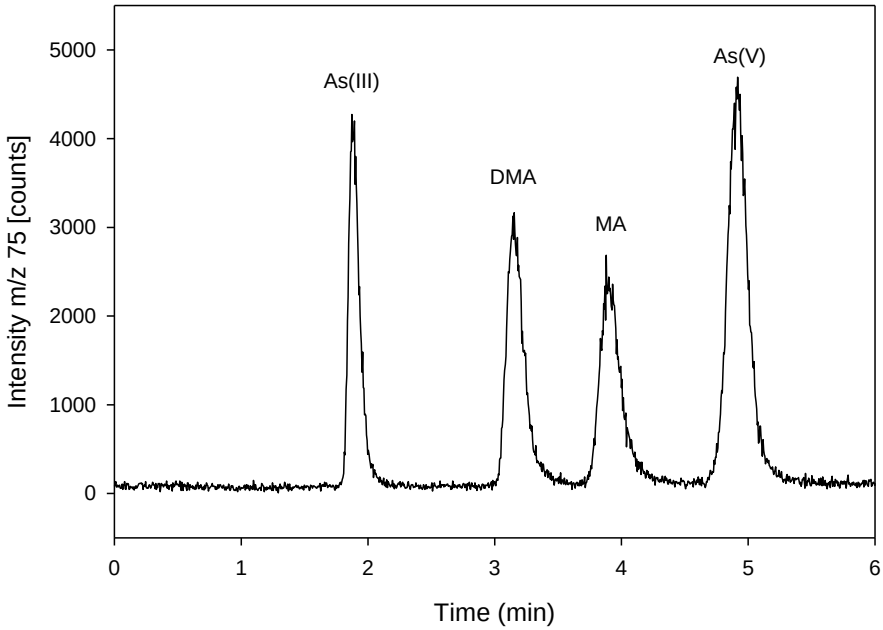
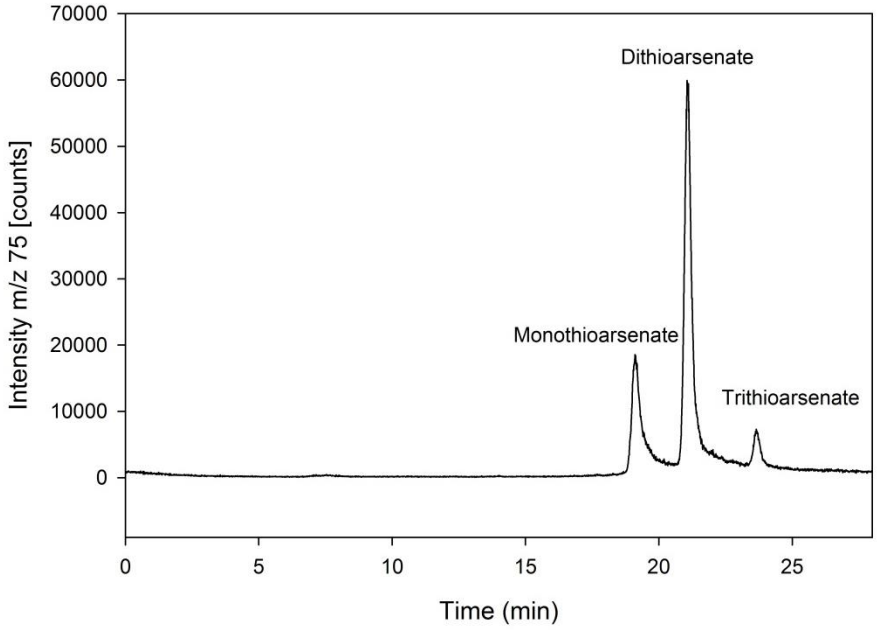


Figure 10: Thio arsenate standards eluted using an Ion Pac AS16 (250 mm x 4-mm, 10 μm particle size) anion column, with a gradient of 20–100 mM NaOH over 20 mins at a flow rate of 1 ml/min, 25 ºC, using a Dionex AERS 300 suppressor (2mm) prior to introduction of the mobile phase into the ICPMS.



References

1. Uthus, E.O., *Arsenic essentiality: A role affecting methionine metabolism.* The Journal of Trace Elements in Experimental Medicine, 2003. **16**: p. 345–355.
2. Cullen, W.R., *Is arsenic an aphrodisiac?: the sociochemistry of an element*2008, Cambridge: Royal Society of Chemistry. 412.
3. Ratnaike, R.N., *Acute and chronic arsenic toxicity.* Postgraduate medical journal, 2003. **79**(933): p. 391.
4. NSW Food Authority. *Inorganic arsenic in seaweed and certain fish 2010*. 2010 23/10/2014]; 1-7]. Available from: http://www.foodauthority.nsw.gov.au/_Documents/science/inorganic_arsenic_seaweed_seafood.pdf.
5. Food Standards Australia and New Zealand. *Mercury in fish Consumer information 2004.* 2004 [cited 2014; Available from: http://www.foodauthority.nsw.gov.au/_Documents/consumer_pdf/fs-ANZ-mercury-fish.pdf.
6. Cannon, J.R., et al., *Isolation, crystal structure and synthesis of arsenobetaine, a constituent of the Western Rock Lobster, the Dusky Shark, and some samples of human urine.* Aust. J. Chem., 1981. **34**: p. 787-798.
7. Kales, S.N., K.L. Huyck, and R.H. Goldman, *Elevated urine arsenic: un-speciated results lead to unnecessary concern and further evaluations.* Journal of analytical toxicology, 2006. **30**(2): p. 80-85.
8. Combs Jr, G., L. Clark, and B. Turnbull, *Reduction of cancer risk with an oral supplement of selenium.* Biomedical and environmental sciences: BES, 1997. **10**(2-3): p. 227.
9. Waxman, S. and K.C. Anderson, *History of the development of arsenic derivatives in cancer therapy.* The Oncologist, 2001. **6**(Supplement 2): p. 3.
10. Urík, M., et al., *Biovolatilization of arsenic by different fungal strains.* Water, air, and soil pollution, 2007. **186**(1-4): p. 337-342.
11. Meyer, J., et al., *Volatilisation of metals and metalloids by the microbial population of an alluvial soil.* Systematic and applied microbiology, 2007. **30**(3): p. 229-238.
12. Maher, W., S. Foster, and F. Krikowa, *Arsenic species in Australian temperate marine food chains.* Marine and Freshwater Research, 2009. **60**(9): p. 885-892.
13. Francesconi, K. and D. Kuehnelt, *Determination of arsenic species: a critical review of methods and applications, 2000-2003.* The Analyst, 2004. **129**(5): p. 373-395.
14. Rumpler, A., et al., *Arsenic-containing long-chain fatty acids in cod-liver oil: a result of biosynthetic infidelity?* Angewandte Chemie (International ed. in English), 2008. **47**(14): p. 2665-2667.
15. Taleshi, M., et al., *Arsenic-containing hydrocarbons: natural compounds in oil from the fish capelin, Mallotus villosus.* Chemical communications (Cambridge, England), 2008(39): p. 4706-4707.
16. Rodriguez, I., B. , G. Raber, and W. Goessler, *Arsenic speciation in fish sauce samples determined by HPLC coupled to inductively coupled plasma mass spectrometry.* Food Chemistry, 2009. **112**(4): p. 1084–1087.
17. Kahn, M., et al., *Two novel thio-arsenosugars in scallops identified with HPLC-ICPMS and HPLC-ESMS.* Environ. Chem., 2005. **2**: p. 171.
18. Jones-Lepp, T.L. and G.M. Momplaisir, *New applications of LC-MS and LC-MS2 toward understanding the environmental fate of organometallics.* TrAC Trends in Analytical Chemistry, 2005. **24**(7): p. 590-595.
19. Segura, M., Y. Madrid, and C. Cámara, *Evaluation of atomic fluorescence and atomic absorption spectrometric techniques for the determination of arsenic in wine and beer by direct hydride generation sample introduction.* Journal of Analytical Atomic Spectrometry, 1999. **14**(2): p. 131-135.

20. Sanchez-Rodas, D., et al., *Health implications of the distribution of arsenic species in airborne particulate matter.* Journal of Inorganic Biochemistry, 2012. **108**.
21. García-Salgado, S., M. Quijano, and M. Bonilla, *Arsenic speciation in edible alga samples by microwave-assisted extraction and high performance liquid chromatography coupled to atomic fluorescence spectrometry.* Analytica chimica acta, 2012. **714**: p. 38-46.
22. Slejkovec, Z., et al., *Analytical artefacts in the speciation of arsenic in clinical samples.* Analytica chimica acta, 2008. **607**(1): p. 83-91.
23. Feldmann, J., et al., *Sample preparation and storage can change arsenic speciation in human urine.* Clinical Chemistry, 1999. **45**(11): p. 1988-1997.
24. Francesconi, K.A. and D. Kuehnelt, *Determination of arsenic species: A critical review of methods and applications, 2000–2003.* Analyst, 2004. **129**: p. 373-395.
25. Ramesh, K.A. and P. Riyazuddin, *Preservation of inorganic arsenic species in environmental water samples for reliable speciation analysis.* TrAC Trends in Analytical Chemistry, 2010. **29**(10): p. 1212-1223.
26. Rubio, R., M.J. Ruiz-Chancho, and J.F. López-Sánchez, *Sample pre-treatment and extraction methods that are crucial to arsenic speciation in algae and aquatic plants.* TrAC Trends in Analytical Chemistry, 2010. **29**(1): p. 53-69.
27. Amaral, C., J. Nóbrega, and A. Nogueira, *Sample preparation for arsenic speciation in terrestrial plants--a review.* Talanta, 2013. **115**: p. 291-299.
28. Niegel, C. and F.M. Matysik, *Analytical methods for the determination of arsenosugars--A review of recent trends and developments.* Analytica Chimica Acta, 2010. **657**(2): p. 83-99.
29. Lewis, A.S., et al., *Speciated arsenic in air: Measurement methodology and risk assessment considerations.* Journal of the Air & Waste Management Association, 2012. **62**.
30. Komorowicz, I. and D. Barałkiewicz, *Arsenic and its speciation in water samples by high performance liquid chromatography inductively coupled plasma mass spectrometry--last decade review.* Talanta, 2011. **84**(2): p. 247-261.
31. Rajaković, L.V., et al., *Analytical methods for arsenic speciation analysis.* Journal of the Serbian Chemical Society, 2013. **78**: p. 1461-1479.
32. Sadee, B., M.E. Foulkes, and S.J. Hill, *Coupled techniques for arsenic speciation in food and drinking water: a review.* Journal of Analytical Atomic Spectrometry, 2015. **30**(1): p. 102-118.
33. Nearing, M.M., I. Koch, and K.J. Reimer, *Complementary arsenic speciation methods: A review.* Spectrochimica Acta Part B: Atomic Spectroscopy, 2014. **99**: p. 150-162.
34. Segura, M., et al., *Stability study of As(III), As(V), MMA and DMA by anion exchange chromatography and HG-AFS in wastewater samples.* Analytical and bioanalytical chemistry, 2002. **374**(3): p. 513-519.
35. Kumaresan, M. and P. Riyazuddin, *Overview of speciation chemistry of arsenic.* Current Science, 2001. **80**(7): p. 837-846.
36. Tian, Y., et al., *Arsenic preconcentration via solid phase extraction and speciation by HPLC-gradient hydride generation atomic absorption spectrometry.* Journal of Analytical Atomic Spectrometry, 2011. **26**: p. 133-140.
37. Gallagher, P., A. , et al., *Preservation of As(III) and As(V) in Drinking Water Supply Samples from Across the United States Using EDTA and Acetic Acid as a Means of Minimizing Iron−Arsenic Coprecipitation.* Environmental Science & Technology, 2004. **38**(10): p. 2919–2927.
38. McCleskey, R.B., D.K. Nordstrom, and S.M. Ann, *Preservation of water samples for arsenic(III/V) determinations: an evaluation of the literature and new analytical results.* Applied Geochemistry, 2004. **19**(7): p. 995-1009.
39. Emett, M. and G. Khoe, *Photochemical oxidation of arsenic by oxygen and iron in acidic solutions.* Water research, 2001. **35**(3): p. 649-656.

40. Hashem, M.A., et al., *Measurements of arsenite and arsenate contained in mining river waters and leached from contaminated sediments by sequential hydride generation flow injection analysis.* Talanta, 2011. **84**(5): p. 1336-1341.
41. Daus, B., et al., *Investigation on stability and preservation of arsenic species in iron rich water samples.* Talanta, 2002. **58**: p. 57-65.
42. Palmer, N.E., J.H. Freudenthal, and R. von Wandruszka, *Reduction of arsenates by humic materials.* Environmental Chemistry, 2006. **3**(2): p. 131-136.
43. Tongesayi, T. and R.B. Smart, *Arsenic speciation: Reduction of arsenic (v) to arsenic (III) by fulvic acid.* Environmental Chemistry, 2006. **3**(2): p. 137-141.
44. Farnfield, H.R., A.L. Marcilla, and N.I. Ward, *Arsenic speciation and trace element analysis of the volcanic río Agrio and the geothermal waters of Copahue, Argentina.* Science of The Total Environment, 2012. **433**.
45. Sigrist, M., et al., *Determination of As (III) and total inorganic As in water samples using an on-line solid phase extraction and flow injection hydride generation atomic absorption spectrometry.* Journal of hazardous materials, 2011. **188**(1): p. 311-318.
46. Gong, Z., et al., *Speciation analysis of arsenic in groundwater from Inner Mongolia with an emphasis on acid-leachable particulate arsenic.* Analytica Chimica Acta, 2006. **555**.
47. Bednar, A., et al., *Field and laboratory arsenic speciation methods and their application to natural-water analysis.* Water research, 2004. **38**(2): p. 355-364.
48. Hansen, H.R., A. Raab, and J. Feldmann, *New arsenosugars metabolite determined in urine by parallel use of HPLC-ICP-MS and HPLC-ESI-MS.* J. Anal. Atom. Spectrom., 2003. **18**: p. 474 - 479.
49. Xie, R., et al., *Arsenic speciation analysis of human urine using ion exchange chromatography coupled to inductively coupled plasma mass spectrometry.* Analytica Chimica Acta, 2006. **578**(2): p. 186-194.
50. Ritsema, R., et al., *Speciation of arsenic compounds in urine by LC-ICP MS.* Applied Organometallic Chemistry, 1998. **12**: p. 591-599.
51. Yoshino, Y., et al., *Speciation of arsenic trioxide metabolites in blood cells and plasma of a patient with acute promyelocytic leukemia.* Analytical and Bioanalytical Chemistry, 2009. **393**(2): p. 689-697.
52. Ito, K., et al., *An interlaboratory study of arsenic speciation analysis of whole blood.* Journal of Analytical Atomic Spectrometry, 2011. **26**.
53. Gong, Z., et al., *Unstable trivalent arsenic metabolites, monomethylarsonous acid and dimethylarsinous acid.* Journal of Analytical Atomic Spectrometry, 2001. **16**.
54. Maher, W.A., et al., *Thio arsenic species measurements in marine organisms and geothermal waters.* Microchemical Journal, 2013.
55. Wallschläger, D. and J. London, *Determination of Methylated Arsenic-Sulfur Compounds in Groundwater.* Environmental Science & Technology, 2008. **42**.
56. Maher, W.A., et al., *Thio arsenic species measurements in marine organisms and geothermal waters.* Microchemical Journal, 2013. **111**: p. 82-90.
57. Suess, E., D. Wallschläger, and B. Planer-Friedrich, *Stabilization of thioarsenates in iron-rich waters.* Chemosphere, 2011. **83**(11): p. 1524-1531.
58. Jay, J., et al., *Arsenic-sulfides confound anion exchange resin speciation of aqueous arsenic.* Water research, 2004. **38**(5): p. 1155-1158.
59. Smieja, J., A. and R. Wilkin, T. , *Preservation of sulfidic waters containing dissolved As(iii).* Journal of Environmental Monitoring, 2003. **5**: p. 913-916.
60. Planer-Friedrich, B., et al., *Thioarsenates in Geothermal Waters of Yellowstone National Park: Determination, Preservation, and Geochemical Importance.* Environmental Science & Technology, 2007. **41**(15): p. 5245-5251.
61. Hollibaugh, J.T., et al., *Arsenic speciation in Mono Lake, California: Response to seasonal stratification and anoxia.* Geochimica et Cosmochimica Acta, 2005. **69**(8): p. 1925-1937.

62. Maher, W., et al., *Thio arsenic species measurements in marine organisms and geothermal waters.* Microchemical Journal, 2013. **111**: p. 82-90.
63. Lewis, J., et al., *Stability of arsenic speciation in fish muscle samples, under different storage and sample preparation conditions.* Microchemical Journal, 2012. **105**: p. 56-59.
64. Molin, M., et al., *Major and minor arsenic compounds accounting for the total urinary excretion of arsenic following intake of blue mussels (Mytilus edulis): A controlled human study.* Food and Chemical Toxicology, 2012. **50**.
65. Dahl, L., et al., *Stability of arsenic compounds in seafood samples during processing and storage by freezing.* Food Chemistry, 2010. **123**(3): p. 720-727.
66. García Salgado, S., M. Quijano Nieto, and M. Bonilla Simón, *Assessment of total arsenic and arsenic species stability in alga samples and their aqueous extracts.* Talanta, 2008. **75**(4): p. 897-903.
67. Whitfield, F.B., D.J. Freeman, and K.J. Shaw, *Trimethylarsine: an important off-flavour component in some prawn species.* Chem. Ind., 1983. **20**: p. 786 - 787.
68. Huang, J.-H. and G. Ilgen, *Factors affecting arsenic speciation in environmental samples: sample drying and storage.* International Journal of Environmental Analytical Chemistry, 2006. **86**.
69. Amaral, C.D., J.A. Nóbrega, and A.R.A. Nogueira, *Investigation of arsenic species stability by HPLC-ICP-MS in plants stored under different conditions for 12months.* Microchemical Journal, 2014. **117**: p. 122-126.
70. Raab, A., et al., *Arsenic–glutathione complexes—their stability in solution and during separation by different HPLC modes.* J. Anal. Atom. Spectrom., 2004. **19**: p. 183-190.
71. Bluemlein, K., A. Raab, and J. Feldmann, *Stability of arsenic peptides in plant extracts: off-line versus on-line parallel elemental and molecular mass spectrometric detection for liquid chromatographic separation.* Analytical and bioanalytical chemistry, 2009. **393**(1): p. 357-366.
72. Munoz, L.P., et al., *Enhanced determination of As–phytochelatin complexes in Chlorella vulgaris using focused sonication for extraction of water-soluble species.* Analytical Methods, 2014. **6**(3): p. 791-797.
73. Sánchez-Rodas, D., et al., *Arsenic speciation of atmospheric particulate matter (PM10) in an industrialised urban site in southwestern Spain.* Chemosphere, 2007. **66**(8): p. 1485-1493.
74. Slejkovec, Z., et al., *Arsenosugars and other arsenic compounds in littoral zone algae from the Adriatic Sea.* Chemosphere, 2006. **63**: p. 1098-1105.
75. Zuccaro, A., et al., *Detection and Identification of Fungi Intimately Associated with the Brown Seaweed Fucus serratus.* Applied and Environmental Microbiology, 2007. **74**.
76. Thomson, D., W. Maher, and S. Foster, *Arsenic and selected elements in marine angiosperms, south-east coast, NSW, Australia.* Applied Organometallic Chemistry, 2007. **21**(6): p. 381-395.
77. Maher, W.A., et al., *Arsenic distribution and species in two Zostera capricorni seagrass ecosystems, New South Wales, Australia.* Environmental Chemistry, 2011. **8**(1): p. 9-18.
78. Smith, P., I. Koch, and K. Reimer, *Uptake, transport and transformation of arsenate in radishes (Raphanus sativus).* The Science of the total environment, 2008. **390**(1): p. 188-197.
79. Mir, K.A., et al., *Extraction and speciation of arsenic in plants grown on arsenic contaminated soils.* Talanta, 2007. **72**(4): p. 1507-1518.
80. Jedynak, L., et al., *Studies on the uptake of different arsenic forms and the influence of sample pretreatment on arsenic speciation in White mustard (Sinapis alba).* Microchemical Journal, 2010. **94**.
81. Maher, W., et al., *Overview of hyphenated techniques using an ICP-MS detector with an emphasis on extraction techniques for measurement of metalloids by HPLC–ICPMS.* Microchemical Journal, 2012. **105**: p. 15-31.
82. Ellwood, M.J. and W.A. Maher, *Measurement of arsenic species in marine sediments by high-performance liquid chromatography-inductively coupled plasma mass spectrometry.* Anal. Chim. Acta, 2003. **477**(2): p. 279-291.

83. Huerga, A., I. Lavilla, and C. Bendicho, *Speciation of the immediately mobilisable As(III), As(V), MMA and DMA in river sediments by high performance liquid chromatography-hydride generation-atomic fluorescence spectrometry following ultrasonic extraction.* Anal. Chim. Acta, 2005. **534**(1): p. 121-128.
84. Zheng, J., et al., *Speciation of arsenic in water, sediment, and plants of the Moira watershed, Canada, using HPLC coupled to high resolution ICP–MS.* Anal. Bioanal. Chem., 2003. **377**: p. 14-24.
85. Pizarro, I., et al., *Evaluation of stability of arsenic species in rice.* Analytical and bioanalytical chemistry, 2003. **376**(1): p. 102-109.
86. Narukawa, T. and K. Chiba, *Heat-assisted aqueous extraction of rice flour for arsenic speciation analysis.* Journal of agricultural and food chemistry, 2010. **58**(14): p. 8183-8188.
87. Alava, P., et al., *Extensive grinding and pressurized extraction with water are key points for effective and species preserving extraction of arsenic from rice.* Analytical Methods, 2012. **4**: p. 1237-1243.
88. Schmidt, A.-C., et al., *Evaluation of extraction procedures for the ion chromatographic determination of arsenic species in plant materials.* J. Chromatogr. A, 2000. **889**(1-2): p. 83-91.
89. Farías, S.S., et al., *On-line speciation and quantification of four arsenical species in rice samples collected in Argentina using an HPLC-HG-AFS coupling.* Microchemical Journal, 2015.
90. Maher, W., et al., *Measurement of trace elements in marine environmental samples using solution ICPMS. Current and future applications.* Aust. J. Chem., 2003. **56**: p. 103 - 116.
91. Larsen, E.H. and S. Stürup, *Carbon-enhanced inductively coupled plasma mass spectrometric detection of arsenic and selenium and its application to arsenic speciation.* J. Anal. At. Spectrom., 1994. **9**(10): p. 1099-1105.
92. Amayo, K., et al., *Identification and quantification of arsenolipids using reversed-phase HPLC coupled simultaneously to high-resolution ICPMS and high-resolution electrospray MS without species-specific standards.* Analytical chemistry, 2011. **83**(9): p. 3589-3595.
93. Wood, B. and J. Feldmann, *Quantification of phytochelatins and their metal(loid) complexes: critical assessment of current analytical methodology.* Analytical and bioanalytical chemistry, 2012. **402**(10): p. 3299-3309.
94. Van Elteren, J.T., et al., *A systematic study on the extractability of arsenic species from algal certified reference material IAEA-140/TM (< i> Fucus</i> sp., Sea Plant Homogenate) using methanol/water extractant mixtures.* Analytica Chimica Acta, 2007. **585**(1): p. 24-31.
95. Whaley-Martin, K.J., I. Koch, and K.J. Reimer, *Arsenic species extraction of biological marine samples (Periwinkles, Littorina littorea) from a highly contaminated site.* Talanta, 2012. **88**.
96. Tukai, R., et al., *Measurement of arsenic species in marine macroalgae by microwave-assisted extraction and high performance liquid chromatography-inductively coupled plasma mass spectrometry.* Anal. Chim. Acta, 2002. **457**(2): p. 173-185.
97. Raab, A., P. Fecher, and J. Feldmann, *Determination of Arsenic in Algae – Results of an Interlaboratory Trial: Determination of Arsenic Species in the Water-Soluble Fraction.* Microchimica Acta, 2005. **151**.
98. Byrne, A.R., et al., *Arsenobetaine and other arsenic species in mushrooms.* Applied Organometallic Chemistry, 1995. **9**.
99. Narukawa, T., et al., *Preparation and certification of hijiki reference material, NMIJ CRM 7405-a, from the edible marine algae hijiki (Hizikia fusiforme).* Analytical and bioanalytical chemistry, 2012. **402**(4): p. 1713-1722.
100. Heitkemper, D.T., et al., *Determination of total and speciated arsenic in rice by ion chromatography and inductively coupled plasma mass spectrometry.* J. Anal. Atom. Spectrom., 2001. **16**: p. 299 - 306.
101. Narukawa, T., et al., *Extraction techniques for arsenic species in rice flour and their speciation by HPLC–ICP-MS.* Talanta, 2014. **130**: p. 213-220.

102. Salido, A., L. and D. Hyatt, *Optimization of Arsenic Speciation Conditions in Plant Material by HPLC-ICPOES.* Spectroscopy Letters, 2007. **40**: p. 493-499.
103. Quaghebeur, M., Z. Rengel, and M. Smirk, *Arsenic speciation in terrestrial plant material using microwaveassisted extraction, ion chromatography and inductively coupled plasma mass spectrometry.* J. Anal. Atom. Spectrom., 2003. **18**: p. 128-134.
104. Anne-Christine, S., A. Julia, and S. Bianca, *Sample preparation strategies for one- and two-dimensional gel electrophoretic separation of plant proteins and the influence on arsenic and zinc bindings.* Journal of Chromatography B, 2009. **877**.
105. Mrak, T., et al., *Use of micro-PIXE in the study of arsenate uptake in lichens and its influence on element distribution and concentrations.* Nuclear Instruments and …, 2007.
106. Schmidt, A., et al., *Evaluation of extraction procedures for the ion chromatographic determination of arsenic species in plant materials.* Journal of chromatography A, 2000. **889**(1-2): p. 83-91.
107. Kirby, J. and W. Maher, *Measurement of water-soluble arsenic species in freeze-dried marine animal tissues by microwave-assisted extraction and HPLC-ICP-MS.* Journal of Analytical Atomic Spectrometry, 2002. **17**.
108. Taleshi, M., et al., *Arsenic-containing lipids are natural constituents of sashimi tuna.* Environmental Science & Technology, 2010. **44**(4): p. 1478-1483.
109. García-Salgado, S., et al., *Arsenosugar phospholipids and arsenic hydrocarbons in two species of brown macroalgae.* Environmental Chemistry, 2012. **9**(1): p. 63-66.
110. Kuehnelt, D., K.J. Irgolic, and W. Goessler, *Comparison of three methods for the extraction of arsenic compounds from the NRCC standard reference material DORM-2 and the brown algae Hijiki fuziforme.* Appl. Organomet. Chem., 2001. **15**(6): p. 445 - 456.
111. Maher, W., et al., *Arsenic concentrations and speciation in the tissues and blood of sea mullet (Mugil cephalus) from Lake Macquarie NSW, Australia.* Mar. Chem., 1999. **68**(1-2): p. 169-182.
112. Kirby, J., et al., *Arsenic concentrations and speciation in a temperate mangrove ecosystem, NSW, Australia.* Applied Organometallic Chemistry, 2002. **16**.
113. Kirby, J. and W. Maher, *Tissue accumulation and distribution of arsenic compounds in three marine fish species: relationship to trophic position.* Applied Organometallic Chemistry, 2002. **16**.
114. Goessler, W., et al., *Arsenic compounds in a marine food chain.* Fresenius J. Anal. Chem., 1997. **359**: p. 434-437.
115. Ruttens, A., et al., *Arsenic speciation in food in Belgium.* Journal of Geochemical Exploration, 2012. **121**.
116. Larios, R., R. Fernández-Martínez, and I. Rucandio, *Comparison of three sequential extraction procedures for fractionation of arsenic from highly polluted mining sediments.* Analytical and Bioanalytical Chemistry, 2012. **402**(9): p. 2909-2921.
117. Larios, R., et al., *A methodological approach to evaluate arsenic speciation and bioaccumulation in different plant species from two highly polluted mining areas.* Science of The Total Environment, 2012. **414**: p. 600-607.
118. Mukai, H. and Y. Ambe, *Determination of methylarsenic compounds in airborne particulate matter by gas chromatography with atomic absorption spectrometry.* Analytica Chimica Acta, 1987. **193**: p. 219-229.
119. Caumette, G., et al., *Arsenic Speciation in Plankton Organisms from Contaminated Lakes: Transformations at the Base of the Freshwater Food Chain.* Environmental Science & Technology, 2011. **45**.
120. Santos, C.M.M., et al., *Evaluation of microwave and ultrasound extraction procedures for arsenic speciation in bivalve mollusks by liquid chromatography–inductively coupled plasma-mass spectrometry.* Spectrochimica Acta Part B: Atomic Spectroscopy, 2013. **86**: p. 108–114.
121. Piñeiro, A.M., et al., *Arsenic species determination in human scalp hair by pressurized hot water extraction and high performance liquid chromatography-inductively coupled plasma-mass spectrometry.* Talanta, 2013. **105**: p. 422–428.

122. Seok-Young, O., et al., *Chemical extraction of arsenic from contaminated soil under subcritical conditions.* Science of The Total Environment, 2011. **409**.
123. Rattanachongkiat, S., G. Millward, and M. Foulkes, *Determination of arsenic species in fish, crustacean and sediment samples from Thailand using high performance liquid chromatography (HPLC) coupled with inductively coupled plasma mass spectrometry (ICP-MS).* Journal of environmental monitoring : JEM, 2004. **6**(4): p. 254-261.
124. Nischwitz, V. and S.A. Pergantis, *Mapping of arsenic species and identification of a novel arsenosugar in giant clams Tridacna maxima and Tridacna derasa using advanced mass spectrometric techniques.* Environ. Chem., 2007. **4**(3): p. 187-196.
125. Fricke, M.W., et al., *Extraction and detection of a new sulfide containing arsenosugar in molluscs by IC-ICP-MS and IC-ESI-MS/MS.* J. Anal. Atom. Spectrom., 2004. **19**: p. 1454-1459.
126. Raber, G., et al., *An improved HPLC–ICPMS method for determining inorganic arsenic in food: Application to rice, wheat and tuna fish.* Food Chemistry, 2012. **134**: p. 524–532.
127. Foster, S., et al., *A microwave assisted technique for the sequential extraction of water and non-water soluble arsenic compounds from estuarine plant and marine animal tissue using dilute nitric acid.* Talanta, 2007. **71**(2): p. 537-549.
128. Zhang, C.H., Y. Wang, and Y. Ge, *Determination of Five Arsenic Species in Porphyra by Microwave-Assisted Water Extraction and High Performance Liquid Chromatography–Atomic Fluorescence Spectrometry.* Analytical Letters, 2013. **46**.
129. Lombi, E., et al., *Speciation and distribution of arsenic and localization of nutrients in rice grains.* New Phytologist, 2009. **184**(1): p. 193-201.
130. Raab, A., J. Feldmann, and A. Meharg, *The nature of arsenic-phytochelatin complexes in Holcus lanatus and Pteris cretica.* Plant physiology, 2004. **134**(3): p. 1113-1122.
131. Wood, B.A., et al., *Arsenic is not stored as arsenite - phytochelatin complexes in the seaweeds Fucus spiralis and Hizikia fusiforme.* Environmental Chemistry, 2011. **8**.
132. Sousa-Ferreira, H., et al., *Screening of Toxic Inorganic Arsenic Species in Garlic (Allium sativum L.).* Food Analytical Methods, 2010. **4**.
133. Reyes, M., et al., *Determination of arsenite, arsenate, monomethylarsonic acid and dimethylarsinic acid in cereals by hydride generation atomic fluorescence spectrometry.* Spectrochimica Acta Part B: Atomic Spectroscopy, 2007. **62**(9): p. 1078-1082.
134. Ackerman, A.H., et al., *Comparison of a Chemical and Enzymatic Extraction of Arsenic from Rice and an Assessment of the Arsenic Absorption from Contaminated Water by Cooked Rice.* Environmental Science & Technology, 2005. **39**: p. 5241–5246.
135. Mieke, Q., R. Zed, and S. Michael, *Arsenic speciation in terrestrial plant material using microwave-assisted extraction, ion chromatography and inductively coupled plasma mass spectrometry.* Journal of Analytical Atomic Spectrometry, 2003. **18**.
136. Liu, W.J., et al., *Arsenic Sequestration in Iron Plaque, Its Accumulation and Speciation in Mature Rice Plants (Oryza Sativa L.).* Environmental Science & Technology, 2006. **40**.
137. Langdon, C.J., et al., *Arsenic-speciation in arsenate-resistant and non-resistant populations of the earthworm, Lumbricus rubellus.* Journal of Environmental Monitoring, 2002. **4**(4): p. 603-608.
138. Williams, P., et al., *Variation in arsenic speciation and concentration in paddy rice related to dietary exposure.* Environmental Science & Technology, 2005. **39**(15): p. 5531-5540.
139. Abedin, M.J., et al., *Arsenic Accumulation and Metabolism in Rice (Oryza sativa L.).* Environmental science & technology, 2002. **36**(5): p. 962-968.
140. Batista, B.L., et al., *Rapid sample preparation procedure for As speciation in food samples by LC-ICP-MS.* Food Additives & Contaminants: Part A, 2012. **29**.
141. Sloth, J.J. and K. Julshamn, *Survey of total and inorganic arsenic content in blue mussels (Mytilus edulis L.) from Norwegian fiords: revelation of unusual high levels of inorganic arsenic.* J. Agric. Food Chem., 2008. **56**(4): p. 1269-1273.

142. Kucuksezgin, F., L.T. Gonul, and D. Tasel, *Total and inorganic arsenic levels in some marine organisms from Izmir Bay (Eastern Aegean Sea): A risk assessment.* Chemosphere, 2014. **112**: p. 311-316.
143. Pétursdóttir, A., et al., *HPLC-HG-ICP-MS: a sensitive and selective method for inorganic arsenic in seafood.* Analytical and bioanalytical chemistry, 2012. **404**(8): p. 2185-2191.
144. Moriarty, M.M., et al., *Arsenic speciation of terrestrial invertebrates.* Environmental Science & Technology, 2009. **43**(13): p. 4818-4823.
145. Stroud, J.L., et al., *Assessing the Labile Arsenic Pool in Contaminated Paddy Soils by Isotopic Dilution Techniques and Simple Extractions.* Environmental Science & Technology, 2011. **45**: p. 4262–4269.
146. Pizarro, I., et al., *Evaluation of stability of arsenic species in rice.* Analytical and Bioanalytical Chemistry, 2003. **376**(1): p. 102-109.
147. Thomas, P., J. Finnie, and J. Williams, *Feasibility of identification and monitoring of arsenic species in soil and sediment samples by coupled high-performance liquid chromatography—inductively coupled plasma mass spectrometry.* Journal of Analytical Atomic Spectrometry, 1997. **12**(12): p. 1367-1372.
148. Ruiz-Chancho, M.J., et al., *New approaches to the extraction of arsenic species from soils.* Microchimica Acta, 2005. **151**(3-4): p. 241-248.
149. Teräsahde, P., M. Pantsar-Kallio, and P.K. Manninen, *Simultaneous determination of arsenic species by ion chromatography-inductively coupled plasma mass spectrometry.* Journal of Chromatography A, 1996. **750**(1): p. 83-88.
150. Maher, W.A., *Mode of occurrence and speciation of arsenic in some pelagic and estuarine sediments.* Chemical Geology, 1984. **47**(3-4): p. 333-345.
151. Orero Iserte, L., A.F. Roig-Navarro, and F. Hernandez, *Simultaneous determination of arsenic and selenium species in phosphoric acid extracts of sediment samples by HPLC-ICP-MS.* Anal. Chim. Acta, 2004. **527**(1): p. 97-104.
152. Castillo, A., et al., *Rapid screening of arsenic species in urine from exposed human by inductively coupled plasma mass spectrometry with germanium as internal standard.* Journal of Analytical Atomic Spectrometry, 2012. **27**(2): p. 354-358.
153. Yang, G., et al., *Levels and speciation of arsenic in the atmosphere in Beijing, China.* Chemosphere, 2012. **87**(8): p. 845-850.
154. Oliveira, V., J.L. Gómez-Ariza, and D. Sánchez-Rodas, *Extraction procedures for chemical speciation of arsenic in atmospheric total suspended particles.* Analytical and Bioanalytical Chemistry, 2005. **382**.
155. González-Castanedo, Y., et al., *Arsenic species in atmospheric particulate matter as tracer of the air quality of Doñana Natural Park (SW Spain).* Chemosphere, 2015. **119**: p. 1296-1303.
156. Pardo-Martinez, M., et al., *Comparison of enzymatic extraction procedures for use with directly coupled high performance liquid chromatography-inductively coupled plasma mass spectrometry for the speciation of arsenic in baby foods.* Anal. Chim. Acta, 2001. **441**(1): p. 29-36.
157. Kohlmeyer, U., et al., *Benefits of high resolution IC-ICP-MS for the routine analysis of inorganic and organic arsenic species in food products of marine and terrestrial origin.* Anal. Bioanal. Chem., 2003. **377**: p. 6-13.
158. Sanz, E., R. Munoz-Olivas, and C. Camara, *Evaluation of a focused sonication probe for arsenic speciation in environmental and biological samples.* J. Chromatogr. A, 2005. **1097**(1-2): p. 1-8.
159. Sanz, E., et al., *Alternative extraction methods for arsenic speciation in hair using ultrasound probe sonication and pressurised liquid extraction.* Journal of Analytical Atomic Spectrometry, 2007. **22**(2): p. 131-139.
160. Amayo, K.O., et al., *Identification of arsenolipids and their degradation products in cod-liver oil.* Talanta, 2014. **118**: p. 217-223.

161. Amayo, K.O., et al., *Arsenolipids show different profiles in muscle tissues of four commercial fish species.* Journal of trace elements in medicine and biology, 2014. **28**(2): p. 131-137.
162. Arroyo-Abad, U., et al., *Detection of arsenic-containing hydrocarbons in canned cod liver tissue.* Talanta, 2010. **82**(1): p. 38-43.
163. Edmonds, J., et al., *Arsenic lipids in the digestive gland of the western rock lobster Panulirus cygnus: an investigation by HPLC ICP-MS.* The Science of the total environment, 1992. **122**(3): p. 321-335.
164. Arroyo-Abad, U., et al., *Determination and identification of hydrophilic and hydrophobic arsenic species in methanol extract of fresh cod liver by RP-HPLC with simultaneous ICP-MS and ESI-Q-TOF-MS detection.* Food Chemistry, 2013. **141**(3): p. 3093-3102.
165. Arroyo-Abad, U., et al., *Arsenolipids in commercial canned cod liver: An occurrence and distribution study.* European Journal of Lipid Science and Technology, 2014. **116**(10): p. 1381-1387.
166. Francesconi, K.A., R.V. Stick, and J.S. Edmonds, *Glycerolphosphorylarsenocholine and phosphatidylarsenocholine in yelloweye mullet (Aldrichetta forsteri) following oral administration of arsenocholine.* Experientia, 1990. **46**: p. 464-466.
167. Duncan, E.G., et al., *The influence of bacteria on the arsenic species produced by laboratory cultures of the marine phytoplankton Dunaliella tertiolecta.* Journal of Applied Phycology, 2014. **18 February 2014**: p. 1-6.
168. Duncan, E.G., et al., *Influence of culture regime on arsenic cycling by the marine phytoplankton Dunaliella tertiolecta and Thalassiosira pseudonana.* Environmental Chemistry, 2013: p. -.
169. Foster, S., D. Thomson, and W. Maher, *Uptake and metabolism of arsenate by anexic cultures of the microalgae Dunaliella tertiolecta and Phaeodactylum tricornutum.* Mar. Chem., 2008. **108**(3-4): p. 172-183.
170. Devalla, S. and J. Feldmann, *Determination of lipid-soluble arsenic species in seaweed-eating sheep from Orkney.* Appl. Organomet. Chem., 2003. **17**: p. 906 - 912.
171. Ebisuda, K., et al., *Arsenic concentrations and speciation in the tissues of the ringed seals (Phoca hispida) from Pangnirtung, Canada.* Appl. Organomet. Chem., 2002. **16**: p. 451-457.
172. Hanaoka, K., et al., *Microbial degradation of arsenobetaine, the major water soluble organoarsenic compound occurring in marine animals.* Chemosphere, 1987. **16**(10-12): p. 2545-2550.
173. Hanaoka, K., et al., *Arsenocholine- and dimethylated arsenic-containing lipids in starspotted shark Mustelus manazo.* Appl. Organomet. Chem., 1999. **13**: p. 765 - 770.
174. Raab, A., et al., *Comprehensive Analysis of Lipophilic Arsenic Species in a Brown Alga (Saccharina latissima).* Analytical Chemistry, 2013. **85**(5): p. 2817-2824.
175. Glabonjat, R.A., et al., *Quantification of Arsenolipids in the Certified Reference Material NMIJ 7405-a (Hijiki) using HPLC/Mass Spectrometry after Chemical Derivatization.* Analytical Chemistry, 2014. **86**(20): p. 10282-10287.
176. Maher, W., et al., *Measurement of Inorganic Arsenic Species in Rice after Nitric Acid Extraction by HPLC-ICPMS: Verification Using XANES.* Environmental Science & Technology, 2013.
177. Bluemlein, K., et al., *Can we trust mass spectrometry for determination of arsenic peptides in plants: comparison of LC-ICP-MS and LC-ES-MS/ICP-MS with XANES/EXAFS in analysis of Thunbergia alata.* Analytical and bioanalytical chemistry, 2008. **390**(7): p. 1739-1751.
178. Schmeisser, E., et al., *Thio arsenosugars identified as natural constituents of mussels by liquid chromatography-mass spectrometry.* Chemical communications 2004. **16**: p. 1824-1825.
179. Soeroes, C., et al., *Thio arsenosugars in freshwater mussels from the Danube in Hungary.* Journal of Environmental Monitoring, 2005. **7**(7): p. 688-692.
180. Button, M., et al., *Arsenic speciation in field-collected and laboratory-exposed earthworms Lumbricus terrestris.* Chemosphere, 2011. **85**: p. 1277–1283.

181. Whaley-Martin, K.J., et al., *Arsenic Speciation in Blue Mussels (Mytilus edulis) Along a Highly Contaminated Arsenic Gradient.* Environmental Science & Technology, 2012. **46**.
182. Smith, P., G. , I. Koch, and K. Reimer, J. , *Arsenic Speciation Analysis of Cultivated White Button Mushrooms (Agaricus bisporus) Using High-Performance Liquid Chromatography–Inductively Coupled Plasma Mass Spectrometry, and X-ray Absorption Spectroscopy.* Environmental Science & Technology, 2007. **41**: p. 6947–6954.
183. Wolf, R., et al., *Simultaneous speciation of arsenic, selenium, and chromium: species stability, sample preservation, and analysis of ash and soil leachates.* Analytical and bioanalytical chemistry, 2011. **401**(9): p. 2733-2745.
184. Alava, P., et al., *HPLC-ICP-MS method development to monitor arsenic speciation changes by human gut microbiota.* Biomedical chromatography : BMC, 2012. **26**(4): p. 524-533.
185. Hansen, H., M. Jaspars, and J. Feldmann, *Arsinothioyl-sugars produced by in vitro incubation of seaweed extract with liver cytosol analysed by HPLC coupled simultaneously to ES-MS and ICP-MS.* The Analyst, 2004. **129**(11): p. 1058-1064.
186. Conklin, S., D. , et al., *Investigation of the pH effects on the formation of methylated thio-arsenicals, and the effects of pH and temperature on their stability.* Journal of Analytical Atomic Spectrometry, 2008. **23**: p. 711-716.
187. Conklin, S., D. , P. Creed, A. , and J. Creed, T. , *Detection and quantification of a thio-arsenosugar in marine molluscs by IC-ICP-MS with an emphasis on the interaction of arsenosugars with sulfide as a function of pH.* Journal of Analytical Atomic Spectrometry, 2006. **21**: p. 869-875.
188. Maher, W., et al., *Measurement of inorganic arsenic species in rice after nitric acid extraction by HPLC-ICPMS: Verification using XANES.* Environmental Science & Technology, 2013. **47**(11): p. 5821-5827.
189. Rahman, M.A., et al., *Accumulation of arsenic in tissues of rice plant (Oryza sativa) and its distribution in fractions of rice grain.* Chemosphere, 2007. **69**(6): p. 942-948.
190. Schmidt, A.-C., N. Haufe, and M. Otto, *A systematic study on extraction of total arsenic from down-scaled sample sizes of plant tissues and implications for arsenic species analysis.* Talanta, 2008. **76**.
191. Dufailly, V., et al., *Validation of a method for arsenic speciation in food by ion chromatography-inductively coupled plasma/mass spectrometry after ultrasonic-assisted enzymatic extraction.* Journal of AOAC International, 2011. **94**(3): p. 947-958.
192. Kirby, J., et al., *Arsenic species determination in biological tissues by HPLC-ICP-MS and HPLC-HG-ICP-MS.* Aust. J. Chem., 2004. **57**: p. 1-11.
193. Schmeisser, E., et al., *Volatile analytes formed from arsenosugars: determination by HPLC-HG-ICPMS and implications for arsenic speciation analyses.* Analytical chemistry, 2004. **76**(2): p. 418-423.
194. Regmi, R., B.F. Milne, and J. Feldmann, *Hydride generation activity of arsenosugars and thioarsenicals.* Analytical and Bioanalytical Chemistry, 2007. **388**(4): p. 775-782.
195. Gómez-Ariza, J., et al., *A comparison between ICP-MS and AFS detection for arsenic speciation in environmental samples.* Talanta, 2000. **51**(2): p. 257-268.
196. Sánchez-Rodas, D., et al., *Determination of an arsenosugar in oyster extracts by liquid chromatography-electrospray mass spectrometry and liquid chromatography-ultraviolet photo-oxidation-hydride generation atomic fluorescence spectrometry.* The Analyst, 2002. **127**.
197. Monasterio, R.P., et al., *Organic solvent-free reversed-phase ion-pairing liquid chromatography coupled to atomic fluorescence spectrometry for organoarsenic species determination in several matrices.* J. Agric. Food Chem., 2011. **59**(8): p. 3566-3574.
198. Ellwood, M.J. and W.A. Maher, *An automated hydride generation-cryogenic trapping-ICP-MS system for measuring inorganic and methylated Ge, Sb and As species in marine and fresh waters.* Journal of Analytical Atomic Spectrometry, 2002. **17**(3): p. 197-203.

199. Matoušek, T., et al., *Selective hydride generation- cryotrapping- ICP-MS for arsenic speciation analysis at picogram levels: analysis of river and sea water reference materials and human bladder epithelial cells.* Journal of analytical atomic spectrometry, 2013. **28**(9): p. 1456-1465.
200. Gunter, I. and H. Jen-How, *An automatic cryotrapping and cryofocussing system for parallel ICP-MS and EI-MS detection of volatile arsenic compounds in gaseous samples.* Journal of Analytical Atomic Spectrometry, 2013. **28**.
201. Yuan, C., et al., *Volatile Arsenic Species Released from Escherichia coli Expressing the AsIII S-adenosylmethionine Methyltransferase Gene.* Environmental Science & Technology, 2008. **42**: p. 3201-3206.
202. Grotti, M., et al., *Influence of chemical species on the determination of arsenic using inductively coupled plasma mass spectrometry at a low liquid flow rate.* Journal of Analytical Atomic Spectrometry, 2013. **28**: p. 1718-1724.
203. Narukawa, T., T. Kuroiwa, and K. Chiba, *Mechanism of sensitivity difference between trivalent inorganic As species [As(III)] and pentavalent species [As(V)] with inductively coupled plasma spectrometry.* Talanta, 2007. **73**(1): p. 157-165.
204. D'Ulivo, A., et al., *Improving the analytical performance of hydride generation non-dispersive atomic fluorescence spectrometry. Combined effect of additives and optical filters.* Spectrochimica Acta Part B: Atomic Spectroscopy, 2001. **56**(10): p. 1893-1907.
205. Mester, Z. and P. Fodor, *High-performance liquid chromatography-hydride generation-atomic fluorescence spectroscopic determination of arsenic species in water.* Journal of Chromatography A, 1996. **756**(1): p. 292-299.
206. Gómez-Ariza, J.L., et al., *Evaluation of atomic fluorescence spectrometry as a sensitive detection technique for arsenic speciation.* Applied Organometallic Chemistry, 1998. **12**: p. 439-447.
207. Howard, A.G. and C. Salou, *Cysteine enhancement of the cryogenic trap hydride AAS determination of dissolved arsenic species.* Anal. Chim. Acta, 1996. **333**(1-2): p. 89-96.
208. Kumar, A. and P. Riyazuddin, *Mechanism of volatile hydride formation and their atomization in hydride generation atomic absorption spectrometry.* Analytical sciences : the international journal of the Japan Society for Analytical Chemistry, 2005. **21**(12): p. 1401-1410.
209. Carrero, P., et al., *Determination of various arsenic species by flow injection hydride generation atomic absorption spectrometry: investigation of the effects of the acid concentration of different reaction media on the generation of arsines.* Anal. Chim. Acta, 2001. **438**(1-2): p. 195-204.
210. Pohl, P. and B. Prusisz, *Ion-exchange column chromatography-an attempt to speciate arsenic.* Trac-Trend. Anal. Chem., 2004. **23**(1): p. 63-69.
211. Karadjova, I., B. , et al., *Continuous flow hydride generation-atomic fluorescence spectrometric determination and speciation of arsenic in wine.* Spectrochimica Acta Part B: Atomic Spectroscopy, 2005. **60**: p. 816–823.
212. Planer-Friedrich, B. and D. Wallschläger, *A Critical Investigation of Hydride Generation-Based Arsenic Speciation in Sulfidic Waters.* Environmental Science & Technology, 2009. **43**: p. 5007-5013.
213. Mamindy-Pajany, Y., et al., *Arsenic in marina sediments from the Mediterranean coast: speciation in the solid phase and occurrence of thioarsenates.* Soil and Sediment Contamination: An International Journal, 2013. **22**(8): p. 984-1002.
214. Wei, C. and J. Liu, *A new hydride generation system applied in determination of arsenic species with ion chromatography-hydride generation-atomic fluorescence spectrometry (IC-HG-AFS).* Talanta, 2007. **73**(3): p. 540-545.
215. Chiba, K. and T. Narukawa, *The Effect of Plasma Reactions on Arsenic Measurement by ICP Spectrometry.* Analytical sciences, 2014. **30**(1): p. 175-181.
216. Sonia, D.I., et al., *Dynamic reaction cell ICP-MS for determination of total As, Cr, Se and V in complex matrices: Still a challenge? A review.* Analytica Chimica Acta, 2011. **698**.

217. An, J., et al., *Combined use of collision cell technique and methanol addition for the analysis of arsenic in a high-chloride-containing sample by ICP-MS.* Microchemical Journal, 2015.
218. Jackson, B.P., A. Liba, and J. Nelson, *Advantages of reaction cell ICP-MS on doubly charged interferences for arsenic and selenium analysis in foods.* Journal of Analytical Atomic Spectrometry, 2015.
219. Raber, G., R. Raml, and W. Goessler…, *Quantitative speciation of arsenic compounds when using organic solvent gradients in HPLC-ICPMS.* Journal of Analytical …, 2010.
220. Wallschläger, D. and C. Stadey, *Determination of (Oxy)thioarsenates in sulfidic waters.* Analytical chemistry, 2007. **79**(10): p. 3873-3880.
221. Prikler, S., D. Pick, and J. Einax, *Comparing different means of signal treatment for improving the detection power in HPLC-ICP-MS.* Analytical and bioanalytical chemistry, 2012. **403**(4): p. 1109-1116.
222. Foster, S., et al., *Arsenic species in a rocky intertidal marine food chain in NSW, Australia, revisited.* Environmental Chemistry, 2006. **3**(4): p. 304-315.
223. Cullen, W.R., et al., *The metabolism of methylarsine oxide and sulfide.* Appl. Organomet. Chem., 1989. **3**(1): p. 71-78.
224. Burrows, G.J. and E.E. Turner, *A new type of compound containing arsenic.* J. Chem. Soc., Trans., 1920. **117**: p. 1373 - 1383.
225. Hansen, H., et al., *Sulfur-containing arsenical mistaken for dimethylarsinous acid [DMA(III)] and identified as a natural metabolite in urine: major implications for studies on arsenic metabolism and toxicity.* Chemical research in toxicology, 2004. **17**(8): p. 1086-1091.
226. Fricke, M., et al., *Chromatographic separation and identification of products from the reaction of dimethylarsinic acid with hydrogen sulfide.* Chemical research in toxicology, 2005. **18**(12): p. 1821-1829.
227. Raml, R., W. Goessler, and K. Francesconi, *Improved chromatographic separation of thio-arsenic compounds by reversed-phase high performance liquid chromatography-inductively coupled plasma mass spectrometry.* Journal of chromatography. A, 2006. **1128**(1-2): p. 164-170.
228. Fricke, M., et al., *Dimethylthioarsinic anhydride: a standard for arsenic speciation.* Analytica chimica acta, 2007. **583**(1): p. 78-83.
229. Reay, P. and C. Asher, *Preparation and purification of< sup> 74</sup> As-labeled arsenate and arsenite for use in biological experiments.* Analytical biochemistry, 1977. **78**: p. 557-560.
230. Nelson, S., et al., *Reactions of arsenic(III) and arsenic(V) species with glutathione.* Chemical Research in Toxicology, 1993. **6**.
231. Yehiayan, L., et al., *Speciation, formation, stability and analytical challenges of human arsenic metabolites.* Journal of analytical atomic spectrometry, 2009. **24**(10): p. 1397-1405.
232. Schwedt, G. and M. Rieckhoff, *Separation of thio-and oxothioarsenates by capillary zone electrophoresis and ion chromatography.* Journal of Chromatography A, 1996. **736**: p. 341-350.
233. Wilkin, R., T. , D. Wallschläger, and R. Ford, G., *Speciation of arsenic in sulfidic waters.* Geochemical Transactions, 2003. **4**: p. 1–7.
234. Traar, P., *The synthesis of arsenic and selenium-containing carbohydrates*, in *Institute of Chemistry – Analytical Chemistry*2006, Karl-Franzens University: Graz, Austria. p. 231.
235. Taleshi, M.S., et al., *Synthesis and Characterization of Arsenolipids: Naturally Occurring Arsenic Compounds in Fish and Algae.* Organometallics, 2014. **33**(6): p. 1397-1403.
236. Ammann, A.A., *Arsenic Speciation Analysis by Ion Chromatography - A Critical Review of Principles and Applications.* American Journal of Analytical Chemistry, 2011. **02**: p. 27-45.
237. Chen, Y.-C., et al., *Stability of arsenic species and insoluble arsenic in human urine.* Cancer epidemiology, biomarkers & prevention : a publication of the American Association for Cancer Research, cosponsored by the American Society of Preventive Oncology, 2002. **11**(11): p. 1427-1433.

238. Davis, W., et al., *Methods for the separation and quantification of arsenic species in SRM 2669: arsenic species in frozen human urine.* Analytical and bioanalytical chemistry, 2010. **396**(8): p. 3041-3050.
239. Valderi, L.D., et al., *As, Hg, I, Sb, Se and Sn speciation in body fluids and biological tissues using hyphenated-ICP-MS techniques: A review.* International Journal of Mass Spectrometry, 2011.
240. Morton, J. and E. Leese, *Arsenic speciation in clinical samples: urine analysis using fast micro-liquid chromatography ICP-MS.* Analytical and bioanalytical chemistry, 2011. **399**(5): p. 1781-1788.
241. Yuan, C., et al., *Arsenic speciation analysis in human saliva.* Clinical Chemistry, 2008. **54**(1): p. 163-171.
242. Raber, G., et al., *Determination of 'arsenosugars' in algae with anion-exchange chromatography and an inductively coupled plasma mass spectrometer as element-specific detector.* Fresenius' journal of analytical chemistry, 2000. **367**(2): p. 181-188.
243. Kirby, J., W. Maher, and D. Spooner, *Arsenic occurrence and species in near-shore macroalgae-feeding marine animals.* Environmental science & technology, 2005. **39**(16): p. 5999-6005.
244. Kohlmeyer, U., J. Kuballa, and E. Jantzen, *Simultaneous separation of 17 inorganic and organic arsenic compounds in marine biota by means of high-performance liquid chromatography/inductively coupled plasma mass spectrometry.* Rapid communications in mass spectrometry : RCM, 2002. **16**(10): p. 965-974.
245. Sloth, J.J., E.H. Larsen, and K. Julshamn, *Determination of arganoarsenic species in marine samples using gradient elution cation exchange HPLC-ICP-MS.* J. Anal. Atom. Spectrom., 2003. **18**: p. 452 - 459.
246. Madsen, A.D., et al., *Characterization of an algal extract by HPLC-ICP-MS and LC-electrospray MS for use in arsenosugar speciation studies.* J. Anal. Atom. Spectrom., 2000. **15**: p. 657-662.
247. Ciardullo, S., et al., *Arsenic speciation in freshwater fish: focus on extraction and mass balance.* Talanta, 2010. **81**(1-2): p. 213-221.
248. Nischwitz, V., K. Kanaki, and S.A. Pergantis, *Mass spectrometric identification of novel arsinothioylsugars in marine bivalves and algae.* J. Anal. Atom. Spectrom., 2006. **21**: p. 33-40.
249. Horváth, C., W. Melander, and I. Molnar, *Liquid chromatography of ionogenic substances with nonpolar stationary phases.* Analytical Chemistry, 1977. **49**(1): p. 142-154.
250. Horvath, C., et al., *Enhancement of retention by ion-pair formation in liquid chromatography with nonpolar stationary phases.* Analytical Chemistry, 1977. **49**(14): p. 2295-2305.
251. Skoog, D.A. and J.J. Leary, *Principles of instrumental analysis, 1992.* Saunders College of Publishing, Philadelphia, London, 1992.
252. Alava, P., et al., *Arsenic undergoes significant speciation changes upon incubation of contaminated rice with human colon micro biota.* Journal of hazardous materials, 2013. **262**: p. 1237-1244.
253. Le, X. and M. Ma, *Speciation of arsenic compounds by using ion-pair chromatography with atomic spectrometry and mass spectrometry detection.* Journal of Chromatography A, 1997. **764**(1): p. 55-64.
254. Guerin, T., A. Astruc, and M. Astruc, *Speciation of arsenic and selenium compounds by HPLC hyphenated to specific detectors: a review of the main separation techniques.* Talanta, 1999. **50**(1): p. 1-24.
255. Beauchemin, D., et al., *Determination of arsenic species by high-performance liquid chromatography-inductively coupled plasma mass spectrometry.* Journal of Analytical Atomic Spectrometry, 1989. **4**(3): p. 285-289.
256. McSheehy, S., et al., *Characterization of arsenic species in kidney of the clam Tridacna derasa by multidimensional liquid chromatography-ICPMS and electrospray time-of-flight tandem mass spectrometry.* Analytical chemistry, 2002. **74**(10): p. 2370-2378.
257. Currier, J.M., et al., *Direct analysis and stability of methylated trivalent arsenic metabolites in cells and tissues.* Metallomics, 2011. **3**(12): p. 1347-1354.

258. de la Calle, M., et al., *Is it possible to agree on a value for inorganic arsenic in food? The outcome of IMEP-112.* Analytical and bioanalytical chemistry, 2012. **404**(8): p. 2475-2488.
259. de la Calle, M.B., et al., *Does the determination of inorganic arsenic in rice depend on the method?* TrAC Trends in Analytical Chemistry, 2011. **30**.
260. Hansen, H., R. , et al., *Identification of tetramethylarsonium in rice grains with elevated arsenic content.* Journal of Environmental Monitoring, 2011. **13**: p. 32-34.
261. Ellwood, M.J. and W.A. Maher, *Measurement of arsenic species in marine sediments by high-performance liquid chromatography–inductively coupled plasma mass spectrometry.* Analytica Chimica Acta, 2003. **477**(2): p. 279-291.
262. Kohlmeyer, U., et al., *Determination of Arsenic Species in Fish Oil After Acid Digestion.* Microchimica Acta, 2005. **151**: p. 249-255.
263. Martin, S., J. , et al., *Arsenosugar Metabolism Not Unique to the Sheep of North Ronaldsay.* Environmental Chemistry, 2005. **2**: p. 190-197.
264. Planer-Friedrich, B., et al., *Arsenic speciation in sulfidic waters: reconciling contradictory spectroscopic and chromatographic evidence.* Analytical chemistry, 2010. **82**(24): p. 10228-10235.
265. Kala, S.V., et al., *The MRP2/cMOAT transporter and arsenic-glutathione complex formation are required for biliary excretion of arsenic.* Journal of Biological Chemistry, 2000. **275**(43): p. 33404-33408.
266. Andrea, R., et al., *Uptake and translocation of inorganic and methylated arsenic species by plants.* Environmental Chemistry, 2007. **4**.
267. Woller, Á., et al., *Simultaneous speciation of redox species of arsenic and selenium using an anion-exchange microbore column coupled with a micro-concentric nebulizer and an inductively coupled plasma mass spectrometer as detector.* Journal of Analytical Atomic Spectrometry, 1998. **13**(2): p. 141-149.
268. Giusti, P., et al., *Development of a nebulizer for a sheathless interfacing of nanoHPLC and ICPMS.* Analytical Chemistry, 2006. **78**(3): p. 965-971.
269. Rappel, C. and D. Schaumlöffel, *Improved nanonebulizer design for the coupling of nanoHPLC with ICP-MS.* Journal of Analytical Atomic Spectrometry, 2010. **25**(12): p. 1963-1968.
270. Le, X., W. Cullen, and K. Reimer, *Speciation of arsenic compounds by HPLC with hydride generation atomic absorption spectrometry and inductively coupled plasma mass spectrometry detection.* Talanta, 1994. **41**(4): p. 495-502.
271. Raber, G., et al., *Determination of 'arsenosugars' in algae with anion-exchange chromatography and an inductively coupled plasma mass spectrometer as element-specific detector.* Fresenius J. Anal. Chem., 2000. **367**: p. 181-188.
272. Terol, A., et al., *High temperature liquid chromatography–inductively coupled plasma mass spectrometry for the determination of arsenosugars in biological samples.* Journal of Chromatography A, 2012. **1262**: p. 1262-1270.
273. Morabito, R., et al., *Towards a new Certified Reference Material for butyltins, methylmercury and arsenobetaine in oyster tissue.* TrAC Trends in Analytical Chemistry, 2004. **23**.
274. Baer, I., et al., *Performance of laboratories in speciation analysis in seafood – Case of methylmercury and inorganic arsenic.* Food Control, 2011. **22**: p. 1928–1934.
275. Briscoe, M.L., J. Creswell, and A. Carter, *2013 Brooks Rand Labs Interlaboratory Comparison Study for Arsenic Speciation in Food and Juice*, 2013.
276. Bluemlein, K., E.M. Krupp, and J. Feldmann, *Advantages and limitations of a desolvation system coupled online to HPLC-ICPqMS/ES-MS for the quantitative determination of sulfur and arsenic in arseno-peptide complexes.* Journal of Analytical Atomic Spectrometry, 2009. **24**(1): p. 108-113.
277. Raab, A., et al., *Pentavalent arsenic can bind to biomolecules.* Angewandte Chemie (International ed. in English), 2007. **46**(15): p. 2594-2597.

278. Roig-Navarro, A., et al., *Simultaneous determination of arsenic species and chromium(VI) by high-performance liquid chromatography-inductively coupled plasma-mass spectrometry.* Journal of chromatography. A, 2001. **912**(2): p. 319-327.
279. Huang, J.-H. and G. Ilgen, *Blank values, adsorption, pre-concentration, and sample preservation for arsenic speciation of environmental water samples.* Analytica Chimica Acta, 2004. **512**(1): p. 1-10.
280. Larsen, E.H., G. Pritzl, and S.H. Hansen, *Speciation of eight arsenic compounds in human urine by high-performance liquid chromatography with inductively coupled plasma mass spectrometric detection using antimonate for internal chromatographic standardization.* Journal of Analytical Atomic Spectrometry, 1993. **8**(4): p. 557-563.
281. Pell, A., et al., *Occurrence of arsenic species in algae and freshwater plants of an extreme arid region in northern Chile, the Loa River Basin.* Chemosphere, 2013. **90**(2): p. 556-564.
282. Bednar, A.J., et al., *Preserving the Distribution of Inorganic Arsenic Species in Groundwater and Acid Mine Drainage Samples.* Environmental Science & Technology, 2002. **36**(10): p. 2213-2218.
283. Samanta, G. and D. Clifford, A., *Preservation of Inorganic Arsenic Species in Groundwater.* Environmental Science & Technology, 2005. **39**.
284. Tallman, D.E. and A.U. Shaikh, *Redox stability of inorganic arsenic (III) and arsenic (V) in aqueous solution.* Analytical Chemistry, 1980. **52**(1): p. 196-199.
285. Kala, S., et al., *The MRP2/cMOAT transporter and arsenic-glutathione complex formation are required for biliary excretion of arsenic.* The Journal of biological chemistry, 2000. **275**(43): p. 33404-33408.
286. Mandal, B., et al., *Speciation of arsenic in biological samples.* Toxicology and applied pharmacology, 2004. **198**(3): p. 307-318.
287. Mandal, B.K., Y. Ogra, and K.T. Suzuki, *Speciation of arsenic in human nail and hair from arsenic-affected area by HPLC-inductively coupled argon plasma mass spectrometry.* Toxicology and Applied Pharmacology, 2003. **189**(2): p. 73-83.
288. Slejkovec, Z., et al., *Speciation of arsenic in coarse and fine urban aerosols using sequential extraction combined with liquid chromatography and atomic fluorescence detection.* Fresenius' journal of analytical chemistry, 2000. **366**(8): p. 830-834.
289. D'Amato, M., et al., *Arsenic speciation in wheat and wheat products using ultrasound-and microwave-assisted extraction and anion exchange chromatography-inductively coupled plasma mass spectrometry.* Journal of Analytical Atomic Spectrometry, 2011. **26**(1): p. 207-213.
290. Yuan, C.-G., et al., *Evaluation of extraction methods for arsenic speciation in polluted soil and rotten ore by HPLC-HG-AFS analysis.* Microchimica Acta, 2007. **159**(1-2): p. 175-182.
291. Geiszinger, A., W. Goessler, and W. Kosmus, *Organoarsenic compounds in plant and soil on top of an ore vein.* Appl. Organomet. Chem., 2002. **16**: p. 245 - 249.
292. Slejkovec, Z., et al., *Speciation analysis to unravel the soil-to-plant transfer in highly arsenic-contaminated areas in Cornwall (UK).* International Journal of Environmental Analytical Chemistry, 2010. **90**: p. 784-796.
293. Hansen, S.H., et al., *Separation of seven arsenic compounds by high-performance liquid chromatography with on-line detection by hydrogen-argon flame atomic absorption spectrometry and inductively coupled plasma mass spectrometry.* Journal of Analytical Atomic Spectrometry, 1992. **7**(4): p. 629-634.
294. Sanz, E., R. Muñoz-Olivas, and C. Cámara, *Evaluation of a focused sonication probe for arsenic speciation in environmental and biological samples.* Journal of chromatography. A, 2005. **1097**(1-2): p. 1-8.
295. Bok Jung, H. and Y. Zheng, *Enhanced recovery of arsenite sorbed onto synthetic oxides by L-ascorbic acid addition to phosphate solution: calibrating a sequential leaching method for the speciation analysis of arsenic in natural samples.* Water Research, 2006. **40**(11): p. 2168-2180.

296. Schmidt, A.-C., et al., *Evaluation of the influence of arsenic species on the nitrogen metabolism of a model angiosperm: nasturtium,Tropaeolum majus.* Applied Organometallic Chemistry, 2005. **19**(5): p. 590-599.
297. He, B., et al., *Optimization of the extraction for the determination of arsenic species in plant materials by high-performance liquid chromatography coupled with hydride generation atomic fluorescence spectrometry.* Spectrochim. Acta B, 2002. **57**(11): p. 1705-1711.
298. Saunders, J., et al., *Arsenic transformations in terrestrial small mammal food chains from contaminated sites in Canada.* Journal of environmental monitoring : JEM, 2011. **13**(6): p. 1784-1792.
299. Wuilloud, R.G., S.S. Kannamkumarath, and J.A. Caruso, *Speciation of essential and toxic elements in edible mushrooms: size-exclusion chromatography separation with on-line UV–inductively coupled plasma mass spectrometry detection.* Applied Organometallic Chemistry, 2004. **18**(4): p. 156-165.
300. Granchinho, S.C.R., et al., *Transformation of arsenic(V) by the fungus Fusarium oxysporum melonis isolated from the alga Fucus gardneri.* Appl. Organomet. Chem., 2002. **16**: p. 721 - 726.
301. Ye, W.-L., et al., *Arsenic speciation in phloem and xylem exudates of castor bean.* Plant physiology, 2010. **154**(3): p. 1505-1513.
302. Van den Broeck, K., C. Vandecasteele, and J.M.C. Geuns, *Speciation by liquid chromatography-inductively coupled plasma-mass spectrometry of arsenic in mung bean seedlings used as a bio-indicator for the arsenic contamination.* Anal. Chim. Acta, 1998. **361**(1-2): p. 101-111.
303. Szakova, J., et al., *Comparison of mild extraction procedures for determination of arsenic compounds in different parts of pepper plants (Capsicum annum, L.).* Applied Organometallic Chemistry, 2005. **19**(3): p. 308-314.
304. Pizarro, I., et al., *Arsenic speciation in environmental and biological samples: Extraction and stability studies.* Anal. Chim. Acta, 2003. **495**(1-2): p. 85-98.
305. Zhu, Y.-G., et al., *High percentage inorganic arsenic content of mining impacted and nonimpacted Chinese rice.* Environmental Science & Technology, 2008. **42**(13): p. 5008-5013.
306. Nam, S., et al., *Preliminary results of extraction, separation and quantitation of arsenic species in food and dietary supplements by HPLC-ICP-MS.* BULLETIN-KOREAN CHEMICAL SOCIETY, 2006. **27**(6): p. 903.
307. Huang, J.H., et al., *Speciation of arsenite and arsenate in rice grain – Verification of nitric acid based extraction method and mass sample survey.* Food Chemistry, 2012. **130**.
308. Sun, G.-X., et al., *Inorganic arsenic in rice bran and its products are an order of magnitude higher than in bulk grain.* Environmental Science & Technology, 2008. **42**(19): p. 7542-7546.
309. Adomako, E., E. , et al., *Inorganic arsenic and trace elements in Ghanaian grain staples.* Environmental Pollution, 2011. **159**(10): p. 2435–2442.
310. Meharg, A., A. , et al., *Speciation and Localization of Arsenic in White and Brown Rice Grains.* Environmental Science & Technology, 2008. **42**(4): p. 1051–1057.
311. Carbonell-Barrachina, A., et al., *Inorganic arsenic contents in rice-based infant foods from Spain, UK, China and USA.* Environmental pollution (Barking, Essex : 1987), 2012. **163**: p. 77-83.
312. Guzmán Mar, J.L., et al., *Simultaneous extraction of arsenic and selenium species from rice products by microwave-assisted enzymatic extraction and analysis by ion chromatography-inductively coupled plasma-mass spectrometry.* J. Agric. Food Chem., 2009. **57**(8): p. 3005-3013.
313. Wolle, M.M., et al., *Speciation analysis of arsenic in prenatal and children's dietary supplements using microwave-enhanced extraction and ion chromatography–inductively coupled plasma mass spectrometry.* Analytica Chimica Acta, 2014. **818**: p. 23-31.
314. Llorente-Mirandes, T., et al., *A need for determination of arsenic species at low levels in cereal-based food and infant cereals. Validation of a method by IC–ICPMS.* Food Chemistry, 2014. **147**: p. 377-385.

315. Yathavakilla, S., et al., *Arsenic speciation and identification of monomethylarsonous acid and monomethylthioarsonic acid in a complex matrix.* Analytical chemistry, 2008. **80**(3): p. 775-782.
316. Vela, N., D. Heitkemper, and K. Stewart, *Arsenic extraction and speciation in carrots using accelerated solvent extraction, liquid chromatography and plasma mass spectrometry.* The Analyst, 2001. **126**(7): p. 1011-1017.
317. Schaeffer, R., et al., *Arsenic speciation in freshwater organisms from the river Danube in Hungary.* Talanta, 2006. **69**(4): p. 856-865.
318. Zhao, F.-J., et al., *Accumulation, distribution, and speciation of arsenic in wheat grain.* Environmental science & technology, 2010. **44**(14): p. 5464-5468.
319. Sánchez-Rodas, D., J. Luis Gómez-Ariza, and V. Oliveira, *Development of a rapid extraction procedure for speciation of arsenic in chicken meat.* Anal. Bioanal. Chem., 2006. **385**(7): p. 1172-1177.
320. Liu, X.-J., et al., *Arsenic speciation in Chinese Herbal Medicines and human health implication for inorganic arsenic.* Environmental pollution (Barking, Essex : 1987), 2013. **172**: p. 149-154.
321. Gómez-Ariza, J.L., et al., *Comparison of biota sample pretreatments for arsenic speciation with coupled HPLC-HG-ICP-MS.* The Analyst, 2000. **125**.
322. Geiszinger, A., et al., *Determination of arsenic compounds in earthworms.* Environmental Science & Technology, 1998. **32**(15): p. 2238-2243.
323. Price, A., et al., *Distribution of arsenic species in an open seagrass ecosystem: relationship to trophic groups, habitats and feeding zones.* Environmental Chemistry, 2012. **9**(1): p. 77-88.
324. Mamindy-Pajany, Y., et al., *Arsenic in marine sediments from French Mediterranean ports: geochemical partitioning, bioavailability and ecotoxicology.* Chemosphere, 2013. **90**(11): p. 2730-2736.
325. Fauser, P., et al., *Occurrence and sorption properties of arsenicals in marine sediments.* Environmental monitoring and assessment, 2013. **185**(6): p. 4679-4691.
326. Foster, S., D. Thomson, and W. Maher, *Uptake and metabolism of arsenate by anexic cultures of the microalgae Dunaliella tertiolecta and Phaeodactylum tricornutum.* Marine Chemistry, 2008. **108**(3-4): p. 172-183.
327. Duncan, E., S. Foster, and W. Maher, *Uptake and metabolism of arsenate, methylarsonate and arsenobetaine by axenic cultures of the phytoplankton Dunaliella tertiolecta.* Botanica Marina, 2010. **53**(4): p. 377-386.
328. Duncan, E.G., et al., *The influence of arsenate and phosphate exposure on arsenic uptake, metabolism and species formation in the marine phytoplankton Dunaliella tertiolecta.* Marine Chemistry, 2013. **157**: p. 78-85.
329. Foster, S., et al., *Distribution and Speciation of Arsenic in Temperate Marine Saltmarsh Ecosystems.* Environmental Chemistry, 2005. **2**.
330. Pell, A., et al., *LC-ICP-MS analysis of arsenic compounds in dominant seaweeds from the Thermaikos Gulf (Northern Aegean Sea, Greece).* Chemosphere, 2013. **93**(9): p. 2187-2194.
331. Meier, J., et al., *The occurrence of thio-arsenosugars in some samples of marine algae.* Environ. Chem., 2005. **2**(4): p. 304-307.
332. Terol, A., et al., *High temperature liquid chromatography-inductively coupled plasma mass spectrometry for the determination of arsenosugars in biological samples.* Journal of chromatography. A, 2012. **1262**: p. 70-76.
333. Foster, S., W. Maher, and F. Krikowa, *Changes in proportions of arsenic species within an Ecklonia radiata food chain.* Environmental Chemistry, 2008. **5**(3): p. 176-183.
334. Thomson, D., W. Maher, and S. Foster, *Arsenic and selected elements in inter-tidal and estuarine marine algae, south-east coast, NSW, Australia.* Applied Organometallic Chemistry, 2007. **21**(6): p. 396-411.
335. Waring, J., et al., *Occurrence and speciation of arsenic in common Australian coastal polychaete species.* Environmental Chemistry, 2005. **2**(2): p. 108-118.

336. Tukai, R., et al., *Occurrence and chemical form of arsenic in marine macroalgae from the east coast of Australia.* Mar. Freshwater Res., 2002. **53**(6): p. 971-980.
337. Foster, S. and W. Maher, *Degradation of arsenoribosides from marine macroalgae in simulated rock pools.* Arsenic in Geosphere and Human Diseases, 2010: p. 230-232.
338. Duncan, E., et al., *The degradation of arsenoribosides from Ecklonia radiata tissues decomposed in natural and microbially-manipulated microcosms.* Environmental Chemistry, 2014.
339. Duncan, E.G., et al., *Arsenoriboside degradation in marine systems: The use of bacteria culture incubation experiments as model systems.* Chemosphere, 2014. **95**: p. 635-638.
340. Yang, G.A.O., et al., *Determination of Arsenic and It's Species in Dry Seafood by High Performance Liquid Chromatography-Inductively Coupled Plasma Mass Spectrometry.* Chinese Journal of Analytical Chemistry, 2009. **37**.
341. Foster, S., et al., *A microwave-assisted sequential extraction of water and dilute acid soluble arsenic species from marine plant and animal tissues.* Talanta, 2007. **71**(2): p. 537-549.
342. Simon, S., et al., *Speciation analysis of organoarsenical compounds in biological matrices by coupling ion chromatography to atomic fluorescence spectrometry with on-line photooxidation and hydride generation.* Analytica Chimica Acta, 2004. **521**(1): p. 99-108.
343. Schaeffer, R., et al., *Determination of arsenic species in seafood samples from the Aegean Sea by liquid chromatography-(photo-oxidation)-hydride generation-atomic fluorescence spectrometry.* Anal. Chim. Acta, 2005. **547**(1): p. 109-118.
344. Thomas, P. and K. Sniatecki, *Inductively coupled plasma mass spectrometry: Application to the determination of arsenic species.* Fresenius' journal of analytical chemistry, 1995. **351**(4-5): p. 410-414.
345. Fernández-Costas, C., I. Lavilla, and C. Bendicho, *Ultrasonic Extraction–Ozonation Sequential Sample Treatment for the Determination of Arsenic in Environmental Certified Reference Materials by Hydride Generation–Atomic Fluorescence Spectrometry.* Spectroscopy Letters, 2006. **39**(6): p. 713-725.
346. Brisbin, J.A. and J.A. Caruso, *Comparison of extraction procedures for the determination of arsenic and other elements in lobster tissue by inductively coupled plasma mass spectrometry.* Analyst, 2002. **127**: p. 921-929.
347. Pétursdóttir, Á.H., et al., *Inorganic arsenic in seafood: Does the extraction method matter?* Food Chemistry, 2014. **150**: p. 353-359.
348. Branch, S., L. Ebdon, and P. O'Neill, *Determination of arsenic species in fish by directly coupled high-performance liquid chromatography–inductively coupled plasma mass spectrometry.* J. Anal. At. Spectrom., 1994. **9**(1): p. 33-37.
349. Mattusch, J. and R. Wennrich, *Determination of anionic, neutral, and cationic species of arsenic by ion chromatography with ICP-MS detection in environmental samples.* Anal. Chem., 1998. **70**: p. 3649-3655.
350. Geiszinger, A.E., W. Goessler, and K.A. Francesconi, *The marine polychaete Arenicola marina: its unusual arsenic compound pattern and its uptake of arsenate from seawater.* Mar. Environ. Res., 2002. **53**(1): p. 37-50.
351. Fujihara, J., et al., *Arsenic accumulation in livers of pinnipeds, seabirds and sea turtles: subcellular distribution and interaction between arsenobetaine and glycine betaine.* Comparative biochemistry and physiology. Toxicology & pharmacology : CBP, 2003. **136**(4): p. 287-296.
352. Ellis, J., et al., *Complementary molecular and elemental detection of speciated thioarsenicals using ESI-MS in combination with a xenon-based collision-cell ICP-MS with application to fortified NIST freeze-dried urine.* Analytical and bioanalytical chemistry, 2008. **390**(7): p. 1731-1737.
353. Heitkemper, D., et al., *Speciation of arsenic in urine using high-performance liquid chromatography with inductively coupled plasma mass spectrometric detection.* J. Anal. At. Spectrom., 1989. **4**(3): p. 279-284.

354. Sheppard, B.S., et al., *Arsenic speciation by ion chromatography with inductively coupled plasma mass spectrometric detection.* Analyst, 1992. **117**(6): p. 971-975.
355. Saverwyns, S., et al., *Speciation of six arsenic compounds using high-performance liquid chromatography-inductively coupled plasma mass spectrometry with sample introduction by thermospray nebulization.* Journal of Analytical Atomic Spectrometry, 1997. **12**(9): p. 1047-1052.
356. Raml, R., et al., *Novel Thioarsenic Metabolites in Human Urine after Ingestion of an Arsenosugar, 2‘,3‘-Dihydroxypropyl 5-Deoxy-5-dimethylarsinoyl-β-D-riboside.* Chemical Research in Toxicology, 2005. **18**(9): p. 1444-1450.
357. Raml, R., et al., *Thio-dimethylarsinate is a common metabolite in urine samples from arsenic-exposed women in Bangladesh.* Toxicology and applied pharmacology, 2007. **222**(3): p. 374-380.
358. Lindberg, A.-L., et al., *Evaluation of the three most commonly used analytical methods for determination of inorganic arsenic and its metabolites in urine.* Toxicology letters, 2007. **168**(3): p. 310-318.
359. Francesconi, K., et al., *Arsenic metabolites in human urine after ingestion of an arsenosugar.* Clinical chemistry, 2002. **48**(1): p. 92-101.
360. Molin, M., et al., *Major and minor arsenic compounds accounting for the total urinary excretion of arsenic following intake of blue mussels (Mytilus edulis): a controlled human study.* Food and chemical toxicology : an international journal published for the British Industrial Biological Research Association, 2012. **50**(7): p. 2462-2472.
361. Contreras-Acuña, M., et al., *Arsenic metabolites in human serum and urine after seafood (Anemonia sulcata) consumption and bioaccessibility assessment using liquid chromatography coupled to inorganic and organic mass spectrometry.* Microchemical Journal, 2014. **112**: p. 56-64.
362. Sloth, J., E. Larsen, and K. Julshamn, *Selective arsenic speciation analysis of human urine reference materials using gradient elution ion-exchange HPLC-ICP-MS.* Journal of Analytical Atomic Spectrometry, 2004. **19**: p. 973-978.
363. Samanta, G., et al., *High performance liquid chromatography inductively coupled plasma mass spectrometry for speciation of arsenic compounds in urine.* Microchemical Journal, 2000. **65**(2): p. 113-127.
364. Heitland, P. and H.D. Köster, *Comparison of different medical cases in urinary arsenic speciation by fast HPLC–ICP-MS.* International journal of hygiene and environmental health, 2009. **212**(4): p. 432-438.
365. Wrobel, K., et al., *Determination of As(III), As(V), monomethylarsonic acid, dimethylarsinic acid and arsenobetaine by HPLC-ICP-MS: analysis of reference materials, fish tissues and urine.* Talanta, 2002. **58**(5): p. 899-907.
366. Reuter, W., et al., *Speciation of five arsenic compounds in urine by HPLC/ICP-MS. Perkin Elmer Application Notes 2003.* 2003.
367. Milstein, L., et al., *Development and application of a robust speciation method for determination of six arsenic compounds present in human urine.* Environmental health perspectives, 2003. **111**(3): p. 293-296.
368. Verdon, C.P., et al., *Determination of seven arsenic compounds in urine by HPLC-ICP-DRC-MS: a CDC population biomonitoring method.* Analytical and Bioanalytical Chemistry, 2009. **393**(3): p. 939-947.
369. Mandal, B.K., Y. Ogra, and K.T. Suzuki, *Identification of dimethylarsinous and monomethylarsonous acids in human urine of the arsenic-affected areas in West Bengal, India.* Chem. Res. Toxicol., 2001. **14**: p. 371-378.
370. Rabieh, S., A.V. Hirner, and J. Matschullat, *Determination of arsenic species in human urine using high performance liquid chromatography (HPLC) coupled with inductively coupled plasma mass spectrometry (ICP-MS).* Journal of Analytical Atomic Spectrometry, 2008. **23**(4): p. 544-549.
371. James, W., et al., *Arsenic speciation: HPLC followed by ICP-MS or INAA.* Journal of Radioanalytical and Nuclear Chemistry, 2008. **278**(2): p. 267-270.

372. Moldovan, M., et al., *Arsenic Speciation in Water and Human Urine by HPLC–ICP-MS and HPLC–MO–HG-AAS.* Microchemical Journal, 1998. **59**(1): p. 89-99.
373. Shibata, Y., *Speciation of arsenic by reversed-phase high performance liquid chromatography-inductively coupled plasma mass spectrometry.* Anal Sci, 1989. **5**: p. 107-109.
374. Le, X.C. and M. Ma, *Short-column liquid chromatography with hydride generation atomic fluorescence detection for the speciation of arsenic.* Analytical Chemistry, 1998. **70**(9): p. 1926-1933.
375. Nakazato, T., et al., *Ion-exclusion chromatography combined with ICP-MS and hydride generation-ICP-MS for the determination of arsenic species in biological matrices.* J. Anal. Atom. Spectrom., 2000. **15**: p. 1546-1552.
376. Inoue, Y., et al., *Determination of arsenic compounds using inductively coupled plasma mass spectrometry with ion chromatography.* Journal of Chromatography A, 1994. **675**(1): p. 149-154.
377. Hansen, H.R., et al., *2-Dimethylarsinothioyl acetic acid Identified in a biological sample: The first occurrence of a mammalian arsinothioyl metabolite.* Angew. Chem. Int. Ed., 2004. **43**: p. 337-340.
378. Shibata, Y., J. Yoshinaga, and M. Morita, *Detection of arsenobetaine in human blood.* Applied Organometallic Chemistry, 1994. **8**: p. 249-251.
379. Raml, R., et al., *Individual variability in the human metabolism of an arsenic-containing carbohydrate, 2', 3'-dihydroxypropyl 5-deoxy-5-dimethylarsinoyl-β-D-riboside, a naturally occurring arsenical in seafood.* Chemical Research in Toxicology, 2009. **22**(9): p. 1534-1540.
380. Farinha, M.M., et al., *Arsenic speciation in lichens and in coarse and fine airborne particulate matter by HPLC–UV–HG–AFS.* Journal of atmospheric chemistry, 2004. **49**(1-3): p. 343-353.
381. Pantsar-Kallio, M. and P.K. Manninen, *Simultaneous determination of toxic arsenic and chromium species in water samples by ion chromatography-inductively coupled plasma mass spectrometry.* Journal of Chromatography A, 1997. **779**(1): p. 139-146.
382. Wallschläger, D. and C. Stadey, J. , *Determination of (Oxy)thioarsenates in Sulfidic Waters.* Analytical Chemistry, 2007. **79**(10): p. 3873–3880.
383. Milstein, L.S., et al., *Selection of a suitable mobile phase for the speciation of four arsenic compounds in drinking water samples using ion-exchange chromatography coupled to inductively coupled plasma mass spectrometry.* Environment international, 2002. **28**(4): p. 277-283.
384. Castillo, A., A. Roig-Navarro, and O. Pozo, *Capabilities of microbore columns coupled to inductively coupled plasma mass spectrometry in speciation of arsenic and selenium.* Journal of Chromatography A, 2008. **1202**(2): p. 132-137.
385. Day, J.A., et al., *A study of method robustness for arsenic speciation in drinking water samples by anion exchange HPLC-ICP-MS.* Anal. Bioanal. Chem., 2002. **373**: p. 664–668.
386. Ronkart, S.N., et al., *Speciation of five arsenic species (arsenite, arsenate, $MMAA^{V}$, $DMAA^{V}$ and AsBet) in different kind of water by HPLC-ICP-MS.* Chemosphere, 2007. **66**(4): p. 738-745.
387. Xie, Q., et al., *Determination of five arsenic species in aqueous samples by HPLC coupled with a hexapole collision cell ICP-MS.* J. Anal. Atom. Spectrom., 2002. **17**: p. 1037–1041.
388. Zheng, J., et al., *Speciation of arsenic in water, sediment, and plants of the Moira watershed, Canada, using HPLC coupled to high resolution ICP-MS.* Analytical and bioanalytical chemistry, 2003. **377**(1): p. 14-24.
389. Daus, B., et al., *Analytical investigations of phenyl arsenicals in groundwater.* Talanta, 2008. **75**(2): p. 376-379.
390. Daus, B., et al., *Concentrations and speciation of arsenic in groundwater polluted by warfare agents.* Environmental Pollution, 2010. **158**(11): p. 3439-3444.
391. Hwang, C.-j. and S.-J. Jiang, *Determination of arsenic compounds in water samples by liquid chromatography-inductively coupled plasma mass spectrometry with an in situ nebulizer-hydride generator.* Analytica Chimica Acta, 1994. **289**(2): p. 205-213.

392. Thomas, P. and K. Sniatecki, *Determination of trace amounts of arsenic species in natural waters by high-performance liquid chromatography–inductively coupled plasma mass spectrometry.* Journal of Analytical Atomic Spectrometry, 1995. **10**(9): p. 615-618.
393. Sathrugnan, K., H. Shizuko, and S.P.I. Chonattumadam, *Determination of arsenic species by microwave-assisted extraction followed by ion-pair chromatography–ICPMS: analysis of reference materials and fish tissues.* International Journal of Environmental Analytical Chemistry, 2004. **84**.
394. Shraim, A., et al., *Speciation of arsenic in tube-well water samples collected from West Bengal, India, by high-performance liquid chromatography-inductively coupled plasma mass spectrometry.* Applied Organometallic Chemistry, 2002. **16**: p. 202-209.
395. Morita, Y., et al., *Study on simultaneous speciation of arsenic and antimony by HPLC-ICP-MS.* Talanta, 2007. **73**(1): p. 81-86.
396. Kinoshita, K., et al., *Determination of diphenylarsinic acid and phenylarsonic acid, the degradation products of organoarsenic chemical warfare agents, in well water by HPLC-ICP-MS.* Appl. Organomet. Chem., 2005. **19**(2): p. 287-293.
397. Yehl, P.M. and J.F. Tyson, *Towards speciation of arsenic in a standard reference river sediment by high-performance ion chromatography coupled with plasma source mass spectrometry.* Analytical Communications, 1997. **34**(2): p. 49-51.
398. Li, Y., et al., *Arsenic speciation in municipal landfill leachate.* Chemosphere, 2010. **79**(8): p. 794-801.
399. Ponthieu, M., et al., *Speciation analysis of arsenic in landfill leachate.* Water Research, 2007. **41**(14): p. 3177-3185.
400. Narukawa, T., et al., *The extraction and speciation of arsenic in rice flour by HPLC-ICP-MS.* Talanta, 2008. **77**(1): p. 427-432.
401. Raab, A., et al., *Uptake and translocation of inorganic and methylated arsenic species by plants.* Environ. Chem., 2007. **4**(3): p. 197-203.
402. Coelho, N.M.M., et al., *High performance liquid chromatography—atomic fluorescence spectrometric determination of arsenic species in beer samples.* Analytica Chimica Acta, 2003. **482**.
403. Coelho, N.M., et al., *Determination of arsenic compounds in beverages by high-performance liquid chromatography-inductively coupled plasma mass spectrometry.* Talanta, 2005. **66**(4): p. 818-822.
404. Moreira, C.M., et al., *Arsenic speciation in white wine by LC–ICP–MS.* Food Chemistry, 2011. **126**(3): p. 1406-1411.
405. Wangkarn, S. and S. Pergantis, A. , *High-speed separation of arsenic compounds using narrow-bore high-performance liquid chromatography on-line with inductively coupled plasma mass spectrometry.* Journal of Analytical Atomic Spectrometry, 2000. **15**(6): p. 627-633.
406. Rodriguez, I.B., G. Raber, and W. Goessler, *Arsenic speciation in fish sauce samples determined by HPLC coupled to inductively coupled plasma mass spectrometry.* Food Chemistry, 2009. **112**(4): p. 1084-1087.
407. Nakazato, T., et al., *Determination of arsenite, arsenate, and monomethylarsonic acid in seawater by ion-exclusion chromatography combined with inductively coupled plasma mass spectrometry using reaction cell and hydride generation techniques.* Talanta, 2002. **58**(1): p. 121-132.
408. Duncan, E.G., et al., *Influence of culture regime on arsenic cycling by the marine phytoplankton Dunaliella tertiolecta and Thalassiosira pseudonana.* Environmental Chemistry, 2013. **10**(2): p. 91-101.
409. Contreras-Acuña, M., et al., *Speciation of arsenic in marine food (Anemonia sulcata) by liquid chromatography coupled to inductively coupled plasma mass spectrometry and organic mass spectrometry.* Journal of chromatography. A, 2013. **1282**: p. 133-141.
410. Granchinho, S.C.R., et al., *Biomethylation and biotransformation of arsenic(V) by marine algae Fucus gardneri.* Appl. Organomet. Chem., 2001. **15**: p. 553-560.

411. Todolí, J.L. and M. Grotti, *Fast determination of arsenosugars in algal extracts by narrow bore high-performance liquid chromatography–inductively coupled plasma mass spectrometry.* Journal of Chromatography A, 2010. **1217**(47): p. 7428-7433.
412. Duncan, E.G., et al., *Total arsenic concentrations and arsenic species present in naturally decomposing Ecklonia radiata tissues collected from various marine habitats.* Journal of Applied Phycology, 2014: p. 1-9.
413. Geiszinger, A., W. Goessler, and K. Francesconi, *The marine polychaete Arenicola marina: its unusual arsenic compound pattern and its uptake of arsenate from seawater.* Marine environmental research, 2002. **53**(1): p. 37-50.
414. Brisbin, J., C. B'Hymer, and J. Caruso, *A gradient anion exchange chromatographic method for the speciation of arsenic in lobster tissue extracts.* Talanta, 2002. **58**(1): p. 133-145.
415. Thomas, P., K. Pereira, and D. Koller, *Improvement in measurement of arsenic and selenium species by coupled high performance liquid chromatography-inductively coupled plasma mass spectrometry using time resolved analysis and chromatographic software.* Analusis, 1997. **25**(1): p. 19-23.
416. Hanaoka, K., et al., *Arsenic in the prepared edible brown alga hijiki, Hizikia fusiforme.* Appl. Organomet. Chem., 2001. **15**: p. 561-565.
417. Hanaoka, K., et al., *Occurrence of a few organo-arsenicals in jellyfish.* Appl. Organomet. Chem., 1999. **13**: p. 95-99.
418. Wrobel, K., K. Wrobel, and J. Caruso, *Pretreatment procedures for characterization of arsenic and selenium species in complex samples utilizing coupled techniques with mass spectrometric detection.* Analytical and bioanalytical chemistry, 2005. **381**(2): p. 317-331.
419. Sele, V., et al., *Arsenic-containing fatty acids and hydrocarbons in marine oils–determination using reversed-phase HPLC–ICP-MS and HPLC–qTOF-MS.* Talanta, 2014. **121**: p. 89-96.
420. Taleshi, M.S., et al., *Arsenic-Containing lipids Are Natural Constituents of Sashimi Tuna.* Environmental Science & Technology, 2010. **44**(4): p. 1478-1483.
421. Ken'ichi, H., et al., *Water-soluble arsenic residues from several arsenolipids occurring in the tissues of the starspotted sharkMusterus manazo.* Applied Organometallic Chemistry, 2001. **15**.
422. Sun, M., et al., *Speciation analysis of inorganic arsenic in coal samples by microwave-assisted extraction and high performance liquid chromatography coupled to hydride generation atomic fluorescence spectrometry.* Talanta, 2013. **106**: p. 8-13.
423. Zheng, J., W. Goessler, and W. Kosmus, *The Chromatographic Behavior of Arsenic Compounds on Anion Exchange Columns with Binary Organic Acids as Mobile Phases.* Chromatographia, 1998. **47**(5-6): p. 257-263.
424. Goessler, W., et al., *Can humans metabolize arsenic compounds to arsenobetaine?* Appl. Organomet. Chem., 1997. **11**: p. 327-335.
425. Pergantis, S.A., W. Winnik, and D. Betowski, *Determination of Ten Organoarsenic Compounds Using MicroboreHigh-performance Liquid Chromatography Coupled With Electrospray MassSpectrometry–Mass Spectrometry.* J. Anal. At. Spectrom., 1997. **12**(5): p. 531-536.
426. Sheppard, B.S., et al., *Elimination of the argon chloride interference on arsenic speciation in inductively coupled plasma mass spectrometry using ion chromatography.* J. Anal. At. Spectrom., 1990. **5**(6): p. 431-435.
427. Story, W.C., et al., *Elimination of the chloride interference on the determination of arsenic using hydride generation inductively coupled plasma mass spectrometry.* Journal of chromatographic science, 1992. **30**(11): p. 427-432.
428. Ding, H., et al., *Arsenic speciation by micellar liquid chromatogrpahy with inductively coupled plasma mass spectrometric detection.* Journal of Chromatography A, 1995. **694**(2): p. 425-431.
429. Zheng, J., et al., *Arsenic speciation in human urine reference materials using high-performance liquid chromatography with inductively coupled plasma mass spectrometric detection.* Journal of trace elements in medicine and biology, 1999. **13**(3): p. 150-156.

430. Wrobel, K., K. Wrobel, and J.A. Caruso, *Liquid Chromatography with Inductively Coupled Plasma Mass Spectrometric Detection for Element Speciation: Clinical and Toxicological Applications.* Chromatographic Methods in Clinical Chemistry and Toxicology, 2007: p. 217.
431. Wei, X., C.A. Brockhoff-Schwegel, and J.T. Creed, *A comparison of urinary arsenic speciation via direct nebulization and on-line photo-oxidation–hydride generation with IC separation and ICP-MS detection.* Journal of Analytical Atomic Spectrometry, 2001. **16**(1): p. 12-19.
432. Slejkovec, Z., J. van Elteren, and A. Byrne, *Determination of arsenic compounds in reference materials by HPLC-(UV)-HG-AFS.* Talanta, 1999. **49**(3): p. 619-627.
433. Mandal, B.K., et al., *Speciation of arsenic in biological samples.* Toxicol. Appl. Pharmacol., 2004. **198**(3): p. 307-318.
434. Cubadda, F., et al., *Speciated urinary arsenic as a biomarker of dietary exposure to inorganic arsenic in residents living in high-arsenic areas in Latium, Italy.* Pure & Applied Chemistry, 2012. **84**(2).
435. Pearson, G.F., et al., *Rapid arsenic speciation using ion pair LC-ICPMS with a monolithic silica column reveals increased urinary DMA excretion after ingestion of rice.* Journal of Analytical Atomic Spectrometry, 2007. **22**(4): p. 361-369.
436. Pearson, G.F., *Elemental speciation and miniaturised sample introduction studies for inductively coupled plasma mass spectrometry*, in *Chemistry*2007, University of Hull. p. 253.
437. Todorov, T.I., et al., *Arsenic speciation in urine and blood reference materials.* Microchimica Acta, 2005. **151**(3-4): p. 263-268.
438. Sanz, E., R. Muñoz-Olivas, and C. Cámara, *A rapid and novel alternative to conventional sample treatment for arsenic speciation in rice using enzymatic ultrasonic probe.* Analytica Chimica Acta, 2005. **535**.
439. Jackson, B.P., et al., *Arsenic concentration and speciation in infant formulas and first foods.* Pure and Applied Chemistry, 2012. **8**(2): p. 215–223.
440. Jackson, B.P., et al., *Arsenic, organic foods, and brown rice syrup.* Environmental Health Perspectives, 2012. **120**(5): p. 623.
441. Batista, B.L., et al., *Speciation of arsenic in rice and estimation of daily intake of different arsenic species by Brazilians through rice consumption.* Journal of hazardous materials, 2011. **191**(1): p. 342-348.
442. D'Amato, M., G. Forte, and S. Caroli, *Identification and quantification of major species of arsenic in rice.* Journal of AOAC International, 2004. **87**(1): p. 238-243.
443. Sun, G.-X., et al., *Survey of arsenic and its speciation in rice products such as breakfast cereals, rice crackers and Japanese rice condiments.* Environment international, 2009. **35**(3): p. 473-475.
444. Le, X.C., S. Yalcin, and M. Ma, *Speciation of submicrogram per liter levels of arsenic in water: On-site species separation integrated with sample collection.* Environmental Science & Technology, 2000. **34**(11): p. 2342-2347.
445. Castlehouse, H., et al., *Biotransformation and accumulation of arsenic in soil amended with seaweed.* Environmental science & technology, 2003. **37**(5): p. 951-957.
446. Almela, C., et al., *Arsenosugars in raw and cooked edible seaweed: characterization and bioaccessibility.* Journal of agricultural and food chemistry, 2005. **53**(18): p. 7344-7351.
447. Yoshinaga, J., et al., *NIES certified reference materials for arsenic speciation.* Accreditation and quality assurance, 1997. **2**(3): p. 154-156.
448. Okamoto, K., J. Yoshinaga, and M. Morita, *Biological and environmental reference materials from the National Institute for Environmental Studies (Japan).* Mikrochimica Acta, 1996. **123**: p. 15-21.
449. Farías, S., et al., *Total and inorganic arsenic in Antarctic macroalgae.* Chemosphere, 2007. **69**(7): p. 1017-1024.
450. García Salgado, S., Q. Nieto, and M. Bonilla Simón, *Optimisation of sample treatment for arsenic speciation in alga samples by focussed sonication and ultrafiltration.* Talanta, 2006. **68**(5): p. 1522-1527.

451. Paproski, R.E. and X.C. Le, *Boric acid-assisted anion-exchange chromatography for separating arsenic species.* Analytica Chimica Acta, 2004. **526**(1): p. 69–76.
452. Lehmann, E., A. Fostier, and M. Arruda, *Hydride generation using a metallic atomizer after microwave-assisted extraction for inorganic arsenic speciation in biological samples.* Talanta, 2013. **104**: p. 187-192.
453. Shibata, Y. and M. Morita, *Characterization of organic arsenic compounds in bivalves.* Appl. Organomet. Chem., 1992. **6**(4): p. 343-349.
454. Lai, V.W.M., et al., *The characterization of arsenosugars in commercially available algal products including aNostoc species of terrestrial origin.* Applied Organometallic Chemistry, 1997. **11**: p. 797-803.
455. Larsen, E.H., *Speciation of dimethylarsinyl-riboside derivatives (arsenosugars) in marine reference materials by HPLC-ICP-MS.* Fresenius' Journal of Analytical Chemistry, 1995. **352**: p. 582-588.
456. Harrington, C.F., et al., *The identification of some water-soluble arsenic species in the marine brown algaeFucus distichus.* Applied Organometallic Chemistry, 1997. **11**: p. 931-940.
457. Devesa, V., et al., *Distribution of arsenic species in the freshwater crustacean Procambarus clarkii.* Applied Organometallic Chemistry, 2002. **16**: p. 123-132.
458. Corr, J.J. and E.H. Larsen, *Arsenic speciation by liquid chromatography coupled with ionspray tandem mass spectrometry.* J. Anal. At. Spectrom., 1996. **11**(12): p. 1215-1224.
459. Geng, W., et al., *Arsenic speciation in marine product samples: comparison of extraction-HPLC method and digestion-cryogenic trap method.* Talanta, 2009. **79**(2): p. 369-375.
460. Muñoz, O., D. Vélez, and R. Montoro, *Optimization of the solubilization, extraction and determination of inorganic arsenic [As(iii) + As(v)] in seafood products by acid digestion, solvent extraction and hydride generation atomic absorption spectrometry.* Analyst, 1999. **124**: p. 601-607.
461. Chatterjee, A., *Determination of total cationic and total anionic arsenic species in oyster tissue using microwave-assisted extraction followed by HPLC-ICP-MS.* Talanta, 2000. **51**(2): p. 303-314.
462. Nischwitz, V. and S. Pergantis, *Liquid chromatography online with selected reaction monitoring electrospray mass spectrometry for the determination of organoarsenic species in crude extracts of marine reference materials.* Analytical chemistry, 2005. **77**(17): p. 5551-5563.
463. Alberti, J., R. Rubio, and G. Rauret, *Arsenic speciation in marine biological materials by LC-UV-HG-ICP/OES.* Fresenius' journal of analytical chemistry, 1995. **351**(4-5): p. 415-419.
464. Georg, R., et al., *Quantitative speciation of arsenic compounds when using organic solvent gradients in HPLC-ICPMS.* Journal of Analytical Atomic Spectrometry, 2010. **25**.
465. Suner, M.A., et al., *Application of column switching in high-performance liquid chromatography with on-line thermo-oxidation and detection by HG-AAS and HG-AFS for the analysis of organoarsenical species in seafood samples.* Journal of Analytical Atomic Spectrometry, 2001. **16**(4): p. 390-397.
466. Suner, M.A., et al., *Speciation of cationic arsenic species in seafood by coupling liquid chromatography with hydride generation atomic fluorescence detection.* J. Anal. Atom. Spectrom., 2000. **15**: p. 1501-1507.
467. Dagnac, T., et al., *Speciation of arsenic in mussels by the coupled system liquid chromatography-UV irradiation-hydride generation-inductively coupled plasma mass spectrometry.* Talanta, 1999. **48**(4): p. 763-772.
468. Larsen, E.H., *Speciation of dimethylarsinyl-riboside derivatives (arsenosugars) in marine reference materials by HPLC-ICP-MS.* Fresenius J. Anal. Chem., 1995. **352**: p. 582-588.
469. Larsen, E., G. Pritzl, and S. Hansen, *Arsenic speciation in seafood samples with emphasis on minor constituents: an investigation using high-performance liquid chromatography with detection by inductively coupled plasma mass spectrometry.* Journal of Analytical Atomic Spectrometry, 1993. **8**: p. 1075-1084.

470. Jorge, M.P., et al., *Assessment of the bioavailability of toxic and non-toxic arsenic species in seafood samples.* Food Chemistry, 2012. **130**.
471. Chaparro, L., et al., *Automated system for on-line determination of dimethylarsinic and inorganic arsenic by hydride generation-atomic fluorescence spectrometry.* Analytical and bioanalytical chemistry, 2012. **404**(5): p. 1589-1595.
472. Leufroy, A., et al., *Determination of seven arsenic species in seafood by ion exchange chromatography coupled to inductively coupled plasma-mass spectrometry following microwave assisted extraction: method validation and occurrence data.* Talanta, 2011. **83**(3): p. 770-779.
473. Sánchez-Rodas, D., et al., *Arsenic speciation in river and estuarine waters from southwest Spain.* The Science of the total environment, 2005. **345**(1-3): p. 207-217.
474. Goessler, W., et al., *Arsenobetaine and other arsenic compounds in the National Research Council of Canada certified reference materials DORM 1 and DORM 2.* J. Anal. Atom. Spectrom., 1998. **13**: p. 183 - 187.
475. Rubio, R., et al., *On-line photolytic decomposition for the determination of organoarsenic compounds.* Trac-Trend. Anal. Chem., 1995. **14**(6): p. 274-279.
476. Branch, S., et al., *Determination of arsenic in samples with high chloride content by inductively coupled plasma mass spectrometry.* J. Anal. Atom. Spectrom., 1991. **6**: p. 151-154.
477. Yang, L., et al., *Determination of arsenobetaine in fish tissue by species specific isotope dilution LC-LTQ-Orbitrap-MS and standard addition LC-ICPMS.* Analytical chemistry, 2011. **83**(9): p. 3371-3378.
478. Shona, M. and M. Zoltan, *Arsenic speciation in marine certified reference materials.* Journal of Analytical Atomic Spectrometry, 2004. **19**.
479. Wahlen, R., et al., *Arsenic speciation in marine certified reference materials Part 2. The quantification of water-soluble arsenic species by high-performance liquid chromatography-inductively coupled plasma mass spectrometry.* J. Anal. Atom. Spectrom., 2004. **19**: p. 876-882.
480. McSheehy, S. and Z. Mester, *Arsenic speciation in marine certified reference materials Part 1. Identification of water-soluble arsenic species using multidimensional liquid chromatography combined with inductively coupled plasma, electrospray and electrospray high-field asymmetric waveform ion mobility spectrometry with mass spectrometric detection.* J. Anal. Atom. Spectrom., 2004. **19**: p. 373-380.
481. Thomson, D., W. Maher, and S. Foster, *Arsenic and selected elements in inter-tidal and estuarine marine algae, south-east coast, NSW, Australia.* Applied Organometallic Chemistry, 2007. **21**(6): p. 396-411.
482. Foster, S.D., *Arsenic cycling in marine ecosystems: Investigating the link between primary production and secondary consumption*, 2007, University of Canberra.
483. Sanchez-Rodas, D., et al., *Arsenic speciation in river and estuarine waters from southwest Spain.* Sci. Total Environ., 2005. **345**(1-3): p. 207-17.
484. Stéphane, S., et al., *Simultaneous determination of twelve inorganic and organic arsenic compounds by liquid chromatography–ultraviolet irradiation–hydride generation atomic fluorescence spectrometry.* Journal of Chromatography A, 2004. **1024**.
485. Schaeffer, R., P. Fodor, and C. Soeroes, *Development of a liquid chromatography/electrospray selected reaction monitoring method for the determination of organoarsenic species in marine and freshwater samples.* Rapid communications in mass spectrometry : RCM, 2006. **20**(19): p. 2979-2989.
486. Foster, S., et al., *Distribution and Speciation of Arsenic in Temperate Marine Saltmarsh Ecosystems.* Environ. Chem., 2005. **2**(3): p. 177-189.
487. Pétursdóttir, Á.H., et al., *Determination of inorganic arsenic in seafood: Emphasizing the need for certified reference materials.* Pure and Applied Chemistry, 2012.

488. Rasmussen, R., et al., *Development and validation of an SPE HG-AAS method for determination of inorganic arsenic in samples of marine origin.* Analytical and bioanalytical chemistry, 2012. **403**(10): p. 2825-2834.
489. Hirata, S., H. Toshimitsu, and M. Aihara, *Determination of arsenic species in marine samples by HPLC-ICP-MS.* Analytical sciences : the international journal of the Japan Society for Analytical Chemistry, 2006. **22**(1): p. 39-43.
490. Raimund, W., et al., *Arsenic speciation in marine certified reference materials.* Journal of Analytical Atomic Spectrometry, 2004. **19**.
491. Larsen, E., et al., *Determination of inorganic arsenic in white fish using microwave-assisted alkaline alcoholic sample dissolution and HPLC-ICP-MS.* Analytical and bioanalytical chemistry, 2005. **381**(2): p. 339-346.
492. Xuan, C., et al., *Sequential extraction combined with HPLC–ICP-MS for As speciation in dry seafood products.* Food Chemistry, 2009. **113**.